OVERVIEW OF FISCHER-TROPSCH SYNTHESIS WITH COBALT CATALYSTS

SUMMARY

This review of the use of cobalt catalysts for the Fischer-Tropsch synthesis emphasizes results of the past thirty years. It is primarily intended to define catalyst formulations, both available to the public and of limited use because of patent coverage, that can be utilized in studies to define relationships between catalyst composition and process variables. To accomplish this literature review, two approaches have been utilized. In the first, a summary is provided by research topics: catalyst preparation, catalyst activation, catalytic activity and productivity, and catalyst aging and rejuvenation. Because of the likelihood that these catalysts will eventually be utilized in bubble column reactors, a brief survey of these reactors is presented. The proposed work will involve both fixed-bed and continuous stirred tank reactors (CSTR) and, at this time, the results from these two types of reactors cannot be directly related to large-scale bubble column reactor operations.

FIRST THIRTY YEARS (1925-1955)

The early work on the conversion of synthesis gas to hydrocarbons using cobalt catalysts has been extensively reviewed [1-3]. The Bureau of Mines review [3] of the literature contains 3771 abstracts and the second part covering patents contains 4017 abstracts; each section has an extensive index. The cobalt catalyst compositions center on those that eventually became the "standard" catalyst for the German Synthine process: Kieselguhr supported cobalt and thorium oxide together with other activating materials. This catalyst defined the use of a support and a nonreducible promoter for cobalt catalyst for the Fischer-Tropsch synthesis. It was demonstrated that the presence of copper, up to about 2 wt.%, significantly decreased the temperature required to reduce the cobalt to the metallic state [4]. This work defined the use of an easily reduced metal oxide as a promoter for reducing cobalt catalysts at lower temperatures than would occur in their absence. However, it was also reported that while the copper allowed reductions to be effected at lower temperatures, the resulting catalyst declined in activity more rapidly [5]. Magnesia has been in use in cobalt catalyst formulation since 1938. The magnesia extends the catalyst life to eight months at normal pressure conditions [6]. The magnesia was added to increase the hardness of the catalyst; it also depressed the methane production and carbon formation.

During this period, the Fischer-Tropsch synthesis was carried out at the commercial scale by the Germans and the Japanese in processes that employed supported cobalt catalysts in fixed-bed reactors [1]. During this period, Kölbel and coworkers completed laboratory and pilot plant operations with a bubble column reactor to directly produce products emphasizing gasoline and diesel range materials using what would be considered today to be low-alpha iron catalysts [7].

MORE RECENT REPORTS OF COBALT CATALYST FORMULATIONS

A representative listing of promoters and supports reported in patents that are covered in **Chemical Abstracts** since 1962 are compiled in Attachments I and II.

For the purpose of the proposed study under this contract, the catalyst preparation and compositions of a patent issued in 1978, and now expired, are of interest [4]. This patent describes a process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane. The process utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst formulation can contain an inert support. The standard cobalt catalyst used in this work was prepared following a recipe that is, or is similar to, the standard German cobalt catalyst and consists of Co, Mg and Th on a kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst for the improved catalyst formulation. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used as support materials can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal, and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in an uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. An interpretation of a phrase from a subclaim, "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." is a demanding task. One could conclude that this patent includes a catalyst with a nonuniform deposition of cobalt within the support particle. The patent covers operating temperatures from 60 to 450^{o}C and pressures from atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application [9].

Another report of interest for the proposed work describes the use of Pt and Pd as promoter for Co-alumina catalysts in which the alumina support does not exhibit an XRD pattern [10]. This disclosure permits the use of these noble metals to compare with catalysts containing Ru as disclosed in the Gulf Res. & Dev. Co. patent described above.

The patents described above utilize a range of metal salts, including cobalt carbonyl, to prepare supported cobalt catalysts that contain a variety of promoters - both easily reducible metal oxides including Ru, Pt, Pd and Cu as well as nonreducible metal oxides including zirconia, titania, alumina and silica.

Air Products utilized impregnation techniques to prepare catalysts during their work under DOE contracts in the 1980s. Catalyst precursors and supports were purchased from commercial sources [11]. The supports (γ-Al_2O_3 (Catapal SB, 217 m^2/g, 45 µm), silica (Davison 952, 339 m^2/g, 70 µm), $MgO \bullet 3.6SiO_2$ (Florisil, 298 m^2/g, 75 µm) and titania (Degussa P-25, 50 m^2/g, 2 µm) were calcined at 500°C for 3 hours in air prior to catalyst preparation. The catalysts and precursors were protected from air and moisture using the Schlenk technique and/or dry box. All solvents were distilled from sodium benzophenone detyl in a nitrogen atmosphere. Prior to use, the supports were further dried at 110°C under vacuum for 1-2 hours. Catalysts were prepared using the incipient wetness technique with separate solutions containing the promoter and metal carbonyl applied to the support in sequential steps. Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No.--------- and is subject to government rights arising therefrom."

CATALYST ACTIVATION

Benson et al. [12] indicate that, "Cobalt required carefully conducted prereduction with hydrogen, followed by an equally rigid schedule of induction with synthesis gas." Induction, as utilized in the reports of work at the Bureau of Mines, refers to the protocol followed during the early stages of exposure of the catalyst to hydrogen, or hydrogen and carbon monoxide, after adding the catalyst to the slurry oil/wax, or vice versa, in the reactor.

The majority of laboratory studies utilized hydrogen reduction followed by transfer of the reduced catalyst to the reactor. The transfer could be conducted by transferring the reduced catalyst to an outgassed start-up solvent in the absence of oxygen sources or by first passivating the catalyst with oxygen/air at low temperatures and then re-reducing the catalyst in the reactor [11].

A process that was claimed to provide a catalyst with superior activity involved the reduction of the dried (or calcined) catalyst in hydrogen, reoxidation, and then re-reduction in hydrogen (the ROR method) [13]. When the ROR method is utilized in a fixed-bed reactor, there are no problems in interpreting the approach since the catalyst can be contacted with synthesis gas in the reactor immediately following the re-reduction, and without exposure to oxygen. The ROR method was employed for testing using a bubble column reactor; however, the method used to transfer the catalyst to the reactor, if indeed it was transferred rather than activated in the bubble column reactor, was not defined in detail [9].

Mitchell [14] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity. The induction utilized by the Bureau of Mines workers was to significantly increase the productivity of the catalyst during the early period of catalyst usage.

While there are a number of patents that cover activation of catalysts in hydrogen, none appear to provide specifics as to the mode of operation with respect to catalyst composition.

In a different approach, Nay et al. [15] claimed an activation that involved the oxidation of a cobalt catalyst followed by a reduction using carbon monoxide. This approach was claimed to produce a catalyst which produced less methane and more C_5+ products than when the same catalyst was activated using hydrogen.

Air Products conducted extensive work with cobalt catalysts during the 1980s, and the results are covered in reports and in patents [16-18]. In these studies they utilized both fixed-bed and CSTRs. The catalyst was loaded into the fixed-bed reactor; this was accomplished in a glove-box with air sensitive catalyst precursors. The reactor was then placed in line after the rest of the system had been flushed with nitrogen for at least 10 minutes. After leak testing, the catalyst was activated following two procedures. In the first, the catalyst was activated using $CO/H_2 = 1.0$. To accomplish this the catalyst precursor was heated to 180^oC in a nitrogen flow at atmospheric pressure. At 180^oC, the flow was switched to the synthesis gas ($CO/H_2 = 1$) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H_2 or syngas ($CO/H_2 = 1$). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels. For the slurry phase tests, catalysts were activated in a separate, 150 cc fixed bed tubular unit using either pure H_2 or 20% syngas in nitrogen. The activated catalyst was then slurried in a deoxygenated paraffin oil in a dry box and transferred to the slurry autoclave under a blanket of nitrogen.

CATALYST ACTIVITY - PRODUCTIVITY

With an iron catalyst the productivity per gram of iron is not independent of CO conversion. Thus, the hydrocarbon productivity is highest at low conversion levels and then declines to about 0.5 g. hydrocarbons/g. Fe/h at the 90%+ CO conversion level (figure 1) [19]. Similar productivity rates are obtained for H_2/CO ratios typical of synthesis gas derived from coal (0.7) or from natural gas (1.7). Based on kinetics, it is anticipated that the productivity of a cobalt catalyst should also be dependent on the CO conversion level, although perhaps not to extent that it is for the iron-based catalyst.

The impact of particle size upon supported catalysts operated in a fixed-bed reactor was demonstrated by work carried out at Gulf Oil (Attachment VIII). As the particle size of the catalyst was decreased in the range from 1.6 to 0.2 mm, the methane production decreased (figure 2) and the C_5+ hydrocarbon fraction increased (figure 3). Likewise, the temperature dependence of synthesis at 185 and 195^{o}C clearly demonstrated that the reaction suffered diffusion limitations in the larger catalyst particle sizes (figure 4). More recent quantitative descriptions of the effect of the catalyst particle size on product selectivity and on activity has been presented (figure 5) [references 20,21].

The results from synthesis in a bubble column slurry reactor showed that the methane production increased and the C_5+ hydrocarbons decreased as the temperature was increased in the 220-240^oC range (figure 6) [9].

It is very difficult to obtain reactor productivity for pilot plant or commercial operations from either the open or patent literature. It is almost always necessary to make one or more assumptions about the operation and this introduces uncertainties in the estimate of productivity. The results summarized in Attachment V suggest that one should be able to obtain productivities in the range of 0.5 g. hydrocarbon/g catalyst/h for either unsupported iron or supported cobalt catalysts.

DECLINE IN CATALYTIC ACTIVITY

Data to define the decline in catalytic activity are not readily available. For a Co-Zr-silica catalyst that is operated with a $H_2/CO = 1$ at 260^oC, the rate of activity decline is about 1% CO conversion per week (figure 7) [22]. On the other hand, a Co-silica catalyst exhibited an activity decline of about 35% CO conversion per week; however, for the same catalyst operated at a higher flow rate so that the CO conversion is only about 10% the activity decline was less than 1% CO conversion per week [23]. This result implies that the activity loss may be conversion dependent, presumably influenced by the partial pressure of water. A recent report indicates that there is a rapid activity decline during the first five days of operation after which the decline becomes much slower (figure 8) [24]. A definition of a series of aging-rejuvenation cycles has been reported (figure 9) [25]. There appears to be a reasonable relationship between the rate of activity decline and the time of the total decline as well as the rate of activity recovery and the time of the total decline. It should be realized that this patent claims to demonstrate a catalyst rejuvenation technique and that accelerated aging conditions may have been employed during the study.

As important as the initial decline in activity is the regeneration (or rejuvenation) of the catalyst. The early work by the Germans and the U.S. Bureau of mines show that the initial activity of a cobalt catalyst can be attained again, or closely approached, by a brief treatment of the aged catalyst with hydrogen.

KINETICS

Several kinetic equations for synthesis gas conversion have been advanced for both iron and cobalt catalysts. For CO conversion levels to about 50%, both catalysts exhibit little dependence on CO partial pressure and a direct dependence on H_2 partial pressure. Thus, at low conversion the data have been fitted with the equation:

$$\text{rate} = k\, P_{H2}\ .$$

Several variations of the inhibition effect of the reactants and products, especially H_2O, on the kinetics at higher conversion levels have been proposed. Unfortunately, the scatter in the experimental data at these high conversion levels makes it impossible to settle on a single kinetic expression.

There are several reports of the activation energy for both iron and cobalt catalysts and these are in the 20-25 kcal/mole range.

SLURRY REACTORS

It was recognized soon after the discovery of the Fischer-Tropsch synthesis that a reactor employing the catalyst in direct contact with a cooling oil was an attractive approach to maintain temperature control of the exothermic reaction. U.S. patents were obtained by I. G. Farbenindustrie A.-G., Standard Oil Development Company and Standard Catalytic Company. The Standard Catalytic Company was established by six

U.S. petroleum companies to develop processes for the production of synthetic fuels, and included an agreement with I. G. Farbenindustrie A.-G. Some of these patents are summarized in Attachment VI. Included in Attachments VII and VIII are the claims of several recent patents covering the use of bubble column reactors for the Fischer-Tropsch synthesis.

Recently, Inga [26] has studied the factors involved in relating data obtained in small-scale laboratory reactors to larger ones that would be utilized in industry. In brief, Inga concludes that the data from small reactors can be related **directly** to large commercial reactors only if the mixing in the small reactor will be the same as encountered in the large bubble column reactor. Thus, the usual results from the small-scale reactor is adequate for a definition of the scientific and engineering principles for bubble column operation but is not appropriate for direct application to any commercial scale bubble column reactor.

REFERENCES

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3. H. C. Anderson, L. L. Wiley and A. Newell, "Bibliography of the Fischer-Tropsch synthesis and related processes (in two parts). I. Review and compilation of the literature on the production of synthetic liquid fuels and chemicals by the hydrogenation of carbon monoxide. II. Patents," Bureau of Mines Bulletin 544, 1954, 1955.
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5. J. F. Schultz, L. J. E. Hofer, E. M. Cohn, K. C. Stein and R. B. Anderson, "Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide,", Bureau of Mines Bulletin 478, 1959.
6. (Technical Oil Mission Report, No. 8, May 15, 1945 (PB 367).
7. H. Kölbel and M. Ralek, Catal. Rev.-Sci. Eng., 21, 225 (1980).
8. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (assigned to Gulf Res. & Dev. Co.).
9. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell; "Conversion of synthesis gas to diesel fuel in controlled particle size fluid system," South Africa Patent 855317, 7/15/85; ZA 8505317, issued 02/26/86.
10. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States), available from NTIS.

11. H. P. Withers, Jr, K. F. Eliezer and J. W. Mitchell, Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production; DOE/PC/70030-T9, Final Report, December 1987.
12. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.
13. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U. S. Patent 4,605,679, August 12, 1986.
14. W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. Patent 5,292,705 (Mar. 1994).
15. B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.
16. P. N. Dyer, R. Pierantozzi and H. P. Withers, Supported Fischer-Tropsch catalyst and method of making the catalyst, US 4,681,867, July 21, 1987.
17. P. N. Dyer and R. Pierantozzi, Catalyst for selective conversion of synthesis gas and method of making the catalyst, US 4,619,910, Oct 28, 1986.
18. P. N. Dyer, R. Pierantozzi and H. P. Withers, Fischer-Tropsch process, US 4,670,472, June 2, 1987.
19. Our work hc/hr vs CO conv
20. E. Iglesia, Appl. Catal. A: General, 161, 59 (1997).
21. E. Iglesia, S. C. Reyes and S. L. Soled, "Reaction-transport selectivity models and the design of Fischer-Tropsch catalysts," "Computer-Aided Design of Catalysts and Reactors," (E. R. Becker and C. J. Pereira, Eds.), Marcel Dekker, Inc., 1992.

22. H. P. Withers, Jr., K. F. Eliezer and J. W. Mitchel, Ind. Eng. Chem. Res., 29, 1807, (1990).

23. Unpublished results, CAER.

24. P. J. van Berge and R. C. Everson, "Cobalt as an alternative Fischer-Tropsch catalyst to iron for production of middle distillates,: Natural Gas Conversion IV (M. de Pontes et al., Eds.), Studies Surf. Sci. Catal., 107, 207 (1997).

25. W. N. Mitchell, "Rejuvenation of hydrocarbon synthesis catalyst," U.S. Patent 5,283,216, February 1, 1994.

26. J. Inga, Ph.D. Thesis, U. Pittsburgh, 1997.

ATTACHMENTS

I. FT Catalyst Promoter - Patents

II. FT Supports - Patents

III. The Preparation of Cobalt Fischer-Tropsch Catalysts - Literature From 1962

IV. Fischer Tropsch - Examples of Activation

V. Productivity - Slurry Phase

VI. Early Slurry Reactors

VII. Tube-in-Shell Fischer-Tropsch Reactor

VIII. Cooling Coils in or outside the Fischer-Tropsch Reactor Shell

IX. Review of Air Products Fischer-Tropsch Synthesis Work

X. Review of Exxon Patents

XI. Listing of Open Literature Description of Exxon FT Work

XII. Review of Fischer-Tropsch Work by Gulf Oil

XIII. Review of Fischer-Tropsch Work by Statoil

XIV. Review of Fischer-Tropsch Work by Rentech

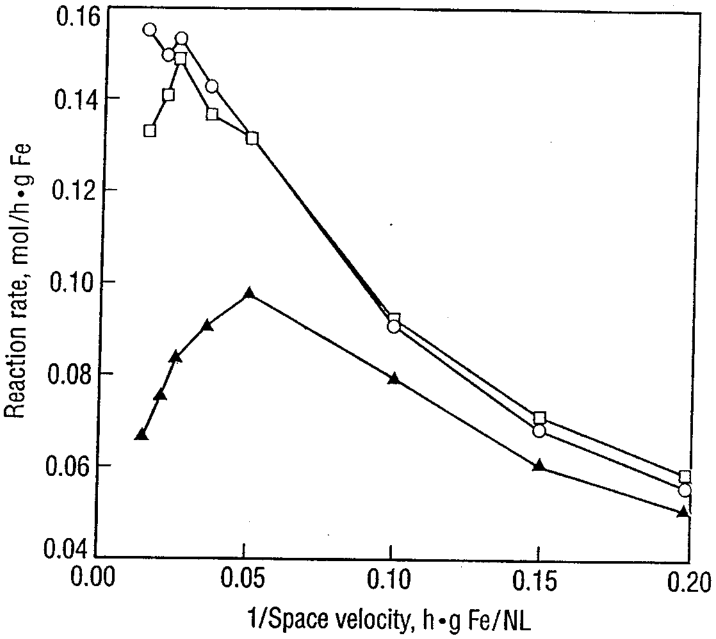

Figure 1. Reaction rate for Fischer-Tropsch synthesis (□, ") and water-gas shift (▲) with an iron catalyst.

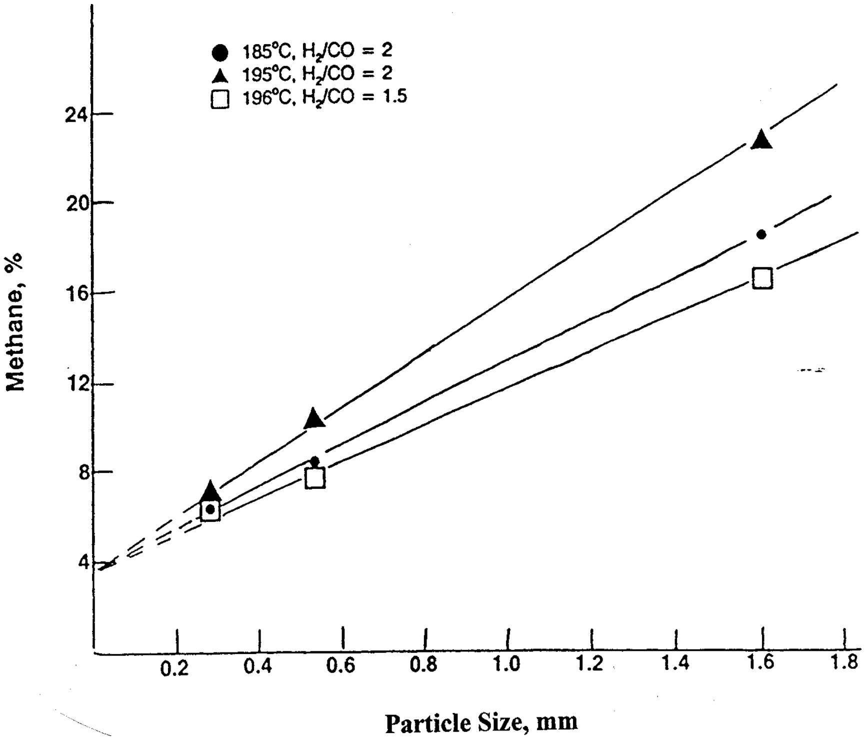

Figure 2. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

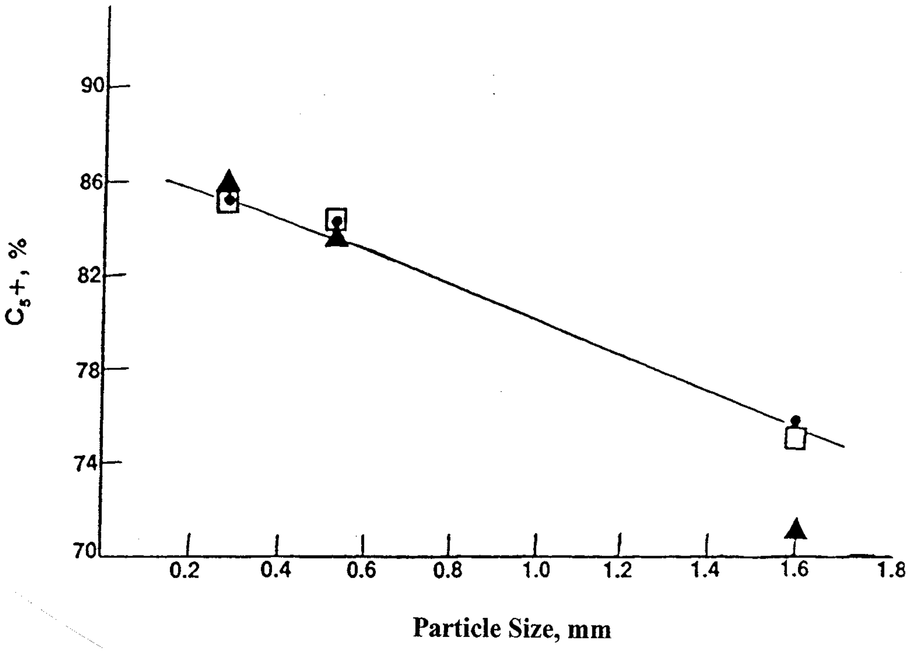

Figure 3. C_5+ product selectivity for three particle size catalysts in fixed-bed reactor (! , 185°C, H_2/CO = 2; ▲, 195°C, H_2/CO = 2; G, 195°C, H_2/CO = 1.5) (from XII.17).

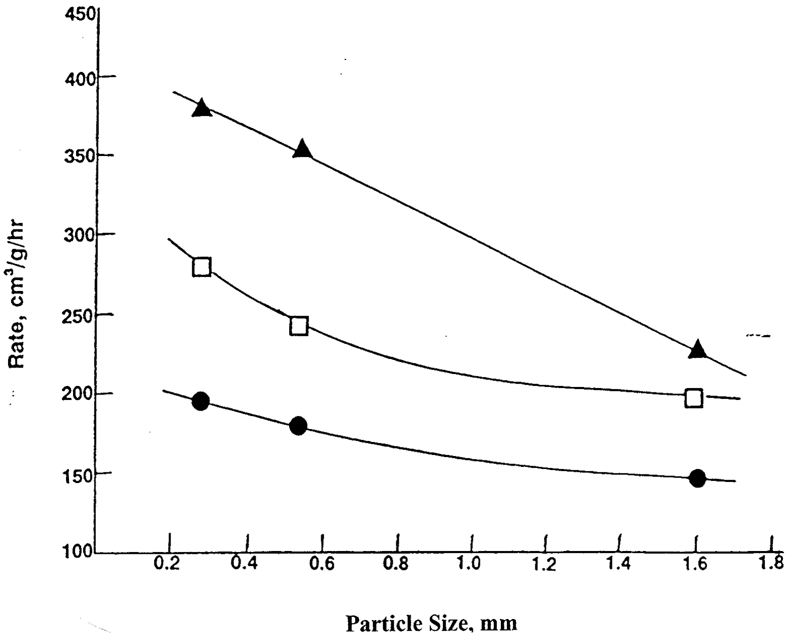

Figure 4. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (! , 185°C, H_2/CO = 2; ▲, 195°C, H_2/CO = 2; G, 195°C, H_2/CO = 1.5) (from XII.17).

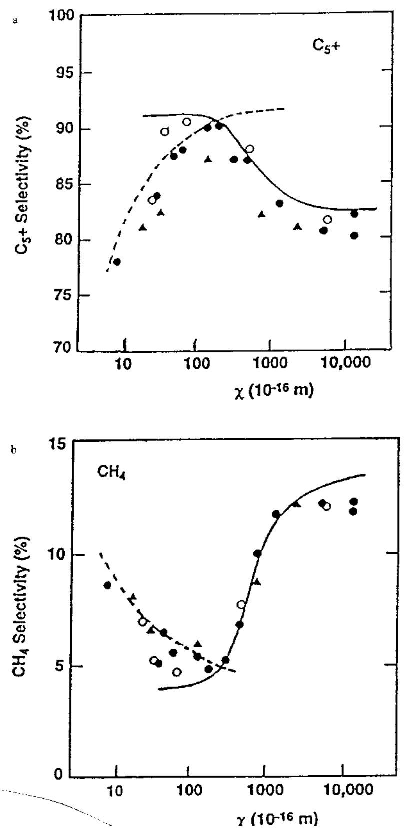

Figure 5. The effect of structural parameters (X) on FTS selectivity. Diffusion-enhanced readsorption (---) and diffusion-inhibited chain growth ( ))))) simulations and experimental data (! , dispersion/support effects; ▲, pellet size variations; F , egghsell thickness variations. Top) C_5+ selectivity; bottom) CH_4 selectivity [473 K, 2000 kPa, H_2/CO = 2.1, 55-65% CO conversion] (X values from eq. 2 with r_p and R_o in m and θ_{Co} in surface Co atoms m^{-2}) (from E. Iglesia in "Natural Gas Conversion IV," (M. De Pontes, R. L. Espinoza, c. Pl. Nicolalides, J. H. Schulz and M. S. Scurrell, eds.), Elsevier, Amsterdam, 1997, pp 153-162).

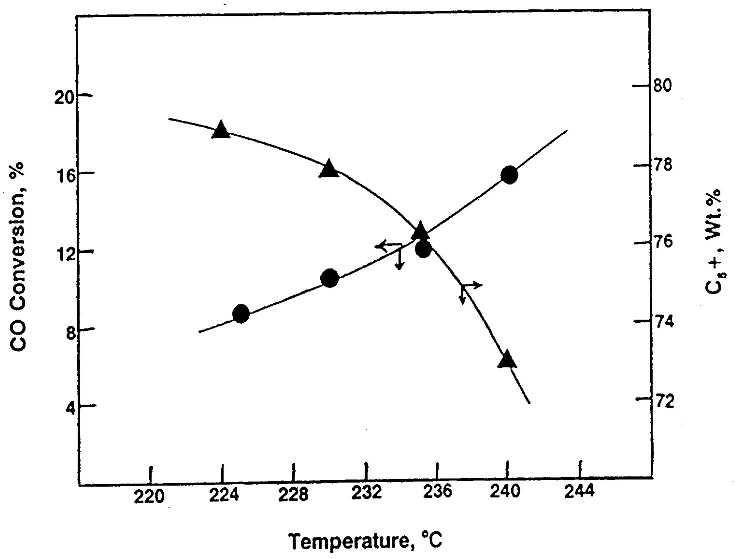

Figure 6. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

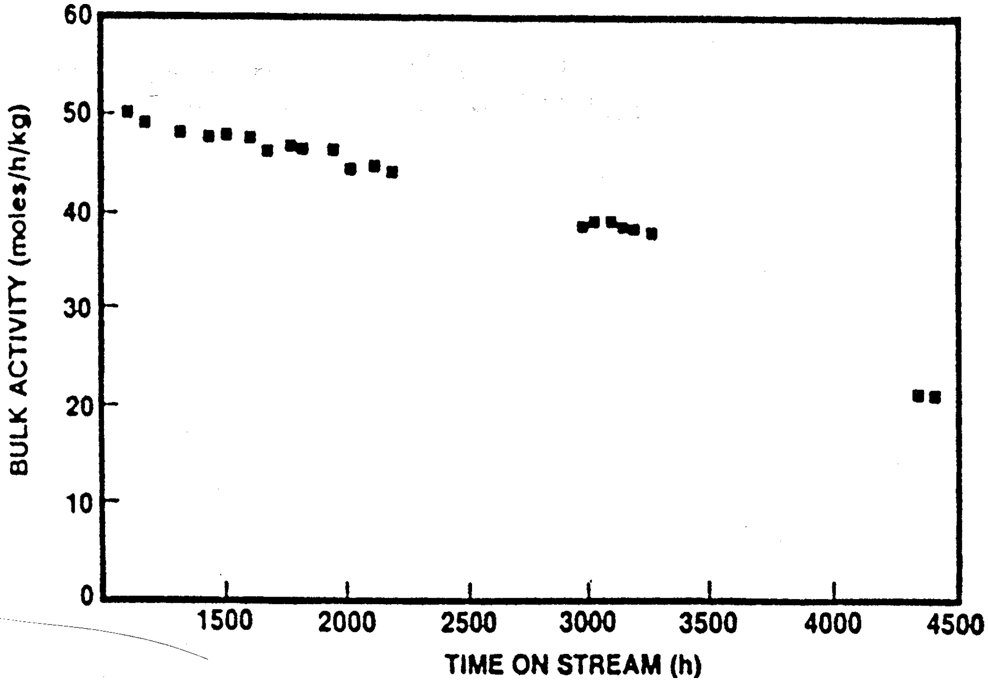

Figure 7. Bulk activity maintenance for extended slurry reactor test of catalyst at baseline conditions (260°C, 2.07 Mpa, CO/H_2 = 1.0, and SV = 2.0 nL/h per g of catalyst).

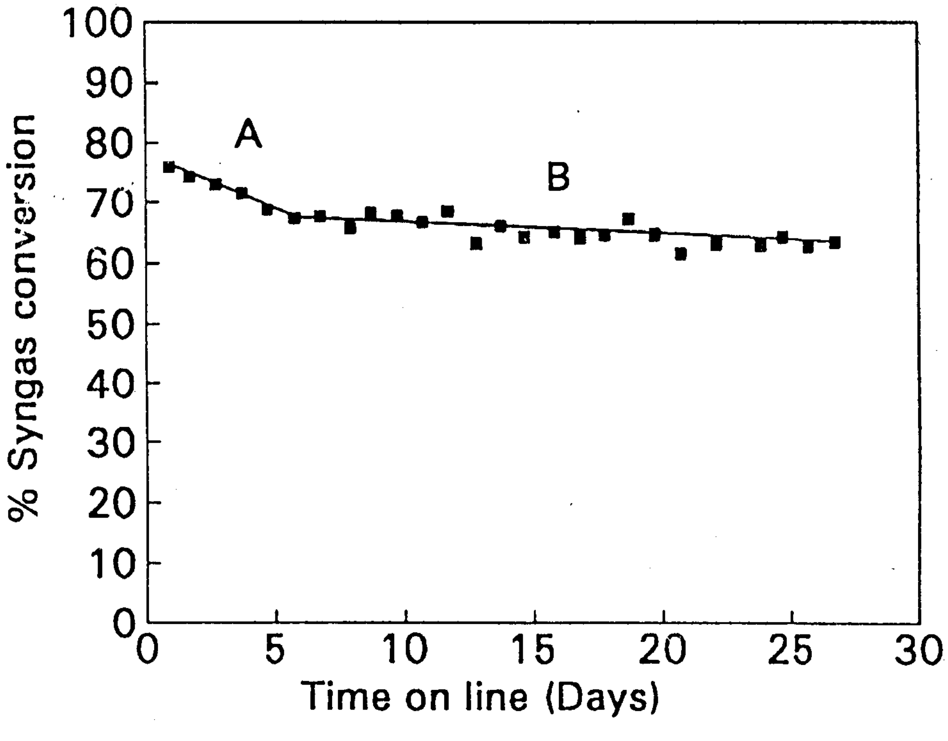

Figure 8. Stability run with a cobalt catalyst (period A, conditioning phase; B irreversible, slow deactivation) (from P. J. van Berge and R. C. Everson, Natural Gas Conversion IV, 107, 207 (1997)).

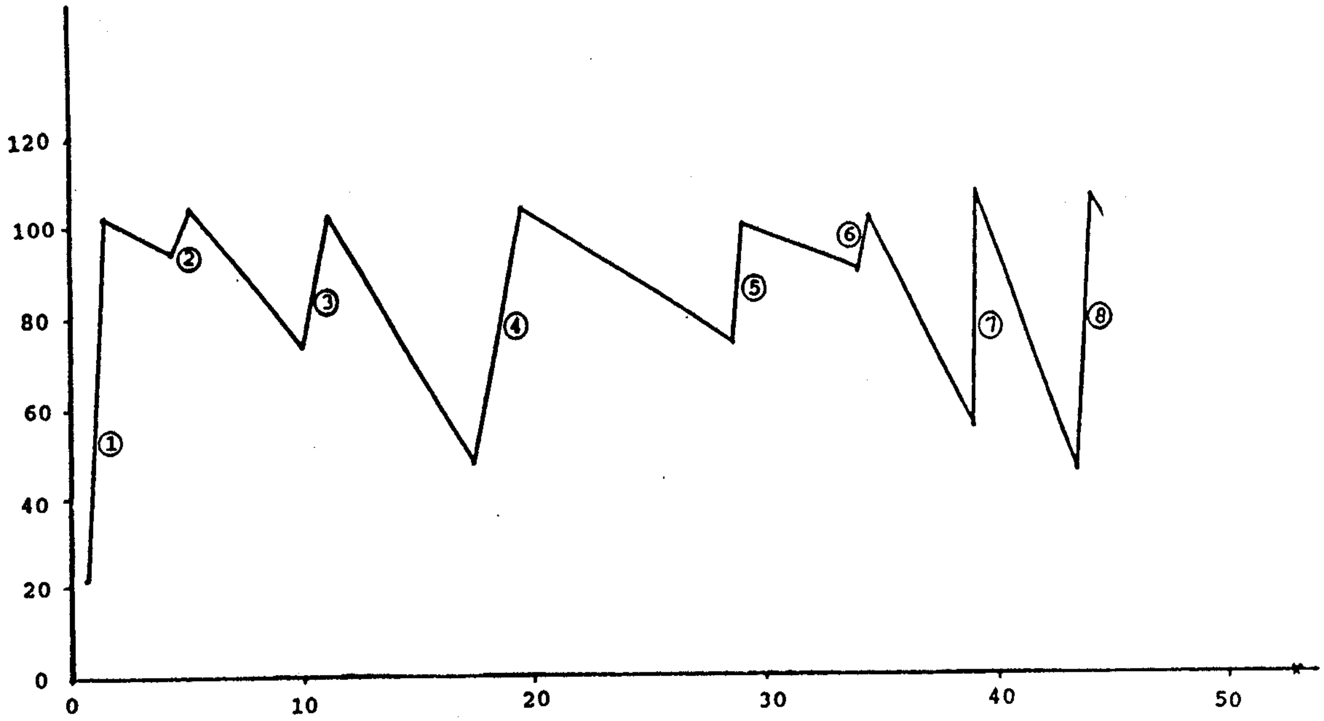

Figure 9. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

ATTACHMENT I

FT Catalyst Promoter - Patents

1. J. J. C. Geerling, A. Hoek, H. M. Huisman, and P. W. Lednor, WO 9825870 A1, 06/18/98 (Shell International). A supported (e.g., titania) cobalt/manganese with a Co/Mn molar ratio of 7-14/1 - shows, at high GHSV and low Co/Mn ratios, a high activity and C_5+ productivity even at relatively high gas hourly space velocity (GHSV).
2. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Paulus and D. Schadenhorst, WO 9700231 A1, 01/03/97 (Shell International). Co + Mn and/or V is supported on a carrier, e.g., TiO_2 is effective for use in a process for the manufacture of hydrocarbons from synthesis gas.
3. P. J. M. Rek and P. Blankenstein, EP 583837 A1, 02/23/94 (Shell International). This patent application provides a method for the preparation of a catalyst or catalyst precursor that comprises a refractory oxide, solvent and peptizing agent that are mixed and neutralized with salt of catalytic active component (e.g., Group VIII metals).
4. C. J. Kim, U.S. Patent 5,227,407, 07/13/93 (Exxon R&E Co.) A syngas with added water is passed over a catalyst containing Co, Ru, or their mixtures, preferably on a TiO_2 support, produces an increased amount of C_5+ and a decreased amount of CH_4, compared to conversions with the same catalyst without added water.
5. B. Sandra and A. L. Chaffee, WO 9305000 A1, 03/18/93 (Broken Hill Pty. Co. Ltd., Australia) A catalyst consists of Co and scandium incorporated into a zeolite.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/28/92 (Shell International). A catalyst composed of a Group VIII metal (Fe, Co, Ni) on refractory oxide (e.g., alumina, silica, titania, zirconia or mixtures of these) and then extruded into shapes is suitable for producing hydrocarbons from syngas.
7. S. L. Soled, E. Iglesia and R. A. Fiato, U.S. Patent 5,162,284, 11/10/92 (Exxon Res. & Eng. Co.). Cu promoted Co-Mn spinel ($Co_{3-x}Mn_xO_4$ with x = 0.5 to 1.2) are effective for converting syngas to a product rich in low molecular weight alkenes. The synthesis includes the use of an α-hydroxy aliphatic carbonylic acid (e.g., citric or glycolic acid) and Cu = 0/1-5 g-atom% of Co + Mn.
8. J. W. Geus and E. Boellaard, EP 466268 A1, 01/15/92 (Shell International). Alloys of 2 or more Group VIB, VIIB and VIII elements, in which the alloys (metals) have negative heat of formation and the metal may be in the form of carbide, are suitable catalyst or catalyst precursor for hydrocarbon synthesis from syngas.
9. J. T. Miller and C. A. Radlowski, CA 2018611 AA, 12/13/90 (Amoco Corp.). Nitrates of Co, Zn and Na were precipitated at pH 10 and calcined and these solids are effective catalysts for the production of olefins or higher alcohols from synthesis gas.
10. Anon. UK, Res. Discl (1991), 323, 180. A honeycomb support for Co promoted with ZrO_2 or Pt or Pd is used to prepare a Fischer-Tropsch catalyst.
11. S. Eri, T. Riis, G. Marcelin and J. G. Goodwin, Jr., WO 9007377 A1, 07/12/90 (Statoil). Co with a second metal (Pt, Ir and/or Rh) on alumina support is used for hydrocarbon synthesis.

12. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. Patent 4,889,763, 11/14/89 (Statoil). Co, Re and alkali (K) are supported on alumina; a metal oxide promoter may also be present. The composite may be used to convert synthesis gas to hydrocarbons.

13. S. Eri and J. G. Goodwin, Jr., U.S. 4,857,559, 08/15/89 (Gas-to-oil, Inc., U.S.A.) Co-Re-alumina which may contain another metal oxide promoter is useful to produce hydrocarbons from synthesis gas.

14. J. G. Miller, G. M. James and J. A. Rabo, ZA 8806952, 05/30/89 (Union Carbide). Co containing LZ-210 zeolite that contains a Mo oxide promoter produce products that exhibit lower methane yield, higher C_5+ hydrocarbons, increased olefins and longer catalyst life..

15. S. L. Soled, R. A. Fiato and E. Iglesia, EP 319625 A1, 06/14/89 (Exxon Res. & Dev. Co.) A catalyst comprised of Co-Ru on TiO_2 support can be regenerated without removal from the reactor: it produces 7.9% CH_4 and 85.7% C_5+ at GHSV 1200 h^{-1}. Co and Ru are dispersed within the same crystallite.

16. S. Eri, J. G. Goodwin, Jr., G. Marcelin and T. Riis, U.S. 4,801,573, 01/31/89 (Statoil). Co-Re on alumina, to which a metal oxide promoter may be added, exhibits a higher activity than either Co or Re alone.

17. W. C. Behrmann, C. H. Mauldin, K. B. Arcuri and M. Herskowitz, EP 266898 A1, 05/11/88 (Exxon Res. & Dev. Co.). A catalyst consisting of a metal film of 0.02-0.25 mm thickness is deposited on the surface of a particulate support; Co and Re are repeatedly deposited on preheated TiO_2 substrate as thin layer (60-160 µm) to prepare the catalyst which is suitable for hydrocarbon production from

syngas. The composite has very high hydrocarbon productivity and low CH_4 selectivities.

18. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,738,948, 04/19/88 (Exxon Res. & Dev. Co.). Co-Ru is deposited on a refractory oxide, and then oxidized and reduced to form a catalyst with the Co and Ru in intimate contact. This catalyst produces 93 mol% C_5+ and 3.4 mole% methane whereas a similar catalyst without Re produces 85 mol% C_5+ and 7 mole% methane.

19. P. N. Dyer, R. Pierantozzi and H. P. Withers, U.S. 4,670,472, 06/02/86 (Air Products & Chemicals, Inc.). An inert carrier was treated with a Group IVB metal compound, then impregnated with decomposable metal compound (e.g., Co, Fe or Ru carbonyls) to produce a catalyst precursor. Reactions with air or water and calcination are specifically avoided. Instead the catalyst was contacted with the synthesis gas.

20. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, EP 221598 A1, 05/13/87 (Shell International) Fe, Ni or Co is deposited on SiO_2 along with one or more Group VIII noble metal promoters and, in addition, may contain Zr. The specific example is Pt-Co-Zr-SiO_2 with 0.1:10:0.9:100 weight parts.

21. C. H. Mcateer and B. Nay, WO 8607350 A1, 12/18/86 (British Petroleum Co.) A catalyst with $Co_aA_bL_{ac}CeO_x$ (A, alkali metal with a = 0-0.25%; b = 0-5%, x = number to satisfy equation) is prepared. A procedure for preparing a pellet also includes an activation procedure.

22. C. J. Kim and R. A. Fiato, U.S. 4,624,968, 11/25/86 (Exxon Res. & Dev. Co.) Fe/Ce/Zn/K, Re-Mn-K or Fe-Co-K catalysts are used in first stage and then the

exit gas is converted to heavier produces over Ru/TiO_2, Ru/SiO_2 or Ru/Al_2O_3 catalyst in a second stage.

23. J. H. Brophy, F. J. J. Font, M. Helena, D. J. H. Smith and C. D. Telford, WO8605775, 10/09/86 (British Petroleum Co.). Hydrocarbons are preferably produced by Fischer-Tropsch reaction over a Group VIII metal oxide or sulfide in presence of 1-40 mole% unsaturated hydrocarbon, preferably ethylene. Support utilized include: alumina, C, silica, zirconia, titania, MgO, ceria, gallia and can contain an acidic component such as a zeolite or amorphous silica-alumina.
24. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, U.S. 4,585,798, 04/29/86 (Gulf Oil). Co and Ru are impregnated by nonaqueous technique on alumina support and can contain another promoter (Ca, Mg, Th, or rare earth or rare earth mixtures).
25. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86 (Shell International). Co + 0-100 wt. parts of element Zr, Ti, Cr and Ru are supported on alumina, silica or silica-alumina and the material formed to be suitable for fixed-bed catalyst.
26. P. K. Coughlin, WO 8600296 A1, 01.16/86 (Union Carbide Corp.). Co with or without Th (1-50 mol%) and an additive (Mo and/or W) on a zeolite or non-zeolite molecular sieve is used as catalyst for converting synthesis gas to hydrocarbons.
27. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, ZA 8505317, 03/26/86 (Gulf Res. & Dev. Co.) Diesel fuel is produced from synthesis gas using a Co(5-25%)-Ru(0.01-0.5) on a support. The support can be alumina or silica and is in the 10-110 µm size range. Data show diffusion limitations in large catalyst particles in fixed bed reactors but not with the small particles in the slurry reactor.

28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85 (Shell International). In first step, syngas is converted to hydrocarbons using a Co(3-60)-Zr(0.1-100)/SiO_2 (100) under specified conversion levels, the water removed and the gaseous products passed to second step using a mixture of two catalysts [Co-Zr/silica and Cu-Zn/alumina].

29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). A catalyst containing silica 100, Co (15-50) and 2nd metal (Zr, Ti, Ru or Cr) is prepared by sequential impregnations with Co and the 2nd metal.

30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudhoelter, EP 142888 A2, 05/29/85 (Shell International). A first stage Ni-Ca-K-alumina catalyst and a second stage Co-Zr-silica catalyst are employed.

31. J. K. Minderhoud and S. T. Sie, GB 2146350 A1, 04/17/85 (Shell International). Zr-Co-silica was used for hydrocarbon synthesis in the first stage of the process.

32. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84 (Shell International). A three-step impregnation of silica with Zr and one-stem impregnation with Co was followed by kneading/calcining to produce catalyst particles active for hydrocarbon synthesis from syngas.

33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702, 05/30/84 (Shell International). Zr- or Ti-promoted Co-silica are used to produce hydrocarbons.

34. A. Hoek, J. K. Minderhoud, M. F. M. Post and P. W. Lednor, EP 110449 A1, 06/13/84 (Shell International). a catalyst is prepared in which a Zr or Ti compound is added to silica by impregnation, then calcined and then impregnated with a Co compound, calcined and reduced.

35. H. Beuther, C. L. Kibby, T. P. Kobylinski, and R. B. Pannell, U.S. 4,413,064, 11/01/83 (Gulf Oil). Finely divided alumina is impregnated with a Co salt, the product is dried and then contacted with aqueous or nonaqueous solution of salts of Ru and Group IIIB or IVB metals is active for the production of hydrocarbons from synthesis gas.

36. T. P. Kobylinski, U.S. 4,088,671, 05/09/1978 (Gulf Res. & Dev. Co.). A process for the conversion of synthesis gas to hydrocarbons having only a minor amount of methane utilizes a catalyst consisting of a major amount of cobalt and a minor amount of ruthenium as the active catalytic components. A sub-claim indicates that the catalyst can contain an inert support. The standard cobalt catalyst was prepared following a recipe that is, or is similar, the standard German cobalt catalyst and consists of Co, Mg and Th on kieselguhr support. Cobalt can comprise from 1 to 50 wt.% of the finished catalyst. The molar ratio of cobalt to ruthenium in the finished catalyst can be from 5:1 to about 200:1. The active catalytic materials are "distended" on a suitable support material. Those metal oxides typically used can be employed to prepare the Co-Ru catalyst. Examples of suitable supports include oxides of the metals of Groups II, III, IV, V and VIB of the Periodic Chart [old style; Group VIB is obviously intended to be IVB as described in a following sentence]. The oxides of Group II, IIIA, and IVB are preferred, e.g., alumina, boria, zinc oxide, magnesia, calcium oxide, strontium oxide, barium oxide, titania, zirconia and vanadia. It is further stated that a combination of these metal oxides, e.g., silica-alumina, can be used. The support can be natural occurring or synthetic, and examples include: kieselguhr, carbon, attapulgite clays, diatomaceous earth, activated carbon, coke, charcoal,

and molecular sieves (both X and Y type). The method employed to deposit the catalytic metals onto the support is not critical, and any technique well known to those having ordinary skills in the art to distend the catalytic metals in a uniform thin layer on the catalyst support is suitable. The catalyst is normally dried, calcined and reduced in a gas such as flowing hydrogen. The interpretation of a phrase from a subclaim is critical: "...with a catalyst consisting essentially of a major amount of cobalt and a minor amount of ruthenium distended in a uniform, thin layer on a catalyst support..." One interpretation of the meaning of the phrase enclosed in quotes is that it includes "rim-loaded" catalysts. The patent covers operating temperatures from 60 to 450^{o}C and pressures from atmospheric to 300 psig. In the body of the patent it is written that, "...using the catalysts of this invention can occur in a fixed, fluid or moving bed type of operation, and the type of operation would not appear to be critical." This patent expired after 17 years from the issue date so that it now falls within the public domain and does not restrict its use. A catalyst falling within this description was used in a bubble column reactor that was reported in a 1985 South African patent application.

ATTACHMENT II

FT Supports - Patents

1. P. Blankenstein, J. J. C. Geerlings, H. M. Huisman, P. W. Lednor and B. J. Van Liemt, WO 9811037 A1, 03/19/98 (Shell International). A catalytically active metal (e.g., Co) is supported on titania having a rutile/anatase ratio less than 2/3 and surface area < 75 m^2/g is used to prepare C_5+ hydrocarbons from synthesis gas.
2. L. A. Rivas, E. Peluso, D. Rojas, J. J. A. Garcia, U.S. 5,648,312, 07/15/97, (Intevep, S.A., Venez.). Spherical particles of a homogeneous mixture of two refractory inorganic carbides, nitrides or mixtures, with surface area > 30 m^2/g and a particle size > 0.1 mm can be used as a support Group IVB and VIII metals in a catalyst system active for the conversion of synthesis gas to C_2+ hydrocarbons.
3. R. Zennaro, A. Gusso and M. G. Clerici, EP 756895 A2, 02/05/97 (Agip Petroli S.P.A., Italy; Institut Francais Du Petrole). A method to prepare a catalyst utilizes an inert support and Co, Ru and a third element, scandium or yttrium. The process includes a sequence of steps for preparation and then calcination, reduction, and passivation steps.
4. J. J. C. Geerlings, M. F. Goes, H. M. Huisman, J.-P. Lange, H. Oosterbeek, P. J. M. Rek and D. Schadenhorst, WO 9700231 A1, 01/03/97, (Shell International). Co and Mn and/or V is supported on a carrier, eg, titania, and is used to convert synthesis gas to hydrocarbons.
5. R. L. Espinoza, J. J. Visagie, P. J. Van Berge and F. H. Bolder, EP 736326 A1, 10/09/96, (Sastech Proprietary Ltd.). A process for preparing Fischer-Tropsch

catalysts is prepared by impregnating alumina with an aqueous salt of Co, Fe and mixtures thereof. The sample is dried below atmospheric pressure, and then calcined.

6. D. Reinalda and P. Blankenstein, EP 510770 A2, 10/18/92, (Shell International). Hydrocarbons are produced by contacting a synthesis gas at 125-350°C and 5-100 bar pressure with a catalyst comprising a Group VIII metal (Fe, Co or Ni) on a refractory oxide carries (alumina, silica, titania, zirconia and mixtures thereof). The catalyst particles are helical lobed shape made by extrusion through a die plate such as a 2 mm helical trilobe.

7. S. L. Soled, E. Iglesia, R. A. Fiato and G. B. Ansell, U.S. 5,169,821, 12/08/92, (Exxon Res. & Eng. Co.). A stable high-temperature Fischer-Tropsch catalyst has the general formula $Co/Ti_xM_{1-x}O_2$ where x = 0.01 to 0.14 selected from Si, Zr, and Ta where titania is anatase. Activation of the composite includes drying and calcining followed by reduction of the Co.

8. D. Reinalda, P. Blankenstein and A. Derking, EP 510771 A1, 10/28/92, (Shell International). A process for the preparation of extruded SiO_2-based catalysts, containing elements from Group VIIB or Group VIII and a promoter from elements in Group IVB is described.

9. A. H. Joustra and B. Scheffer, EP 455308 A1, 11/06/91 (Shell International). The preparation of alumina-based extrudates containing Co, Fe, or Ni is described.

10. E. Iglesia, H. Vroman, S. L. Soled, J. Baumgartner and R. A. Fiato, EP 434284 A2, 06/26/91 (Exxon Res. & Dev. Co.). Supported Co catalysts are prepared by depositing a metal on a suitable support, eg, silica. Rim-loaded catalysts are

obtained by contacting the support with a molten salt. Non-rim-loaded catalysts may be prepared in a similar manner.

11. D. Reinalda and J. Dars, EP 421502 A2, 04/10/91, (Shell International). A Co compound is applied on a porous inert support, dried and then calcined in an atmosphere with greater than 20 volume% NO_x.

12. C. H. Mauldin and K. L. Riley, U.S. 4,977,126, 12/11/90, (Exxon Res. &. Eng. Co.). A film layer of catalytically effective amounts of Co is deposited on the peripheral outer surface of a porous inorganic oxide, especially TiO_2.

13. E. Iglesia, S. L. Soled and R. A. Fiato, U.S. 4,960,801, 10/02/90 (Exxon Res. &. Dev. Co.). A catalyst with Co present on a TiO_2 support that contains up to 15 wt.% SiO_2 is described.

14. C. H. Mauldin and K. L. Riley, EP 370757 A1, 05/30/90, (Exxon Res. & Dev. Co.). A catalyst support with 0.1-20% of inorganic metal oxide binder (alumina, silica, zirconia or titania) is utilized. A Group VIII metal, preferably Co or Co plus additional metal or metals, is deposited on the support.

15. J. G. Miller and J. A. Rabo, U.S. 4,874,732, 10/17/89, (UOP). A catalyst having improved selectivity for C_5+ hydrocarbons consists of a Co containing acid zeolite that additionally contains Mn oxide or Mn oxide and Zr oxide promoters.

16. E. Iglesia, S. Soled and R. A. Fiato, U.S. 4,794,099, 12/27/88, (Exxon Res. & Dev. Co.). Silica (to 15%) or silica precursor is incorporated into a Co-containing catalyst on an inorganic refractory titania support. Re can also be present.

17. W. C. Behrmann, C. H. Mauldin, B. K. Arcuri and M. Herskowitz, EP 266898 A2, 05/11/88, (Exxon Res. & Dev. Co.). Metal is deposited alone or with a promoter as film on support.

18. K. P. De Jong, J. H. E. Glezer and M. F. M. Post, (Shell International). A Fischer-Tropsch catalyst contains Fe, Ni or Co deposited on silica with additional Group VIII metal(s). The catalyst may also contain Zr.

19. T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy, U.S. 5,605,679, 08/12/86, (Chevron Res. Co.). A Co-based catalyst is prepared by impregnation of Co carbonyl on alumina or silica and then activating in sequential steps of reduction in hydrogen, oxidation, and re-reduction in hydrogen.

20. P. F. Meier and F. Pennella, U.S. 4,623,669, 11/18/86, (Phillips Petroleum Co.). A metal is vaporized in the presence of a solvent and condenses to form a solid mixture; this is warmed to form a metal-solvent slurry which is then contacted with a support and then the solvent is removed. Co evaporation into toluene followed by deposition on a silica support was the example preparation.

21. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,605,680, 08/12/86, Chevron Research Co.). Alumina is used to support Co and one or more Group VIII or IVB metal oxide promoters.

22. E. J. R. Sudhoelter, EP 180269, 05/07/86, (Shell International). Co-silica catalyst preparation procedure is described wherein silica is obtained from a Si halogen, alkoxy and/or acyloxy).

23. A. I. Foster, R. W. Joyner, J. J. McCarroll, S. R. Partington, R. G. L. Spiers and S. R. Tennison, WO 8601499 A1, 03/13/86, (British Petroleum Co.). Co or Fe (with option of including Pt) is deposited on a C support.

24. D. Bode and S. T. Sie, EP 188304 A1, 07/23/86, (Shell International). Co, and one or more of Zr, Ti, Cr and Ru is deposited on a silica, alumina or silica-alumina support.

25. P. K. Coughlin, WO 8600296, 01/16/86, (Union Carbide Corp.). Co with Th promoter and 1-50 mole% (based on Co) of an additive (e.e, Mo and/or W) supported on a zeolite, SAPO or non-zeolite molecular sieve.

26. H. Beuther, T. P. Kobylinski, C. L. Kibby and R. B. Pannell, ZA 8505317, 03/26/86, (Gulf Res. & Dev. Co.). Co (5-25 WT.%) and Ru (or other promoters, 0.01-0.5 wt%) is deposited on a support. The average particle diameter is 10-110 micron size and is suitable for use as slurry phase conversion of synthesis gas to hydrocarbons.

27. V. L. Payne and C. H. Mauldin, U.S. 4,595,703, 06/17/86, (Exxon Res. & Eng. Co.). Co is dispersed on a TiO_2 or ThO_2 support that, when titania, has greater than 2:3 rutile-anatase ratio.

28. M. F. M. Post and S. T. Sie, EP 153781 A2, 09/04/85, (Shell International). A two step process for converting synthesis gas to diesel range fuels. In the first stage a Fischer-Tropsch catalyst containing Co (3-60)-Zr(0.1-100)-SiO_2(100) so that conversion is in range $(F - 0.5)/(F + 2)(150) < C < (F - 0.5)/(F + 1)(250)$, where F is syngas flow and C is syngas conversion. After water removal, the gaseous products are separated and contacted in the second step with two catalysts (e.g., Co-Zr-SiO_2 (I) and Cu-Zn-alumina (II).

29. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142887 A2, 05/29/85 (Shell International). Hydrocarbon steam reforming produces a syngas that is converted with a Fischer-Tropsch catalyst containing SiO_2 (100), Co (15-50) and a second metal (chosen from Zr, Ti, Ru or Cr) (> 0.1). The catalyst is prepared by sequential impregnation.

30. J. K. Minderhoud, M. F. M. Post, S. T. Sie and E. J. R. Sudholter, EP 142888 A2, 05/29/85, (Shell International). C_9+ hydrocarbons are manufactured in a two stage process consisting of steam reforming of C_1-C_4-hydrocarbons with a Ni-containing catalyst followed by Fischer-Tropsch synthesis with a Co-containing catalyst (e.g., Co:Zr:SiO_2 = 25:18:100).

31. J. K. Minderhoud and M. F. M. Post, EP 127220 A2, 12/05/84, (Shell International). Fischer-Tropsch catalysts were prepared by a three-step impregnation of silica with a solution of zirconium tetrapropoxide in a propanol-benzene, then aqueous cobalt nitrate, kneading and then calcination.

32. R. S. Sapienza, M. Sansone and W. A. R. Slegier, U.S. Patent Application 482372, 06/22/84, (United States). A catalyst for converting synthesis gas to hydrocarbons contains 0.1-10:10-70 (wt.%) Pd or Pt-Co-alumina where alumina does not show an XRD peak for alumina. The catalyst was prepared by impregnating a Pd/Al_2O_3 catalyst with Co_2(CO_8 in the reactor and then heating with synthesis gas to the reaction temperature.

33. J. K. Minderhoud, M. F. M. Post and S. T. Sie, EP 109702 A1, 05/30/84, (Shell International). A catalyst with the composition 0.9:25:100 wt Zr-Co-silica was used for Fischer-Tropsch synthesis.

34. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. 4,413,064, 11/01/83, (Gulf Res. & Dev. Co.). A catalyst suitable for use in a fluidized reactor was prepared by impregnating finely divided alumina support with a Co salt, drying, and then contacting with a nonaqueous solution containing salts of Ru and a Group IIIB or IVB metal.

ATTACHMENT III

The Preparation of Cobalt Fischer-Tropsch Catalysts - Literature from 1962

Cobalt Fischer-Tropsch catalysts has been widely investigated in recent years due to its high activity and selectivity for the synthesis of long-chain hydrocarbons. In this review, we summarize preparation methods of cobalt Fischer-Tropsch catalysts. The effect of precursors, promoters, support materials and pretreatment conditions are covered. These effects arise at the level of a catalytic site and reflect the influence of site structure, composition and electronic properties on the rate of the primary chain growth and the selectivity of catalysts. Such modifiers for metal catalysts have been hypothesized to act by the structural modification of the metal surfaces that is induced by a promoter (III.1-III.3), by blockage of the active catalytic sites by the modifier (III.4), by charge transfer between the modifier and the metal (III.5,III.6), by direct chemical interactions between the modifier and the active intermediates (III.7) and/or by the effect of the electrostatic field of the modifier ions (III.8-III.10). As to cobalt catalysts, work has been done on the promotion effect of potassium, zirconium, ruthenium, platinum, rhenium, etc.

The noble metal promoter has been suggested to have a number of different ways of affecting catalyst performance. It has been proposed that it acts as a source of hydrogen spillover (III.11), that it increases the reducibility of cobalt (many), that it preserves activity by preventing the buildup of carbonaceous deposits (III.12), that it exhibits cluster and ligand effects (III.13), and that it provides a combination of enhanced cobalt reducibility and dispersion (III.14). It has even been reported that the addition of a second metal component may have no, or a detrimental, effect on CO hydrogenation activity (III.15).

Ruthenium promoters have been reported (III.13, III.16-III.20). Two papers (III.16,III.20) indicate the use of alumina as support material and the preparation of the catalyst using an incipient wetness impregnation method. Cobalt nitrate hexahydrate, ruthenium nitrosyl nitrate and ruthenium chloride were used as precursors. The incipient wetness impregnation was carried out in a single step followed by drying and calcination. Some catalysts, however, were prepared by sequential impregnation of cobalt and ruthenium with intermediate drying, calcination, or reduction in order to determine the ways that differences in catalyst preparation influence catalyst performance. Co-Ru/Al_2O_3 catalysts described in these references contained 20 wt% cobalt and 0.5 wt% ruthenium. Their results indicate that the addition of small amounts of ruthenium on alumina-supported cobalt catalysts facilitate the reduction of the cobalt. This conclusion was based on the lowering of the reduction temperatures during temperature programmed reduction (TPR) by approximately 100^{o}C and essentially complete reduction of the Ru-promoted catalyst (CoRu/Al_2O_3) at 350^{o}C compared to only a 60% reduction of the unpromoted Co/Al_2O_3 catalyst. In parallel, the amount of metal atoms exposed on the surface, determined by hydrogen chemisorption, increased by a factor of three upon ruthenium promotion.

Catalyst activity was obtained by the conversion of a helium diluted H_2/CO mixture (H_2/CO = 10; 20 cc/min H_2; 2 cc/min CO; total flow 100 cc/min; H_2 = 8 NL/hr•g-cat.; CO = 0.8 NL/hr•g-cat; total flow 40 NL/hr•g-cat). The catalyst bed consisted of 15 mg catalyst diluted with 15 mg of quartz powder. The reaction was conducted in a fixed-bed reactor at 220^{o}C and 1.8 atm. The catalyst contained 20 wt.% cobalt and, if present, 0.5 wt.% ruthenium. If the rate (µmole/gCo•s) is assumed to be based on CO, we calculate that 25 µmole/gCo•s corresponds to 0.25 gCH_2/hr•g-cat and 50 µmole/gCo•s corresponds to 0.5 gCH_2/hr•g-cat (Figure III.1). From the data shown in Figure III.2, the temperature of reduction (300, 350 and 400^{o}C) does not impact the reaction rate; however, the calcination temperature does and the catalyst calcined at 300^{o}C is about twice as active as the material after calcination at 400^{o}C.

An increase in surface exposed metal atoms was paralleled by an equivalent increase in the rate of CO hydrogenation, yielding practically constant turnover frequencies (Figure III.3). Steady-state isotopic transient kinetic analysis (SSITKA) results indicated constant intrinsic activities but an increase in the number of reaction intermediates at constant coverages when a Ru-promoted catalyst was compared to the unpromoted cobalt catalyst. There was little change in product selectivity. Promotion with more than 0.5% Ru improved the catalyst characteristics only marginally. From these results they conclude that ruthenium acts only as a reduction promoter for cobalt by increasing the reducibility and dispersion of the cobalt. These results for Ru promotion are compatible with those recently reported for Pt-promoted cobalt FTS catalysts (III.21).

As shown in Figure III.4, the presence of ruthenium increases the rate of hydrocarbon production by up to a factor of four. Iglesia et al. (III.13) reported that ruthenium promotion of silica- and titania-supported cobalt catalysts caused a synergistic effect since the specific rates for CO hydrogenation, expressed as turnover frequencies (TOFs) based on hydrogen chemisorption, increased with addition of small amounts of ruthenium. They attributed this improvement to the hydrogenation activity of ruthenium and its ability to decrease, or prevent, carbon formation on the surface of cobalt. In contrast to Iglesia et al., Kogelbauer et al. (III.16) conclude that surface enrichment of ruthenium is unlikely for the alumina supported cobalt-ruthenium catalysts.

Belambe et al. (III.20) reported methane selectivities in the range of 70-85% for the cobalt catalysts tested in Goodwin's laboratory (Table III.1) and attributed this to the high H_2/CO ratio (=10) that they used. The Anderson-Schulz-Flory (ASF) alpha values obtained by Belambe et al. were in the range of 0.37 for the aged, steady-state catalysts and 0.4-0.42 for the fresh catalyst (Table III.1). Ruthenium appeared to inhibit the formation of highly irreducible cobalt species (cobalt oxide strongly interacting with the support to form cobalt aluminates) or to promote their reduction, indicated by the absence of the broad, high-temperature TPR feature observed with Co/Al_2O_3 and the greater degree of reduction. Calcination of Ru/Al_2O_3 or Co/Al_2O_3 precursors prior to a sequential impregnation of cobalt or ruthenium, respectively, impeded the intimate mixing of the metal components. Coimpregnation of the metal salts appeared to produce catalysts slightly more active for CO hydrogenation.

They (III.20) also investigated the effect of calcination and reduction temperatures on the activity of a Ru-promoted 20 wt% Co/Al_2O_3 catalyst for the CO hydrogenation reaction by steady-state reaction and SSITKA (III.20). While reduction temperature in the range 300-450°C had at most a negligible effect, calcination temperature was found to have a significant effect on the overall activity of this catalyst. The overall catalyst activity decreased with increasing temperature of calcination (Figure III.2). However, pretreatment temperatures did not affect the intrinsic activity of the catalyst sites. The decrease in CO hydrogenation rate with increasing calcination temperature was found to be attributable to a decrease in the number of surface active sites due to a decrease in the reducibility of the catalyst. The SSITKA results, which showed no change in the surface residence time for CH_4 intermediates with increasing calcination temperature, as well as the TOF results, confirmed that there was no change in the intrinsic activity of the sites producing methane. Neither the reduction nor the calcination conditions had any effect on chain growth probability. Calcination temperature did have, however, a small effect on CH_4 selectivity.

A study of CO hydrogenation on La^{3+}-promoted Co/SiO_2 catalysts (La/Co atomic ratios of 0-0.75; Cab-O-Sil silica support) has been performed by Haddad et al. (III.21) using both global rate measurement and SSITKA. The prereduced and passivated base catalyst containing 20% cobalt was impregnated by incipient wetness with the appropriate amount of an aqueous solution of $La(NO_3)_3{\bullet}5H_2O$ to obtain catalysts with La/Co atomic ratios of 0.0, 0.05, 0.1, 0.2, 0.3, 0.5 and 0.75. After impregnation, the catalyst was allowed to dry in an oven overnight at 90^{o}C. Finally, it was re-reduced in hydrogen at 350^{o}C for 22 h and passivated at 25^{o}C.

Aqueous impregnation of Co/SiO_2 with La^{3+} led to a significant decrease in the number of intermediates leading to methane during CO hydrogenation (Figure III.5), but it did not alter the nature of the active sites (III.21). In a previous characterization paper (III.21a) La^{3+} promotion of Co/SiO_2 was shown to moderate strong Co-support interactions brought about by aqueous impregnation of the Co/SiO_2 and to enhance the reducibility of the cobalt oxide. La^{3+} addition to the Co/SiO_2 catalyst was found to lead to a significant increase in the activity for Fischer-Tropsch synthesis (on a per gram cobalt basis) (Figure III.6). It appears that the impregnation to produce the B-La0 (0 means no La^{3+} promoter) catalyst from the B catalyst caused a decrease in the amount of CO adsorbed and in the TON; the reason for this was not given. The SSITKA results showed that the concentration of active intermediates leading to methane increased with increase in La/Co ratio. However, the TOF, the pseudo-first-order rate constant, the reactivity distribution function, and the activation energy were not affected by La^{3+} addition. Thus, it can be concluded that La^{3+} did not change the nature of the active sites, just their concentration. This increase in the concentration of active sites follows exactly the increase in surface Co^o. La^{3+} promotion also caused the chain growth probability (Figure III.7) and the olefin/paraffin ratio (Figure III.8) to increase significantly at 220°C for $H_2/CO=2$.

Ali et al. (III.22) also investigated the influence of zirconia promotion of 20 wt% Co/SiO_2 on FTS using catalysts prepared in different ways and having different loadings of zirconia (up to 8.5 wt%). The catalysts were investigated using FTS ($H_2/CO=2$), H_2-D_2 exchange, and CO dissociation to provide insight into how zirconia modifies the cobalt properties. The Zr-promoted catalysts exhibited higher overall rates of FTS compared to unpromoted Co/SiO_2 (Figure III.9). The sequentially impregnated $Co/Zr/SiO_2$ catalysts appeared to be the most active. However, the coimpregnation method of preparation appeared to result in higher cobalt dispersion. While zirconia promotion did not appear to promote or inhibit hydrogen activation, hydrogen spillover may have been partly responsible for enhancing the activity of the sequentially impregnated $Zr/Co/SiO_2$ catalysts. Zirconia also possibly created an active interface with cobalt that increased catalyst activity by facilitating CO dissociation. Although high levels of promotion tended to increase the selectivity for higher hydrocarbons, zirconia appears to primarily function as an excellent rate promoter for Co/SiO_2.

Huffman et al. (III.23) studied the promotion effect of potassium on cobalt catalysts. The K-promoted Co/Al_2O_3 catalyst was prepared by impregnating the passivated 9.0 wt% Co/Al_2O_3 catalyst with a solution of potassium nitrate in order to have an atomic ratio of K/Co=1. In situ XAFS spectroscopy studies were conducted at reaction conditions on the potassium-promoted cobalt catalysts supported on SiO_2 and Al_2O_3, and on similar samples without potassium. Measurements were conducted at temperatures up to 200^{o}C under both reducing and simulated FTS reaction conditions. Potassium and cobalt K-edge XANES spectra indicate that potassium interacts with both the cobalt phase and the SiO_2 support, and that potassium promotion inhibits the reduction of the Co/SiO_2 catalyst in hydrogen at 200^{o}C. However, under CO hydrogenation conditions in the presence of water vapor, the differences in degree of reducibility are less since the unpromoted catalyst becomes more oxidized. For the K-promoted Co/Al_2O_3 catalyst, Co K-edge XANES and EXAFS spectra show that cobalt is initially present as a mixture of Co_3O_4 and CoO. Under hydrogen at 200^{o}C, these oxides are reduced to a mixture of CoO and cobalt metal. During reaction at 200^{o}C in H_2/CO, the cobalt phases are reconverted to a mixture of Co_3O_4 and CoO. Without potassium, the cobalt in Co/Al_2O_3 is reduced almost completely to cobalt metal under hydrogen at 200^{o}C and remains in that form even during reaction at 200^{o}C in H_2/CO. Only a minor trace of CoO is observed.

Schanke et al. (III.24) undertook studies directed toward explaining the role of platinum as a promoter for hydrocarbon synthesis on alumina-supported and silica-supported cobalt catalysts. In addition to conventional measurements of kinetics and metal surface areas, direct information on reaction rates and surface coverage of reaction intermediates has been obtained by the use of SSITKA experiments. Al_2O_3 and SiO_2 supported catalysts containing 9 wt% cobalt and 0 or 0.4 wt% platinum were prepared by incipient wetness coimpregnation of the supports with aqueous solutions of

$Co(NO_3)_2{\bullet}6H_2O$ and $Pt(NH_3)_4(NO_3)_2$. At T = 483K, P = 1 bar and $H_2/CO = 7$, CO hydrogenation rates (based on weight of cobalt) of Pt-promoted catalysts were 3-5 times higher than those on their unpromoted analogues. The selectivity was not influenced by the presence of platinum. TPR-studies shown that the presence of platinum strongly influences the reducibility of the catalysts, with TPR-peaks shifting to lower temperatures for all catalysts. This effect is most pronounced on the Al_2O_3 supported catalysts, where the highly dispersed and otherwise difficult to reduce surface cobalt oxides are readily reduced at normal reduction temperature in the presence of platinum. The dispersion of metallic cobalt for platinum promoted catalysts increased compared to that on the unpromoted catalysts, with Al_2O_3 supported catalysts showing the largest effect due to the reduction of highly dispersed surface cobalt oxide. Apparent turnover numbers (based on H_2-chemisorption) were higher for Pt-promoted catalysts than for their unpromoted analogues by a factor of two. Decoupling coverage and intrinsic reactivity effects on the apparent turnover number by the use of SSITKA revealed essentially constant true turnover numbers on all catalysts. Thus, the increased apparent turnover numbers on Pt-promoted catalysts are due to a higher surface coverage of reactive intermediates.

In another paper (III.15), they reported the preparation of Pt- and Re-promoted 8.7 wt% Co/Al_2O_3 (1.0 wt% platinum or 1.0 wt% rhenium) by impregnating Al_2O_3 with an aqueous solution of $Co(NO_3)_2{\bullet}6H_2O$ using the incipient wetness technique. The sample was dried and calcined for 2 h at 573 K. Portions of the calcined base catalyst were then modified by impregnating with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ or Re_2O_7. An investigation of the CO hydrogenation of the two promoted catalysts has been carried out at two different conditions: 473 K, 5 bar, $H_2/CO=2$ and 493 K, 1 bar, $H_2/CO=7.3$.

The addition of platinum or rhenium significantly increases the CO hydrogenation rate (based on weight of cobalt), but the selectivity was not changed by the presence of platinum or rhenium. The results show that the observed increases in the reaction rates are caused by increased reducibility and increased number of surface exposed Co-atoms. SSITKA with carbon tracing was used to decouple the effects of the concentration of active surface intermediates and the average site reactivity of intermediates during steady-state CO hydrogenation. The SSITKA results show that the concentration of active surface intermediates leading to CH_4 increased as a result of the addition of a noble metal promoter. However, the average site activity was not significantly affected upon rhenium or platinum addition.

Holmen (III.25) also studied the effect of small amounts of Re on the reduction properties of alumina supported cobalt catalysts by TPR. An intimate mixture of Co/Al_2O_3 and Re/Al_2O_3 catalysts showed a promoting effect of rhenium similar to that for coimpregnated $Co\text{-}Re/Al_2O_3$. A loose mixture of Co/Al_2O_3 + Re/Al_2O_3 did not show any effect of rhenium on the reduction of cobalt. However, when the loose mixture of Co/Al_2O_3 + Re/Al_2O_3 was pretreated with argon saturated with water before the TPR, a promoting effect of rhenium on the reduction of cobalt was observed. It is suggested that rhenium promotes the reduction of cobalt oxide by hydrogen spillover, and that no direct contact between rhenium and cobalt seems to be necessary in order to obtain the promoting effect as observed by TPR. It is also shown that the presence of a high temperature TPR peak at 1200 K assigned to cobalt aluminate is mainly a result of Co-ion diffusion during the TPR and not during calcination. It would appear that another possibility would be water assisted transport of rhenium onto the $Co\text{-}Al_2O_3$ particles.

Iglesia (III.13) has reported work on TiO_2 and SiO_2 supported Ru-promoted cobalt catalysts. The catalytic activity was obtained using a fixed-bed reactor with H_2/CO = 2.05, 453-523 K, 0.01-2 MPa and 2-10 g catalyst with an average diameter of less than 0.2 mm to avoid diffusional effects. Their Co-Ru/TiO_2 catalysts were prepared by adding a ruthenium nitrate/acetone solution to an acetone slurry containing the pretreated, calcined, reduced and passivated Co/TiO_2 catalyst, followed by evaporation of the acetone solvent while stirring. The cobalt and ruthenium contents were 11.6 and 0.14% wt., respectively, corresponding to an atomic Ru/Co ratio of about 0.0067. SiO_2 supported bimetallic Co-Ru/SiO_2 catalyst was prepared from formerly prepared Co/SiO_2 using the synthesis and pretreatment procedures described above for TiO_2-supported catalysts. Cobalt and ruthenium contents were 23.0 and 0.26 wt.%, respectively, corresponding to an atomic Ru/Co ratio of about 0.0070. It seems the addition of small amounts of ruthenium to Co/TiO_2 or Co/SiO_2 catalysts (Ru/Co, 0.008 atm) increase their turnover rate (Figure III.10) and C_5+ selectivity (Figure III.11) for FTS. The methane make was much lower than Kogelbauer et al. (III.16) reported and the alpha-values were much higher. Also, deactivated bimetallic Co-Ru catalysts can be regenerated by a hydrogen treatment at the reaction temperature whereas monometallic cobalt catalysts cannot. On Co/TiO_2, ruthenium addition increases the turnover rates by a factor of three and C_5+ selectivities from 84.5 to 91.1%, without an apparent change in cobalt dispersion. Activation energies (88 ± 6 kJ/mol) and kinetic pressure orders (n = 0.6-0.65 for CO) are unaffected by ruthenium addition. These data suggest that the presence of ruthenium leads to higher cobalt site density during reaction without modifying the chemical reactivity of exposed cobalt surface atoms. Ruthenium appears to inhibit the deactivation of surface cobalt ensembles. Ruthenium atoms at the surface of cobalt crystallites increase the rate of removal of carbon and oxygen species during reaction and during regeneration of deactivated cobalt catalysts. The resulting higher cobalt site density leads to higher apparent turnover rates and to enhanced readsorption of olefins. As a result, Co-Ru catalysts yield a heavier and more paraffinic product than monometallic cobalt catalysts with a similar initial dispersion. The observed bimetallic interactions require intimate contact between cobalt and ruthenium, a state that forms during oxidation of the bimetallic precursors at high temperature. This treatment induces migration of ruthenium oxide species and leads to mixed Co-Ru oxides. The reducibility and the carbon deposition rates on well-mixed bimetallic Co-Ru catalysts are very different from those of monometallic cobalt catalysts. Electron microscopy, X-ray absorption spectroscopy, and thermogravimetric studies confirm the intimate mixing required for catalytic rate and C_5+ selectivity enhancements, for faster reduction of the cobalt oxide precursor, and for inhibition of carbon deposits during reactions of H_2/CO mixtures.

Turney (III.19) prepared a Ru-promoted coprecipitated cobalt/ceria catalyst. A mixture of ammonium ceric nitrate and cobalt nitrate hexahydrate in water was slowly added to an aqueous solution of ammonium carbonate, while stirring vigorously and bubbling carbon dioxide through the reaction vessel. After addition, the pH dropped to 7.1; the resultant dark brown precipitate was collected by centrifugation and washed five times with 4 L aliquots of water and then twice with 2 L aliquots of acetone. Residual acetone was removed in vacuo at ambient temperature. Further drying at 120^{o}C for 16 h in air and then calcination at 600^{o}C gave a black powder. Promotion was effected by adsorption of $Ru_3(CO)_{12}$ from solution in n-heptane onto the support; on stirring under nitrogen for 2 h, the solution was fully decolorized, indicating complete uptake of the ruthenium carbonyl. FTS using the catalysts indicates the addition of ruthenium lowers the reduction temperature of both Co_3O_4 and CeO_2 further, presumably via hydrogen spillover reduction. Consequently there is more Co^o in the ruthenium-promoted catalyst than the unpromoted catalyst leading to higher activity.

Bianchi et al. (III.18) prepared a Ru-doped cobalt titanium silicate (ETS-10) catalyst by a slurry impregnation of the ion-exchanged ETS-10 with a solution of $Ru(NO)(NO)_3$ in pure ethanol. The result indicates that the presence of small amounts of ruthenium introduced by wet-impregnation leads a complete reduction of the surface cobalt species and an increase of CO conversion and of the selectivity to iso-products. Upon increasing the amount of ruthenium, a further increase of the CO conversion and an interesting decrease of the C_1 fraction was found.

Kiviaho et al. (III.17) prepared a Co-Ru/SiO_2 catalyst from the carbonyl cluster. $Co_{4n}Ru_nH_n(CO)_x/SiO_2$ and $(Co_4(CO)_{12}+Ru_4H_4(CO)_{12})/SiO_2$ catalysts were prepared and their TPR and FT-IR properties were studied. $Co_{4n}Ru_nHn(Co)_x/SiO_2$ and $(Co_4(CO)_{12}$ + $Ru_4H_4(CO)_{12})/SiO_2$ catalysts were prepared from the carbonyl cluster and their TPR and FT-IR properties were studied by Kiviaho et al. (III.17). The FT-IR studies suggested that $Ru_4H_4(CO)_{12}$, $CoRu_3H_3(CO)_{12}$ and $Co_3RuH(CO)_{12}$ clusters on silica were more stable in room temperature than $Co_4(CO)_{12}$, $Co_2Ru_2H_2(CO)_{12}$ and $Co_2Ru_2(CO)_{13}$ clusters. The FT-IR measurements also indicated that all precursors decomposed during thermal treatment, but the distinct temperature of decarbonylation was not necessarily noticeable. On the other hand, in TPR, the CO desorption peak maxima for the precursors were 123^{o}C for $(Co_4(CO)_{12}+Ru_4H_4(CO)_{12})$, 127^{o}C for $CoRu_3H_3(CO)_{12}$, 133^{o}C for $Co_2Ru_2(CO)_{13}$, 137^{o}C for $Co_4(CO)_{12}$, 144^{o}C for $Co_2Ru_2H_2(CO)_{12}$, 148^{o}C for $Co_3RuH(CO)_{12}$ and 185^{o}C for $Ru_4H_4(CO)_{12}$. Thus, the catalysts with 1:1 atomic ratio of

Co:Ru decarbonylated at different temperatures. The temperature of decarbonylation was lower for $Co_2Ru_2(CO)_{13}/SiO_2$ than for $Co_2Ru_2h_2(CO)_{12}/SiO_2$, i.e., cobalt influenced the decarbonylation more in the first case. In accordance, the CO hydrogenation activity and selectivity results for the decarbonylated catalysts suggested that $Co_2Ru_2(CO)_{13}/SiO_2$ exhibited the characteristics of cobalt more than $Co_2Ru_2H_2(CO)_{12}/SiO_2$ did.

Effects of activation on the surface properties of silica-supported cobalt catalysts were studied by Coulter and Sault (III.26). Drying and calcining effects for 16-19 wt% Co/SiO_2 FTS catalysts, prepared by impregnation with cobalt nitrate, have been examined using ultrahigh vacuum surface analysis and conventional catalyst characterization techniques. Drying in air at 110^{o}C or under vacuum at 100^{o}C and then calcining in air at 400^{o}C causes large Co_3O_4 particles to form, which easily reduce under hydrogen at 300^{o}C. In contrast, dried samples annealed under UHV prior to calcining exhibit dramatically different characteristics. The decomposition of cobalt nitrate during drying initiates the formation of a surface cobalt silicate. Prolonged air drying eventually converts the surface silicate into Co_3O_4, while vacuum drying disperses the nitrate precursors on the support, forming cobalt silicate islands. Annealing air-dried samples in UHV stabilizes the surface silicate against reduction or oxidation through the migration of Co^{2+} ions into the support to form a well-ordered bulk cobalt silicate. Annealing of vacuum dried samples to 200^{o}C in UHV produces a continuous, conductive surface silicate that sinters upon heating to temperatures above 250^{o}C. Analysis of species generated during the decomposition of the $Co(NO_3)_2 \bullet 6H_2O$ precursor indicates that the concentration of gas phase CO near the surface determines the nature of the cobalt surface phase. The formation of an intermediate surface cobalt silicate under specific activation conditions maximizes the amount of reducible cobalt surface area available for FTS reactions.

The precursor can significantly influence the property of the catalyst. Loosdrechtf et al. (III.27) prepared alumina-supported cobalt catalysts from different cobalt precursors to study its influence on the ultimate metal particle size. Furthermore, the effect of the particle size on the catalytic performance (activity and selectivity) during FTS was investigated. The preparation by incipient wetness impregnation, using cobalt EDTA and ammonium cobalt citrate precursors, of low-loaded cobalt catalysts (2.5 wt%) resulted initially in very small cobalt oxide particles, as determined by XPS. The small oxide particles reacted during the thermal treatment in a reducing gas flow with the alumina support to form cobalt aluminate, which was neither active nor selective during FTS. The catalysts prepared with cobalt nitrate had larger particles that could be easily reduced to metallic cobalt. These catalysts were active under reaction conditions (fixed-bed reactor, 523 K, H_2/CO = 2, 30 ml/min, 1 atm). Higher-loaded cobalt catalysts (5.0 wt%) prepared using ammonium cobalt citrate showed a larger particle size than the lower-loaded catalyst prepared from the citrate precursor. The extent of reduction to metallic cobalt that could be achieved with the higher-loaded catalyst was significantly higher than that with the lower-loaded catalyst, as shown by magnetic measurements. Accordingly, the authors report that "the higher-load catalyst exhibited a reasonable activity and, in addition, an interesting and remarkably high selectivity toward higher hydrocarbons, and also a very high Schulz-Flory parameter." This statement must be viewed as a relative comparison since the methane selectivities varied from 36 to 64% and the alpha values were in the range of 0.45 to 0.69, low values for a cobalt catalyst.

The effect of the precursor on the characteristics of the Co/SiO_2 catalysts prepared from $Co(NO_3)_2$, $Co(CO)_8$ and $Co_4(CO)_{12}$ was determined by Niemela et al. (III.28). The near-surface reduction was clearly lower for the $Co_2(CO)_8$ derived catalyst than for the $Co_4(CO)_{12}$ based one. The hydrogen chemisorption, CO desorption, XRD and XPS measurements indicated that the dispersion of the metallic species decreased in the precursor order $Co_2(CO)_8 > Co_4(CO)_{12} >> Co(NO_3)_2$. The TPD studies showed that CO was more strongly adsorbed on catalysts derived from carbonyls than on those based on nitrate, resulting in greater initial activity for CO hydrogenation. In pulsed CO hydrogenation reactions, the selectivity of the $Co_2(CO)_8$ derived catalyst differed from the other two. Thus, despite the well documented transformation of the $Co_2(CO)_8$ to $Co_4(CO)_{12}$ on the silica support, the supported catalysts derived from these two precursors exhibited distinct characteristics and reactivity.

The activity of the Co/SiO_2 catalyst in relation to pretreatment of the catalyst was investigated by Niemela et al. (III.29). With increasing reduction temperature (300-450^oC), the extent of reduction increased. The increase was not, however, accompanied with increased chemisorption capacity. Namely, the hydrogen chemisorption was highest at a reduction temperature of approximately 300^oC. Also, carbon monoxide adsorption was almost constant at 200-400^oC, and decreased drastically when the catalyst was heated to higher temperatures. Thus, the results suggest that cobalt agglomerated at temperatures above 400^oC. The activity for toluene hydrogenation correlated well with the hydrogen uptake for reduction temperatures above 300^oC. Also, the CO hydrogenation activity (235^oC; 5 bar, $H_2/CO/Ar = 3/1/3$, GHSV = 2600 h^{-1}) of the catalyst increased with increasing temperature of reduction (400-450^oC) due to the decrease in the number of active sites (figure III.12). These results are in contradiction to the results of Moon and Yoon (III.30) who obtained a higher extent of reduction and catalytic activity by increasing the reduction temperature in the range 325-525°C. Johnson et al. (III.31) also obtained increasing activity (expressed as CO turnover frequency) with increasing percentage of reduction, although the specific activity of the well reduced catalyst sample did not depend upon cobalt dispersion.

Iglesia (III.32) found that catalyst productivity and selectivity to C_5+ hydrocarbons are critical design criteria in the choice of FTS catalysts and reactors. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbons from CO/H_2 mixtures. Optimum catalysts with high cobalt concentration and site density can be prepared by controlled reduction of nitrate precursors introduced via melt or aqueous impregnation methods. FTS turnover rates are independent of cobalt dispersion and support identity over the accessible dispersion range (0.01-0.12) (Figure III.10) at typical FTS conditions. At low reactant pressures or conversions, water increases FTS reaction rates and the selectivity to olefins and to C_5+ hydrocarbons. These water effects depend on the identity of the support and lead to support effects on turnover rates at low CO conversions. Turnover rates increase when small amounts of ruthenium (Ru/Co < 0.008 atm) are added to cobalt catalysts. C_5+ selectivity increases with increasing cobalt site density because diffusion-enhanced readsorption of α-olefins > β-hydrogen abstraction steps and inhibits chain termination. The readsorption of α-olefins merely has the effect of reversing the predominant chain termination pathways of small surface chains (β-hydrogen abstractions) by reinitiating surface chains that continue to grow and ultimately desorb as larger hydrocarbons. In effect, termination of alkyl chains via β-hydrogen abstraction becomes increasingly reversible as olefin concentration or residence time increases; the readsorption reaction also becomes faster as reactive olefins are retained longer within liquid-filled catalyst pellets. This well known secondary reaction leads to an increase in the selectivity to C_5+ hydrocarbons and to lower selectivities to methane and olefins as bed residence time increases. Clearly, readsorption effects become more influential as olefin concentrations increase with increasing bed residence time and CO conversion. Severe diffusional restrictions, however, can also deplete CO within moderate diffusional restrictions. Diffusional constraints depend on pellet size and porosity and on the density and radial location of cobalt sites within catalyst pellets. Slurry bubble column reactors and the use of eggshell catalyst pellets in packed-bed reactors introduce design flexibility by decoupling the characteristic diffusion distance in catalyst pellets from pressure drop and other reactor constraints.

Catalytic rates and selectivity can reflect the intrinsic behavior of a metal surface. Sometimes, this surface chemistry changes because metal crystallites of different size expose surface ensembles with unique structures (III.33); strong interactions with a metal oxide support can also perturb the electronic density and structure of metal crystallites (III.34). The effect of titania, silica, alumina, zirconia and ZSM-5 on the specific activity and selectivity properties of cobalt for carbon monoxide hydrogenation has been studied by different authors under different conditions.

Bessell (III.35) examined a range of cobalt catalysts supported on kieselguhr, silica, alumina, bentonite, Y-zeolite, mordenite and ZSM-5 for catalytic activity and product selectivity for FTS at 240°C, 2 MPa using a GHSV of 1000 h^{-1} in a microreactor. These results were correlated with catalyst reducibility and adsorptive properties, as well as support acidity, surface area and structure. In order to maximize the activity of cobalt-based Fischer-Tropsch catalysts, it is necessary to choose high surface area supports and to obtain high cobalt dispersions. However, possible interactions between cobalt and the support must be taken into account as they can lead to lower catalyst activity. This was evidenced by the alumina,Y-zeolite and mordenite supported catalysts which did not undergo complete reduction under standard conditions due to the formation of irreducible surface species or ion exchanged cobalt within the support. Incomplete reduction, while producing a more dispersed catalyst, will limit the availability of active cobalt sites. Pore structure of the support is also important as pore diffusion or blocking effects can prevent reactants accessing active cobalt sites. All supports examined showed similar methane, carbon dioxide and higher hydrocarbon selectivities, and in all cases carbon dioxide selectivity was low. However, the nature of the higher hydrocarbons depended very much on the acidity of the support. The low acidity kieselguhr, silica, alumina and bentonite supports produced the traditional straight chained Fischer-Tropsch products, and are thus the preferred type of support if a straight chained product, such as a wax or diesel fuel, is desired. If gasoline production is targeted, zeolite supported catalysts are to be preferred as a lighter, more highly branched, and at sufficiently high temperatures aromatic, product results. However, the primary formed Fischer-Tropsch products must have access to the zeolitic acid sites if these secondary isomerization and aromatization reactions are to occur. This places some constraints on the channel system and ion exchange properties of the zeolite in question.

Reuel and Bartholomew (III.36) investigated the effect of support and dispersion on the CO hydrogenation activity/selectivity properties of cobalt. Specific activities and selectivities of unsupported cobalt and cobalt supported on alumina, silica, titania, carbon, and magnesia carriers for CO hydrogenation were measured in a single-pass differential reactor at low conversion, 1 atm, and 175-350^{o}C. The results indicate that specific activity and selectivity of cobalt vary with support, dispersion, metal loading, and preparation method. The order of decreasing CO hydrogenation activity at 1 atm and 225^{o}C for catalysts containing 3 wt% cobalt is Co/TiO_2, Co/SiO_2, Co/Al_2O_3, Co/C, and Co/MgO (Figure III.13). The specific activity of cobalt decreases significantly with increasing dispersion (Figure III.14). Product selectivity is best correlated with dispersion and extent of reduction (Figure III.15), i.e., the molecular weight of hydrocarbon products is lower and the CO_2/H_2O ratio is higher for catalysts having higher dispersions and lower extent of reduction. This effect may be due to stable oxides in the well-dispersed, poorly reduced catalysts, which catalyze the water-gas-shift reaction thereby increasing the H_2/CO ratio at the surface. In the Co/Al_2O_3 system, activity and selectivity for high molecular weight hydrocarbons increase very significantly with increasing cobalt loading. A 15% Co/Al_2O_3 is 20 times more active than 3% Co/Al_2O_3; moreover, 86 wt% of its hydrocarbon fraction is in the C_5-C_{12} (gasoline) range compared to 18 wt% for 3% Co/Al_2O_3.

Silica is a very popular support for cobalt; it exhibits high surface area and it does not readily form spinels during the reduction process. However, according to Goodwin's results (III.37), the formation of cobalt silicates in Co/SiO_2 has been found to occur during FTS, whether conducted in gaseous or the liquid phase. In order to explore the role of vapor in causing this formation, the Co/SiO_2 catalyst was studied using conditions simulating those present during FTS. It was found that, depending on exposure time and gas phase concentration, a loss of the catalytically active phase and the formation of cobalt silicates occurred. The cobalt silicates formed were not completely reducible even during TPR to 900°C. The formation of silicates occurred rapidly for the in situ reduced catalyst and even more rapidly in the presence of hydrogen. The presence of air retarded this effect. On the contrary, when the cobalt was present as the oxide, hydrothermal treatment had little effect. It is concluded that the presence of cobalt metal is necessary for Co-silica reactions to occur forming both `reducible' and `nonreducible' (<900°C) cobalt silicate. The results point out a type of catalyst change which can occur during reaction. The authors did not indicate how Co_o can react to form a cobalt silicate.

Khodakov et al. (III.38) studied the reducibility of cobalt species that are present in silica-supported Fischer-Tropsch catalysts using in situ XRD, in situ EXAFS, and FTIR spectroscopy with carbon monoxide as a molecular probe. Crystalline cobalt phases in the oxidized catalysts were characterized using XRD. In the oxidized samples with a large concentration of amorphous phase, EXAFS showed the presence of small oxide clusters including several cobalt atoms. It was found (in-situ XRD, EXAFS) that calcination of oxidized cobalt catalysts under an inert atmosphere resulted in a selective transformation of Co_3O_4 to CoO at 623-673 K. FTIR spectroscopy, with CO as a molecular probe, revealed the presence of different sites associated with cobalt after the reduction of the catalysts with hydrogen at 723 K: cobalt metal sites, Co^{2+} ions in the crystalline phase of CoO, and Co^{n+} species in an amorphous phase. The results (XRD, EXAFS, FTIR) showed that the hydrogen reduction properties of particles of cobalt oxide on silica depended on the size of the Co_3O_4 crystallites. The ease of reduction to metal decreased from larger (200-700Å) to smaller (60Å) particles.

The long-term performance of Co/SiO_2 catalysts in CO hydrogenation was investigated by Neimela and Krause (III.39). The catalysts were prepared from nitrate

(N) and carbonyl (CO) precursors. The activity in terms of conversion of carbon monoxide was determined over a reaction time of 120 h. The activity was obtained using a fixed-bed reactor, 0.5 MPa, 235-290°C, Ar:CO:H_2 = 3:1:3 and GHSV = 5200 h^{-1}. The conversion decreased rapidly during the first five hours (Figure III.16), and thereafter at a moderate rate that was related to dispersion, i.e, the higher the dispersion the higher the rate of decrease. These catalysts produced 58-65 mole% methane and had alpha values in the range of 0.69-0.81. The active sites were blocked by wax and coke formed during the reaction, although some agglomeration of particles probably took place on the Co(CO)/SiO_2 catalysts. More carbon was accumulated on Co(CO)/SiO_2 during the reaction suggesting a need for frequent regeneration. The reduction-oxidation-reduction treatments indicated, however, that the regenerability of the Co(CO)/SiO_2 in terms of hydrogen uptake is poor, although the amounts adsorbed still remained higher than those for Co(N)/SiO_2.

The influence of water on alumina-supported cobalt catalysts has been studied by Schanke et al. (III.40). The deactivation of supported cobalt catalysts was studied in a fixed-bed reactor using synthesis gas feeds containing different concentration of water vapor. Supporting model studies were carried out using H_2O/H_2 feeds in conjunction with XPS and gravimetry. Rapid deactivation occurs on Re-promoted Co/Al_2O_3 catalysts when H_2/CO/H_2O feeds are used, whereas unpromoted Co/Al_2O_3 shows more stable activity (Figure III.17). The results from the gravimetric studies suggest that only a small fraction of the bulk cobalt metal initially present reoxidizes to cobalt oxide during reaction. However, the XPS results indicate significant reoxidation of surface cobalt atoms in highly dispersed cobalt phases, which is likely to be the cause of the observed deactivation. Rhenium is shown to have a marked effect by decreasing the extent of reoxidation of alumina-supported cobalt catalysts and a smaller decrease in the catalytic activity.

Lapidus and co-workers (III.41-III.43) studied the physical properties and FT performance of 10% cobalt catalysts supported on alumina, silica and alumina-silica, respectively. They found that properties of impregnated cobalt catalysts depend on the nature of the support and on the temperature of pretreatment. The decomposition of dried 10% Co/Al_2O_3 and 10% Co/SiO_2 in an inert gas proceeds in two steps: water evolution and decomposition of cobalt nitrate. In a reducing atmosphere, the endothermic decomposition was accompanied by exothermic reduction of cobalt nitrate, and the whole process strongly depended on the nature of the support. On SiO_2, the formation of cobalt surface compounds with the support was much more limited than on Al_2O_3. The amount of adsorbed CO increases with calcination temperature, while both the degree of cobalt reduction and the cobalt dispersion decrease. CO was adsorbed in four different states on the 10% Co/Al_2O_3 catalyst: as linear forms on Co^{2+}, Co.delta.$^+$, and CoO, bridged form on CoO. Their relative amounts depended on the temperature of pretreatment. Catalyst pretreatment with a CO and hydrogen mixture under hydrocarbon synthesis conditions causes a certain modification of the metal surface which leads to variations of the CO adsorption states. The influence of the nature of the support and the pretreatment temperature on the activity of cobalt catalysts in FTS at atmospheric pressure are presented. Pretreatment by calcination in air led to a decrease in cobalt reducibility and dispersion. The degree of reduction was higher with Co/SiO_2 than with Co/Al_2O_3 at all calcination temperatures. Except for the dried samples, cobalt dispersions were higher with Co/Al_2O_3. The variations in the catalytic properties of Co/Al_2O_3 and Co/SiO_2 in FTS with the pretreatment temperature differed for both supports. When the calcination temperature was increased, the total hydrocarbon yield decreased over Co/SiO_2 catalysts and increased over Co/Al_2O_3 catalysts. The C_{5+} fraction selectivities over Co/Al_2O_3 catalysts increased with the pretreatment temperature, whereas over Co/SiO_2 catalysts, they remained practically constant. The resistance of cobalt catalysts to the action of air was higher with samples previously used in Fischer-Tropsch synthesis than with freshly reduced ones. For freshly reduced Co/Al_2O_3 catalysts, an increase of catalytic activity was found up to a certain level after repeated doses of air were passed through the catalyst bed. The nature of the oxide phases are thought to be responsible for the variation of catalytic properties. On the Co/SiO_2 catalyst surface, the formation of Co_3O_4 supposedly reduces the total hydrocarbon yield. In spite of the decrease of cobalt dispersion, the Co-support surface compounds cause an increase in the total hydrocarbon yield and the C_5+ fraction selectivity on the Co/Al_2O_3 catalysts.

The physicochemical properties of 10% Co/SiO_2-Al_2O_3 catalysts prepared by impregnation were studied by temperature programmed reduction, thermoanalysis and CO adsorption (III.41-III.43). The temperature at which the catalyst was pretreated has a great influence on its adsorption capacity for CO. Both reduced and unreduced samples calcined in air at relatively high temperatures adsorbed CO, but the reduced ones adsorbed much larger amounts. The adsorption capacity tended to increase with increasing pretreatment temperature. The character of CO temperature programmed desorption profiles and the proportions of the individual adsorption forms depend on the pretreatment temperature and the degree of cobalt reduction. CO was adsorbed in three forms on species originating in Co-support interactions, metallic cobalt, and on Co_3O_4. Calcination in air caused a decrease of both cobalt reduction and the activity for hydrocarbon synthesis. While the yield of gaseous products remained constant, liquid yield decreased substantially with increasing pretreatment temperature, reaching a maximum value when the degree of cobalt reduction was approximately 40-50%. The average carbon number decreased with increasing cobalt reduction. The catalytic properties of Co/SiO_2-Al_2O_3 are resemble more closely those of Co/SiO_2 than of Co/Al_2O_3, but Co/SiO_2-Al_2O_3 catalysts are less efficient in polymerization than either Co/SiO_2 or Co/Al_2O_3. The hypothesis, suggesting that the adsorption centers of weakly bonded CO were involved in the production of liquid hydrocarbons and that the cobalt oxide species act directly in this synthesis, was confirmed.

A particularly interesting scheme is to react synthesis gas mixture over a bifunctional catalyst (III.44-III.46). The catalyst would be a combination of Fischer-Tropsch catalyst and a shape-selective zeolite. For example, the combination of metal oxides with the medium pore (ca. 6.0 Å) ZSM-5 zeolite (III.47-III.50) and the use of metal nitrate or organometallic impregnated ZSM-5 (III.51-III.55) catalysts have been shown to produce gasoline range hydrocarbons containing a high percentage of aromatics from synthesis gas. Physical and chemical properties as well as the activity and selectivity of Co/HZSM-5 zeolite bifunctional catalysts have been studied by Calleja (III.56) for conversion of synthesis gas. These catalysts were prepared by incipient wetness impregnation with different conditions of drying, calcination and reduction. The cobalt content in the catalyst and the effect of thoria, as a promoter, were also studied. The catalysts were characterized and tested in a fixed bed continuous reactor system. The results show that drying is the most important step in the preparation, having more active catalysts with fast drying conditions, probably due to the formation of smaller cobalt particles. The interaction between the metal and the zeolite surface seems to contribute significantly to the catalyst activity. Maximum activity of the catalyst is obtained with 1.5 wt% of thorium, resulting in an increase of C_{6+} selectivity. This was explained in terms of a shift in chemisorption properties of the catalyst. The basic character of the promoter affects the zeolite acidity, decreasing the aromatic proportion in the liquid hydrocarbon fraction. [It is not clear how either ThO_2 or Rh^{4+} can exchange could do this. For example, exchange of a zeolite with La^{3+} does not appreciably change the number of acid sites of a zeolite.] Finally, the optimum bifunctional catalyst selected in this study is compared with a physical mixture of a commercial Fischer-Tropsch catalyst and HZSM-5 zeolite. The results achieved under the usual reduction conditions with both catalysts show that, for the same value of conversion, selectivity towards C_6+ hydrocarbons was notably greater for the optimum catalyst. Although the amount of aromatic hydrocarbons was slightly lower, the percentage of C_{6+} hydrocarbons was about two-fold higher. Also, an increase could be observed in the olefinic nature of C_3 hydrocarbon fraction obtained using the selected catalyst. The most important reason for these differences may be a decrease in the acidity of the zeolite due to the basicity of ThO_2, which reduces aromatization reactions of light alkenes. Therefore, the selected catalyst yields a higher liquid hydrocarbon fraction compared to physical mixture catalyst. Moreover, the mixture of hydrocarbons had an acceptable composition to be used as high octane number fuel.

Yin et al. (III.57) studied CO hydrogenation with PdCo/NaY catalysts. NaY-encapsulated Pd-Co bimetallic catalysts of various Co/Pd ratios and pretreatment conditions were used for carbon monoxide hydrogenation. Preparation conditions have an overwhelming effect on the active phases and the catalyst selectivity. In Pd/NaY and bimetal samples with very a low extent of cobalt reduction, the formation of palladium carbide is detected by XRD. On these catalysts, methane is formed when particles are very small, but after some agglomeration, methanol is the dominant primary product of CO hydrogenation; secondary reactions (MTG) on strong Brønsted-acid sites lead to dimethyl ether and heavier hydrocarbons. For bimetallic PdCo/NaY samples, calcination and reduction conditions are critical for the formation of PdCo alloy particles, which prevents the formation of palladium carbide, and methane selectivity is high. For higher cobalt contents, alloy particles are obtained following reduction at high temperature; these samples show a signature reminiscent of Fischer-Tropsch catalysts.

McMahon et al. (III.58) studied dispersed cobalt-containing zeolite Fischer-Tropsch catalysts. Microwave discharge methods were used to prepared highly dispersed cobalt clusters in zeolites. Ferromagnetic resonance, electron microscopy, and hydrogen chemisorption experiments have been used to determine the particle sizes of the cobalt clusters. These materials were also studied as Fischer-Tropsch catalysts. Catalytic results suggest that these cobalt zeolite catalysts show high selectivity for the production of low-molecular-weight olefin. Evidence of shape selective catalysts with a cut off at the C_6 chain length has also been observed according to their analysis. McMahon et al.'s data indicate that CO hydrogenation on Co/zeolite catalysts is a structure-sensitive reaction. These highly dispersed catalysts are not as active as catalysts with larger cobalt particles but show higher selectivities toward light hydrocarbons than cobalt-alumina catalysts. FTIR, SEM, and hydrogen chemisorption experiments indicate that the cobalt clusters are extremely small. H_2 chemisorption experiments indicate a 100% dispersion and a particle size of about 9Å prior to catalytic experiments. At 512 K, the hydrocarbon product is 26% C_2-C_4 olefins. A tail-off in Anderson-Schulz-Flory plots at C_6-C_9 is indicative of a shape-selective effect. However, in a later review, Bartholomew (III.59) provided data obtained by Ungar and Baird that is still unpublished that conclusively show that because of the holdup of heavy hydrocarbons in the zeolite structure, one must wait for a longer time period than most of the reported data to ensure that steady-state products are obtained.

Stencel et al. (III.60) prepared a metal-impregnated Co/ZSM-5 catalysts with $Co(NO_3)_2\,6H_2O$ using an incipient wetness technique. These catalysts were shown to contain highly dispersed, ion-exchanged, non-reducible Co^{2+} species in the interior of the ZSM-5 particle, and large, reducible cobalt oxide crystallites on the exterior as determined from the number of pyridine molecules that coordinately bond to each of these ions, estimated using infrared data. The crystalline forms of cobalt on the surface of the ZSM-5 are identified and their sizes estimated after O_2 calcination, H_2 reduction, and $CO+H_2$ exposure. These data are then scrutinized for correlations of chemical and physical properties of the Co/ZSM-5 catalysts with conversion activity and selectivity for synthesis of hydrocarbons from $CO+H_2$ gas. The use of surface sensitive and bulk experimental techniques have enabled the differentiation of two distinct cobalt species in Co/ZSM-5 catalysts. Cobalt interior to the ZSM-5 is in an irreducible, ionic Co^{2+} form created during ion exchange for H^+, cobalt exterior to the ZSM-5 is in the form of large Co_3O_4 crystallites that are reducible under hydrogen at 350^oC to hcp cobalt metal and CoO. By varying the preparation methods, either of these cobalt forms can be obtained. It may now be of interest to study the conversion of other reactants over these types of catalysts and possibly to investigate the effect of particle size of the exterior-located cobalt on $CO+H_2$ conversion activity and selectivity.

Investigation of bifunctional zeolite supported cobalt Fischer-Tropsch catalysts has been done by Bessell (III.61). ZSM-5, ZSM-11, ZSM-12 and ZSM-34 were examined as supports for cobalt bifunctional Fischer-Tropsch catalysts in order to determine the influence of zeolite pore structure on the synthesis. All supports produced reasonably active catalysts, with the activity increasing with the channel size of the zeolite support (i.e, in the order of ZSM-34 < ZSM5, ZSM-11 < ZSM-12 supported catalysts). Lack of observable differences in methane and higher hydrocarbon selectivities indicated that this increased activity was not due to an electronic cobalt-support effect. It was more likely a result of increased cobalt dispersion due to an enhancement of some small cobalt crystallite formation within the larger-channeled zeolites. The absence of a channel-size dependent cut-off in the product distributions indicated a lack of shape selective behavior, and that significant hydrocarbon chain growth was occurring on cobalt crystallites on the zeolite surface. Ammonia TPD measurements indicated that the acidity of these zeolites, in terms of both acid strength and acid site concentration, decreased in the order ZSM-34 > ZSM-5 > ZSM-11 > ZSM-12. Contrary to initial expectations, the hydrocarbon products became lighter, and contained less n-alkanes, as the acidity of the zeolite was reduced (which was in the same order as when the channel size of the zeolite was increased). This indicated that for this strongly acidic series of zeolites, accessibility to internal acid sites was more important in influencing the degree of secondary acid catalyzed restructuring reactions of the primary Fischer-Tropsch products than was the strength or concentration of these acid sites.

Metal dispersion and support effects on FTS rate and selectivity were studied at conditions that favor the formation of C_5+ hydrocarbons (>80% selectivity) by Iglesia et al. (III.62). On cobalt, hydrocarbon synthesis rates are proportional to metal dispersion (0.0045-0.095) and independent of the metal oxide support (SiO_2, Al_2O_3, TiO_2, and ZrO_2-

modified SiO_2 and TiO_2). Site-time yields (1.6-3.0x $10^{-2}s^{-1}$) are independent of cobalt dispersion and support (473 K, 2.0 MPa, H_2/CO=2.1). Dispersion and support influence C_5+ selectivity slightly; these changes reflect transport-enhanced secondary reactions and not modifications of intrinsic chain growth kinetics. Specifically, transport restrictions imposed by the physical structure of the support and by a high site density within catalysts pellets increase the residence time and the readsorption probability of reactive α-olefins and lead to higher C_5+ yields and more paraffinic products.

FTS site-time yields and intrinsic chain growth kinetics depend only weakly on cobalt dispersion and on the oxide support (SiO_2, Al_2O_3, TiO_2). Dispersion and support effects on C_5+ selectivity arise from changes in the extent of α-olefin readsorption as changes in site density and support structure modify the rate of intrapellet olefin removal (III.63).

Fu and Bartholomew (III.64) determined the activities and selectivities of cobalt/alumina catalysts for CO hydrogenation as a function of metal loading, reduction temperature, and preparation. Specific activities and average carbon number of the hydrocarbon product were found to significantly vary with metal loading, reduction temperature, and preparation. These changes were also found to be linearly correlated with changes in dispersion indicating that CO hydrogenation on Co/Al_2O_3 is structure-sensitive (Figure III.18). The changes in specific activity with dispersion can be explained by variations in the distribution of low and high coordination sites and by changes in the nature of adsorbed CO species available for reaction. High specific activity is apparently favored on sites to which CO is strongly coordinated. Variations in the average carbon number of the product can be explained by changes in the rate of termination relative to the rate of propagation. High-molecular-weight products are favored by catalysts having high rates of propagation and low rate of termination.

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Table III.1

Effect of Calcination Temperature on CO Hydrogenation (reduction temperature = 300°C, H_2/CO = 10, T = 220°C, P = 1.8 atm) (from ref. III.20)

	% CO conversion		Rate[d] (µmole/g Co_{Tot}/S)		CH_4 Selectivity (%)		α		TOF[e] x 10^2 (1/s)	
T_C (°C)[a]	Initial[b]	S-S[c]	Initial	S-S	Initial	S-S	Initial	S-S	Initial	S-S
Uncalcined	9.7	7.5	44.0	32.2	70	75	0.42	0.37	---	---
200	15.1	11.1	68.6	50.4	86	84	0.40	0.36	---	---
250	12.3	9.2	55.9	41.9	86	80	0.41	0.36	3.0	2.2
300	10.9	8.4	49.8	38.2	73	76	0.40	0.38	2.9	2.3
350	8.2	6.4	37.2	29.2	70	74	0.42	0.37	3.0	2.3
400	6.4	5.1	29.2	23.0	68	73	0.41	0.37	3.3	2.6

a. Calcination temperature.
b. After 5 min. of reaction.
c. After 7 hr. of reaction.
d. Error in rate measurement was ± 5%.
e. Based on total hydrogen chemisorption.

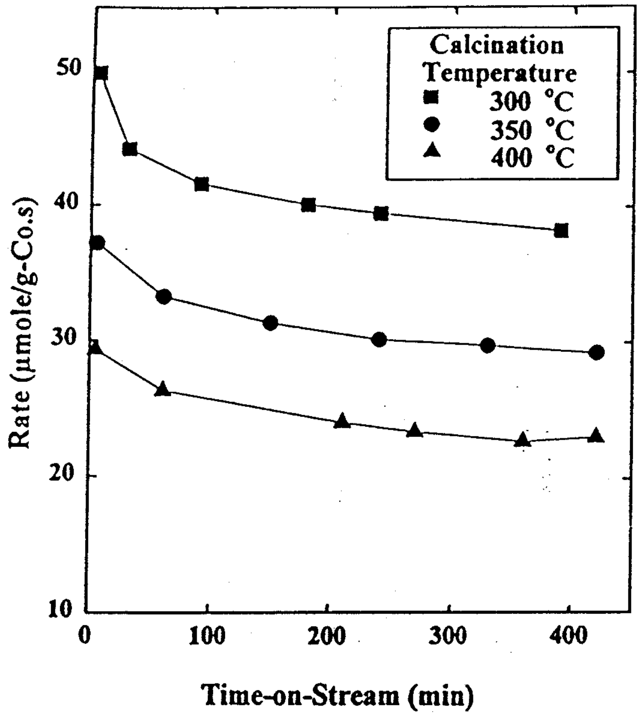

Figure III.1. Time-on-stream behavior of the overall rate of CO hydrogenation for the catalyst reduced at 300°C and calcined at various temperatures (from ref. III.20).

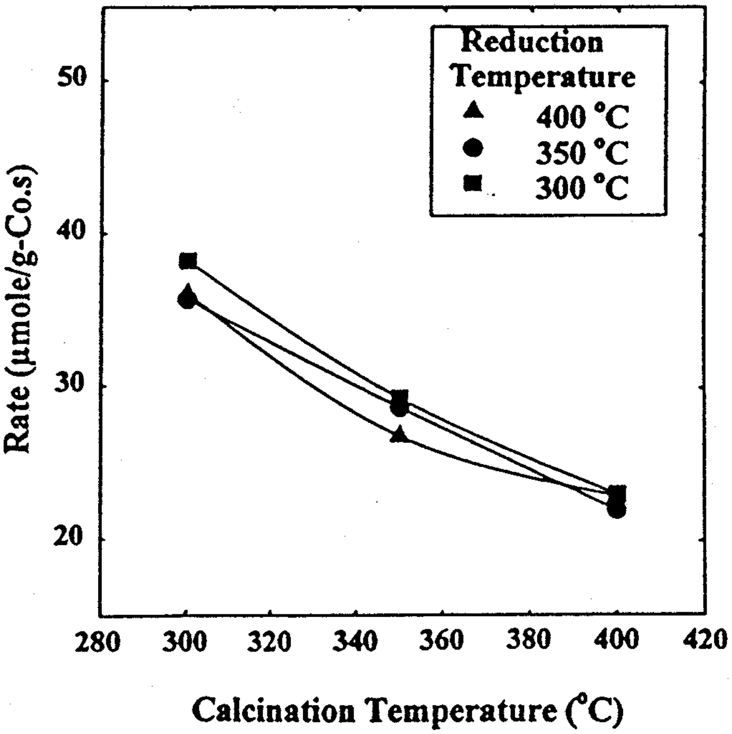

Figure III.2. Effect of pretreatment temperatures on overall catalyst activity of $Ru/Co/Al_2O_3$ (from ref. III.20).

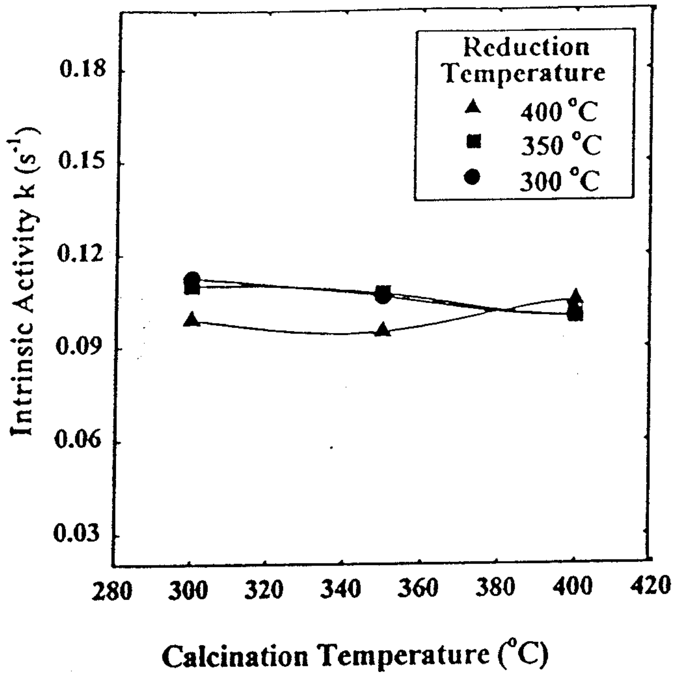

Figure III.3. Effect of pretreatment temperatures on intrinsic activity of Ru/Co/Al_2O_3 for methane formation (from ref. III.20).

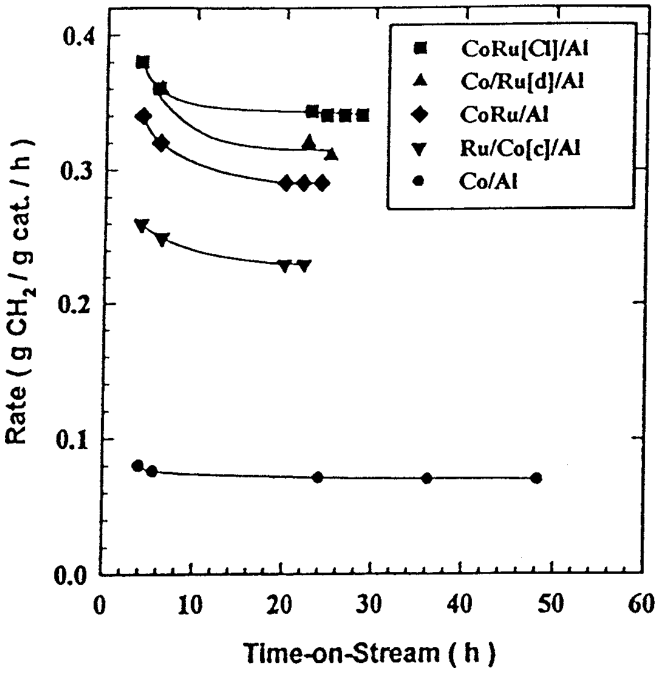

Figure III.4. Rates of F-T synthesis at 220°, 1 atm. and H_2/CO = 2 versus time-on-stream for selected catalysts (in inset d = dried, c = calcined, r = reduced, Cl = prepared from $RuCl_3$) (figure from ref. III.16).

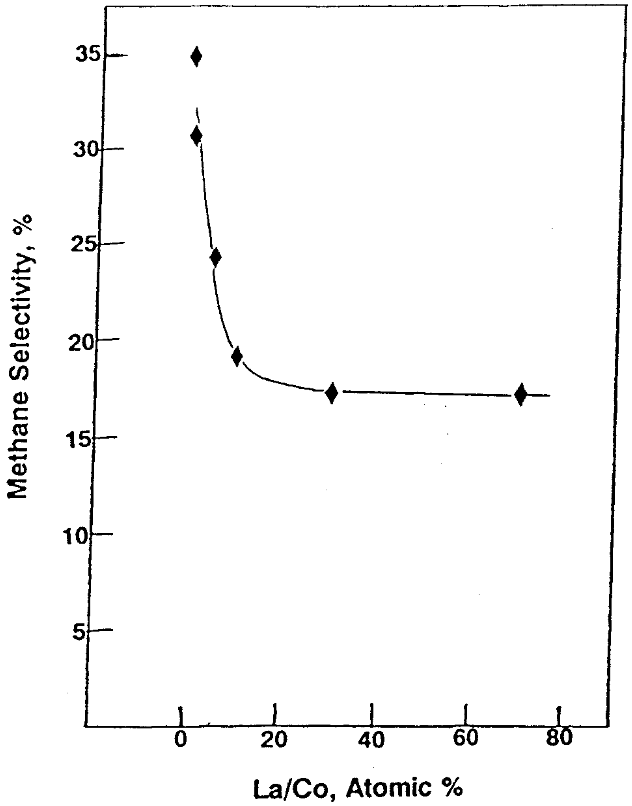

Figure III.5. Influence of La^{3+} content on the fraction of methane produced by a Co/SiO_2 catalyst (220°C, 1 atm., $H_2/CO = 2$) (from ref. III.23) Plot from table 2 of reference.

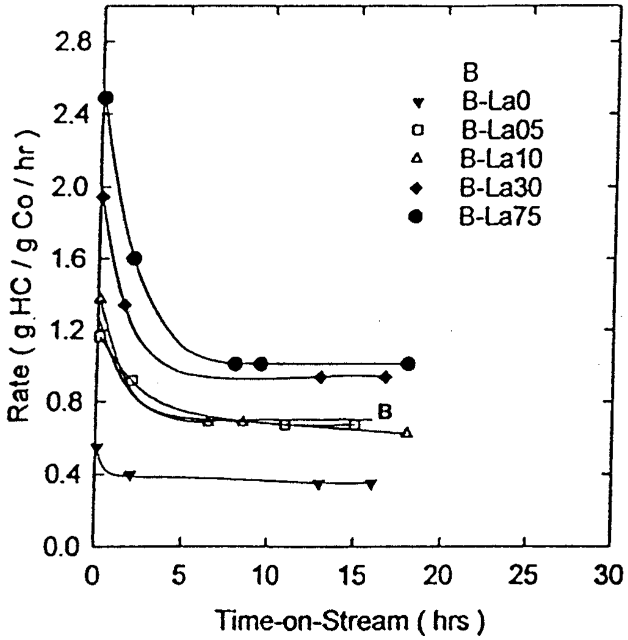

Figure III.6. Initial CO hydrogenation reaction for $(La)Co/SiO_2$ catalysts (220°C, 1 atm., $H_2/CO = 2$) (from ref. III.23).

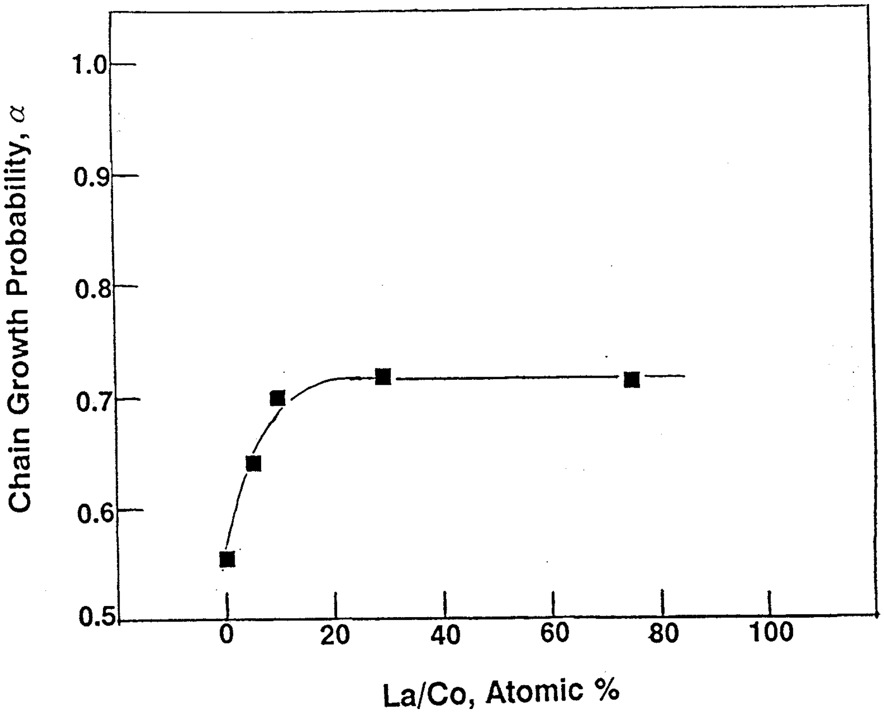

Figure III.7. Dependence of the chair growth probability (alpha) on the La^{3+} content for a Co-SiO_2 catalyst (220°C, 1 atm., H_2/CO = 2) (from ref. III.23). drawn from table 2.

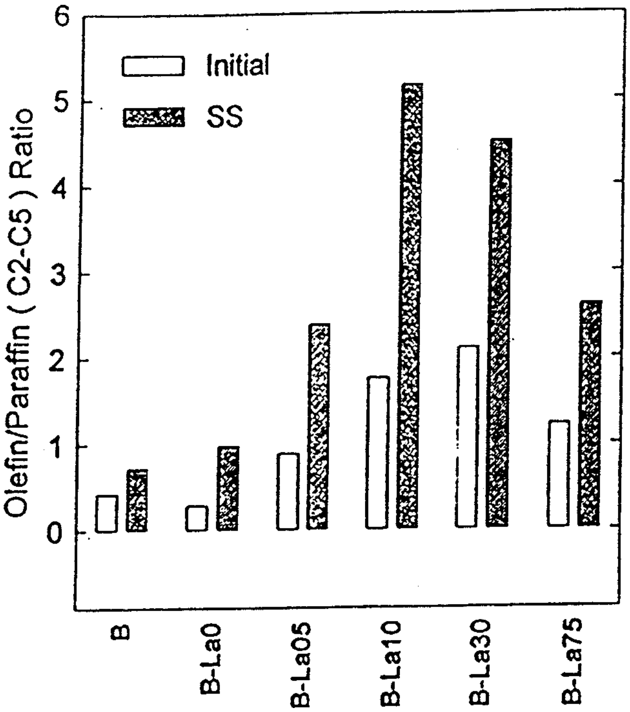

Figure III.8. C_2-C_5 olefin/paraffin ratios for La-promoted Co/SiO_2 catalysts (220°C, 1 atm., H_2/CO = 2) (from ref. III.23).

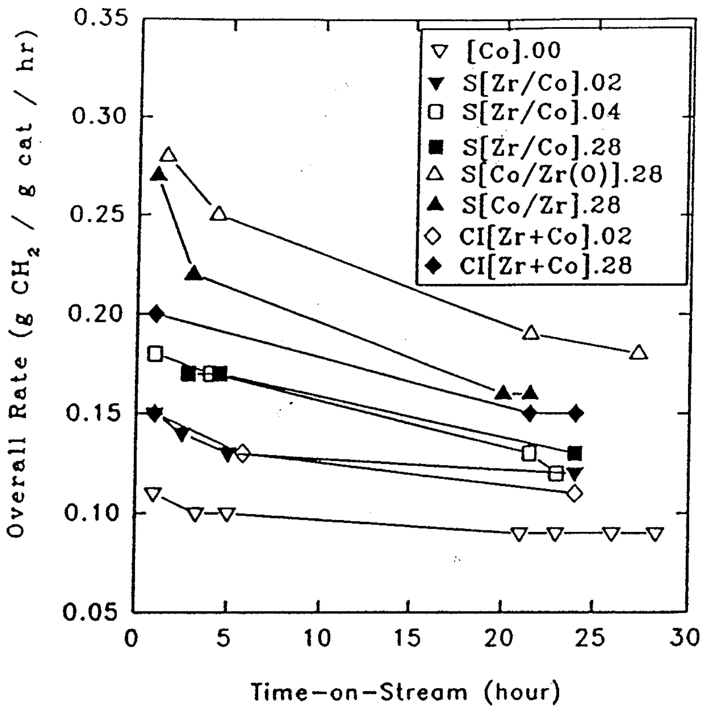

Figure III.9. Overall rate vs time-on-stream during FTS (220°C, 1 atm., $H_2/CO = 2$) (from ref. III.24).

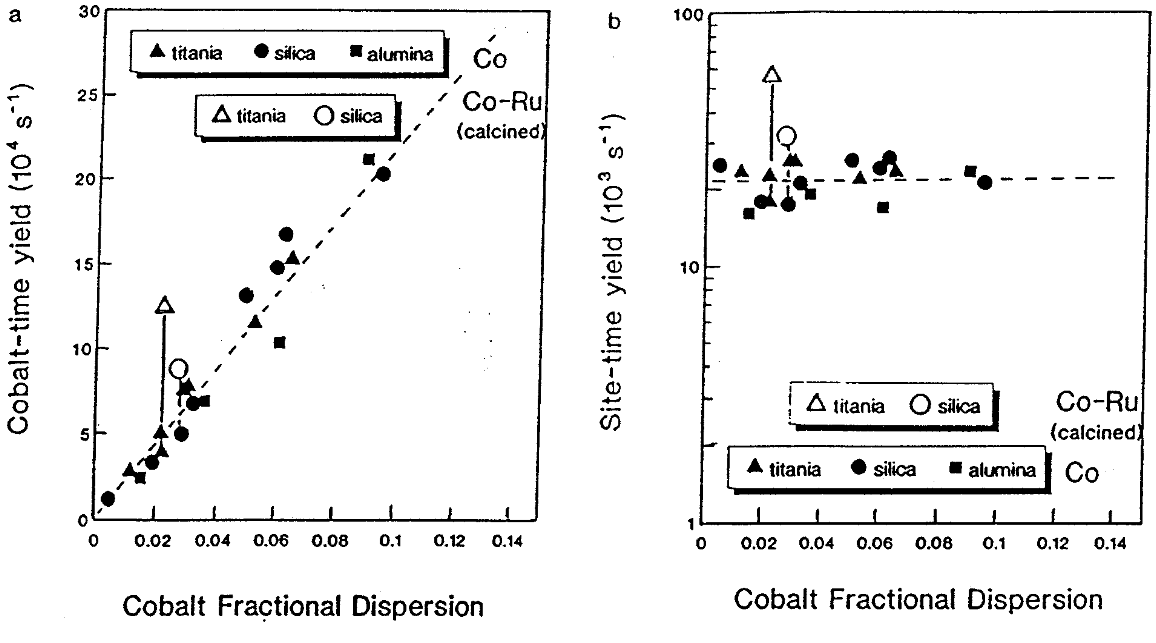

Figure III.10. Effects of cobalt dispersion and support on Fischer-Tropsch synthesis rates (473 K, $H_2/CO = 2.1$, 2.0 MPa, 50-60% CO conversion: (a) metal-time yields and (b) site-time yields (from ref. III.13).

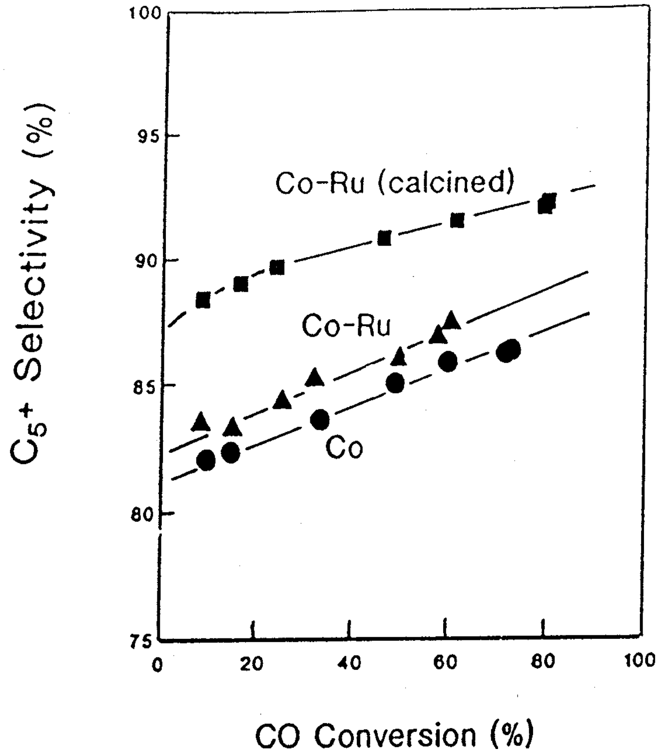

Figure III.11. C_5+ selectivity on Co/TiO_2 and $Co-Ru/TiO_2$ (Ru/Co = 0.0067 at.) catalysts (473 K, 2.0 MPa, H_2/CO = 2.05, 11.6 wt.% Co) (from ref. III.13).

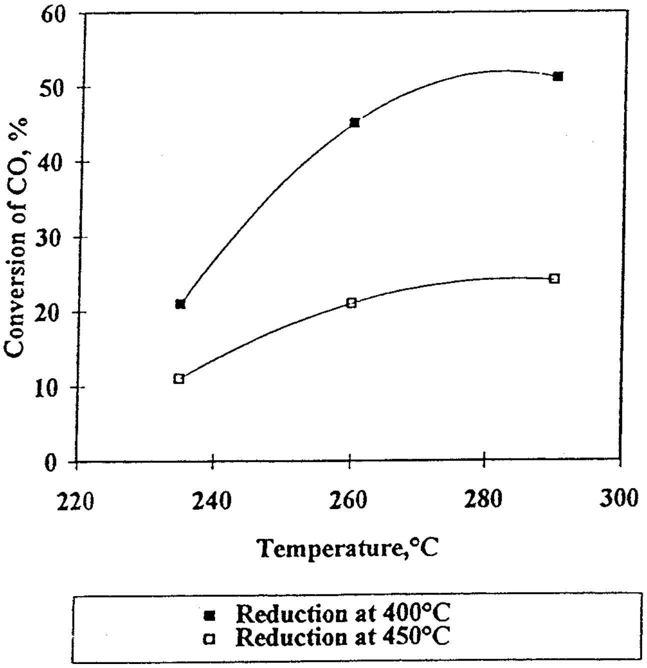

Figure III.12. The effect of reduction temperature on the activity of Co/SiO_2 hydrogenation at 235°C, 5 bar, 1g of catalyst, GHSV of 2600 h^{-1} and H_2:CO:Ar = 3:1:3 (from ref. III.29).

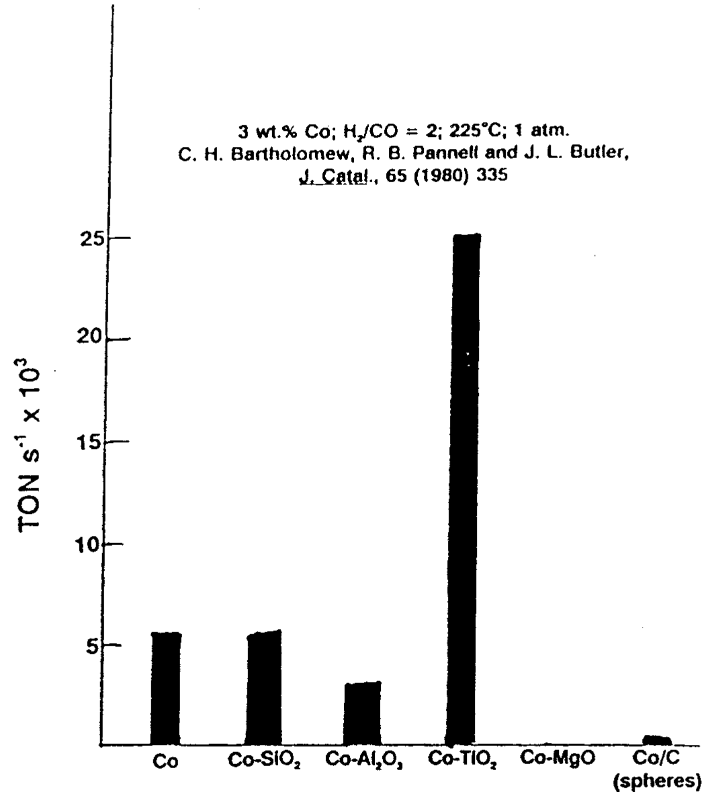

Figure III.13. The activity of the indicated catalysts for CO hydrogenation at atmospheric pressure (drawn using data in C. H. Bartholomew, R. B. Pannell and J.L. Butler, J. Catal., 65 (1980) 335).

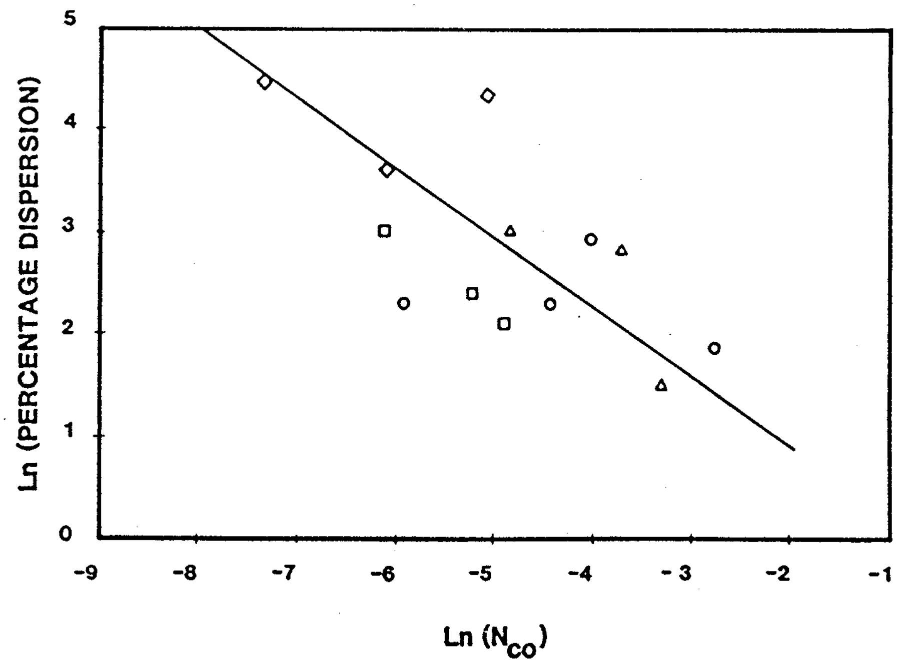

Figure III.14. Percentage dispersion vs CO turnover frequency at 225°C for impregnated, precipitated, and evaporatively deposited catalysts (G, Co/SiO$_2$; F, Co/Al$_2$O$_3$, △, Co/TiO$_2$, ◇, Co/C) (from ref. III.34).

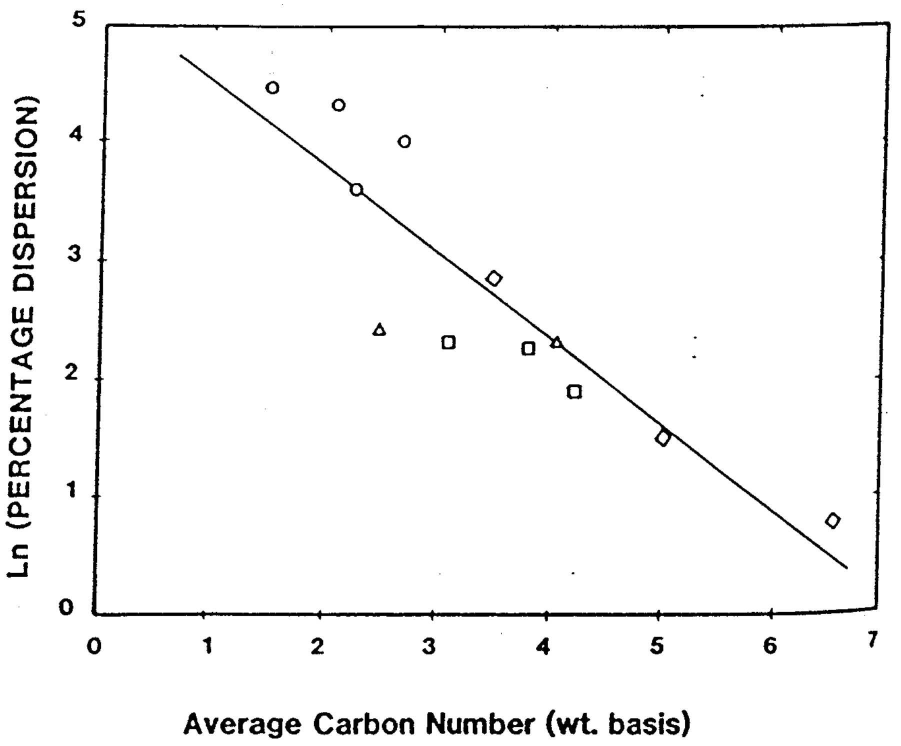

Figure III.15. Average carbon number of hydrocarbons produced at 225°C and 1 atm for 3 and 10 wt.% supported cobalt catalysts as a function of dispersion. (△, Co/SiO_2 (impregnated); G, Co/Al_2O_3 (impregnated); ◇, Co/TiO_2 (impregnated); F, Co/C (evaporatively deposited) (from ref. III.34).

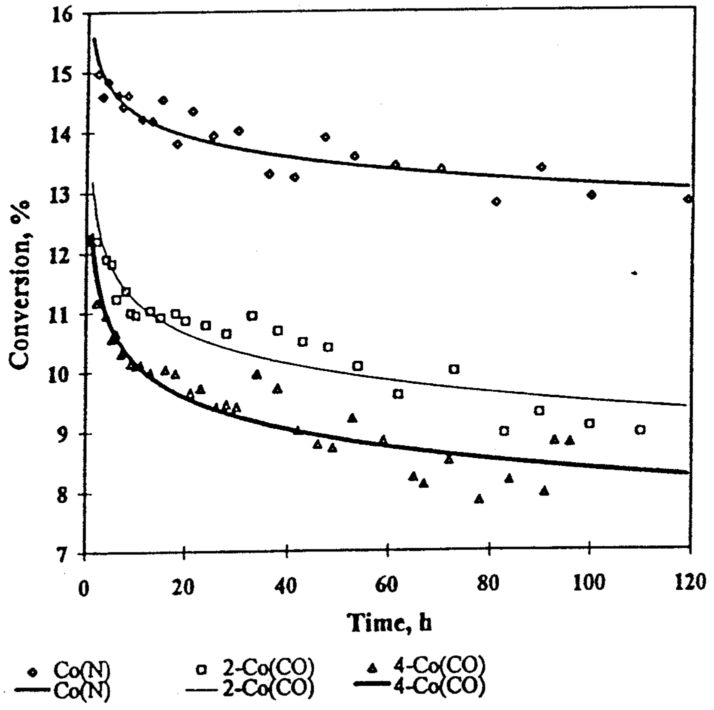

Figure III.16. The activity of Co/SiO_2 at 235°C for 120 h of reaction time (from ref. III.37).

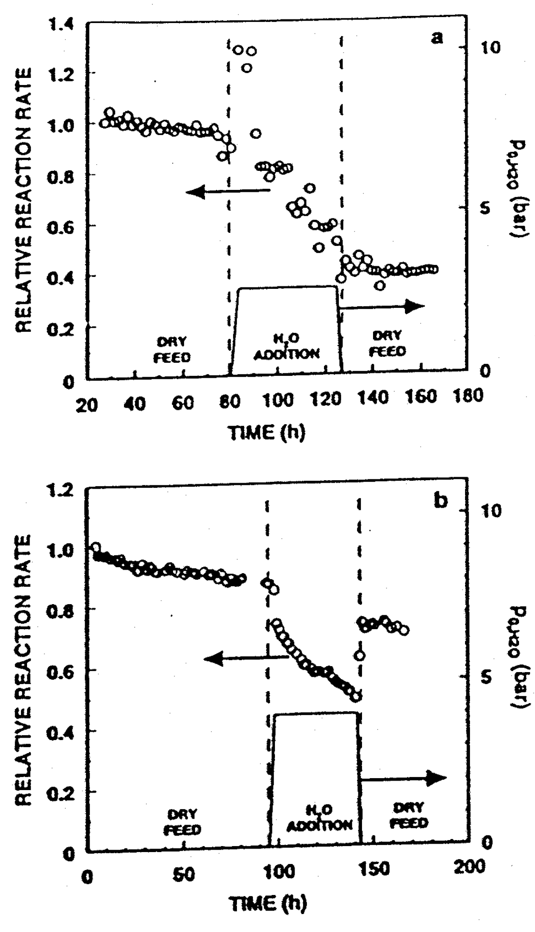

Figure III.17. Observed reaction rate relative to the initial rate for hydrocarbon formation as a function of time during simulated high conversion conditions. $p_{o,H2O}$ = partial pressure of water at reactor inlet. Feed composition: 50 mole% H_2 + CO, $H_2/CO=2$, balance N_2+He or N_2 + He + H_2O. CO conversion before addition of water: 20-28%. (a) Catalyst: 21%Co-1%Re/γ-Al_2O_3 (Puralox). %=483K, P=13bar. (b) Catalyst: 20%Co/γ-Al_2O_3 (Vista-B). T=493 K, P = 8 bar. (from ref. III.38).

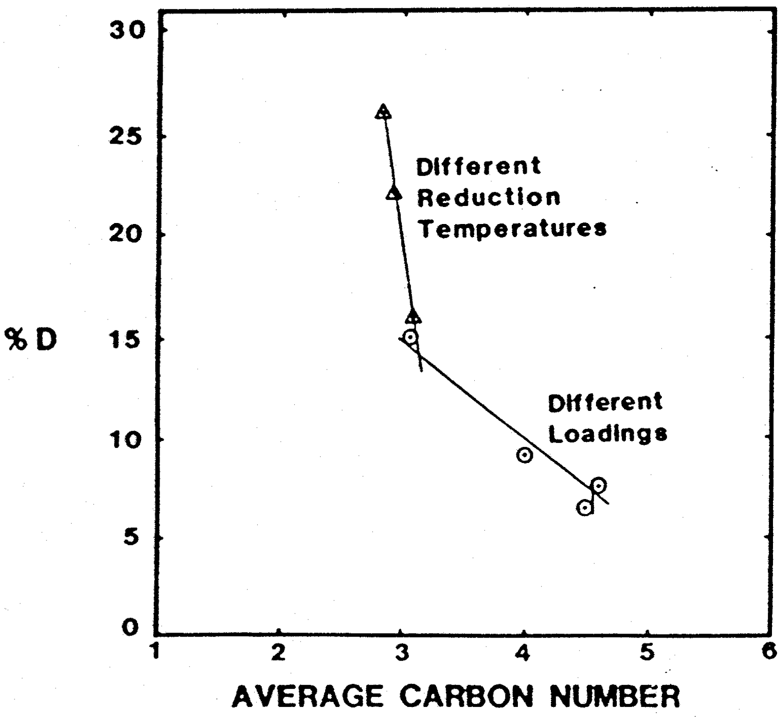

Figure III.18. Correlations of dispersion with average carbon number for Co/Al_2O_3 catalysts of different loading and reduction temperature. (△, different reduction temperatures; F, different loadings) (from ref. III.61).

ATTACHMENT IV

Fischer Tropsch - Examples of Activation

EX-SITU

1. Oukaci et al. [R. Oukaci, J. G. Goodwin, Jr., G. Marcelin and A. Singleton, ACS Fuel Chem Preprint, 39, (1994) 1118] reported that the catalyst is first reduced ex-situ in a fluidized bed assembly and then transferred into a glove box for weighing and subsequent transfer into the slurry bubble column reactor.
2. Beuther et al. reported a procedure known as ROR [H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, South Africa Patent Application No. 855317, July 15, 1985.] in which a reduction in hydrogen, oxidation, and rereduction (ROR) procedure was utilized. The rereduction was conducted the same as the first reduction. The reduction procedure was conducted so that the water vapor pressure did not exceed 1% of the exit gas. The catalyst particles were then suspended in a liquid medium but details of catalyst transfer not given nor were the details of any in-situ treatment prior to the synthesis.
3. Iglesia et al. [E. Iglesia, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patent 4,738,948 (Apr. 1988).] claim a hydrocarbon synthesis catalyst prepared by a process that comprises an impregnation of a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides. It appears

that this procedure is either the same as or very similar to the ROR procedure utilized by Beuther et al. (IV.1).

4. Nay et al. [B. Nay, M. R. Smith and C. D. Telford, "Catalyst treatment;" U.S. Patent 5,585,316, December 17, 1996.] claimed a process for reducing a catalyst containing cobalt, suitable for use in a Fischer Tropsch process for converting synthesis gas into hydrocarbons, which comprises pretreating said cobalt catalyst at 200-600°C with a gas containing molecular oxygen to produce an oxidized cobalt catalyst, a majority of said cobalt being in an oxide form, and then contacting said oxidized cobalt catalyst at elevated temperatures with a gas containing carbon monoxide substantially free of hydrogen, to produce a reduced cobalt containing catalyst. In one example, a 10% Co on ZnO and one portion treated at 500°C in air for 6 hr and then hydrogen for 9 hr at 320°C. The other portion was treated with air for 50 hr and then with CO for 3 hr at 250°C. Conversion was obtained in fixed bed at 30 bar, GHSV 1250 h^{-1}.

Catalyst Treatment	Hr. on Stream	Mean Bed Temp (°C)	CO Conv %	% CH_4	CO_2	C_5+
Air/H_2	214	214	87	7.5	2.5	76.8
Air/CO	213	212	87	4.6	1.9	91.0

During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas (CO/H_2 = 1) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H_2 or syngas (CO/H_2 = 1). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (Figure VI.1; Table VI.1).

IN-SITU

The reduction procedure used by the U.S. Bureau of Mines [6. H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, J. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch oil-recycle process," Bureau of Mines Bulletin 568, 1957.] was conducted at atmospheric pressure. To begin the reduction the temperature was raised to 360^{o}C as rapidly as possible, maintaining a flow of about 40 GHSV. At 360^{o}C the hydrogen flow was increased to 500 to 1,000 GHSV, and was maintained for four hours. The flow was then reduced to 20 GHSV and the temperature reduced to 150^{o}C. Process oil was then added to the reactor, nitrogen replaced the hydrogen flow and the pressure was increased to about 40 psig. When the reflux and readdition of process oil stabilized, the nitrogen flow was replaced by synthesis gas. The pressure was slowly increased which in turn slowly increased the temperature inside the reactor. During 48 h. the temperature remained below 175^{o}C and the gas contraction held to a maximum of 50%. The temperature was increased to 180^{o}C during 24 h. after which the induction period had been completed and the temperature was adjusted to obtain maximum productivity.

Mitchell [W. N. Mitchell, "Activation of hydrocarbon synthesis catalyst;" U.S. patent 5,292,705 (Mar. 1994).] claimed a method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

REFERENCES

IV.1. H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell, U.S. patent 4,605,680, Aug. 12, 1986.

Table VI.1

Effect of syngas vs. hydrogenation activation on the hydrocarbon selectivity using a 4% Co on Zr/Al_2O_3 catalyst utilized in a slurry CSTR.

	Syngas	H_2
Space velocity, NL/gcat/hr	1.6	2.0
CO/H_2	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt.%		
C_1	11.5	7.2
C_{2-4}	10.4	10.8
C_{5-11}	29.2	34.1
C_{12-18}	15.3	27.9
C_{19-23}	12.5	8.6
$C_{24}+$	21.1	11.4
C_{5-23}	57.0	70.6

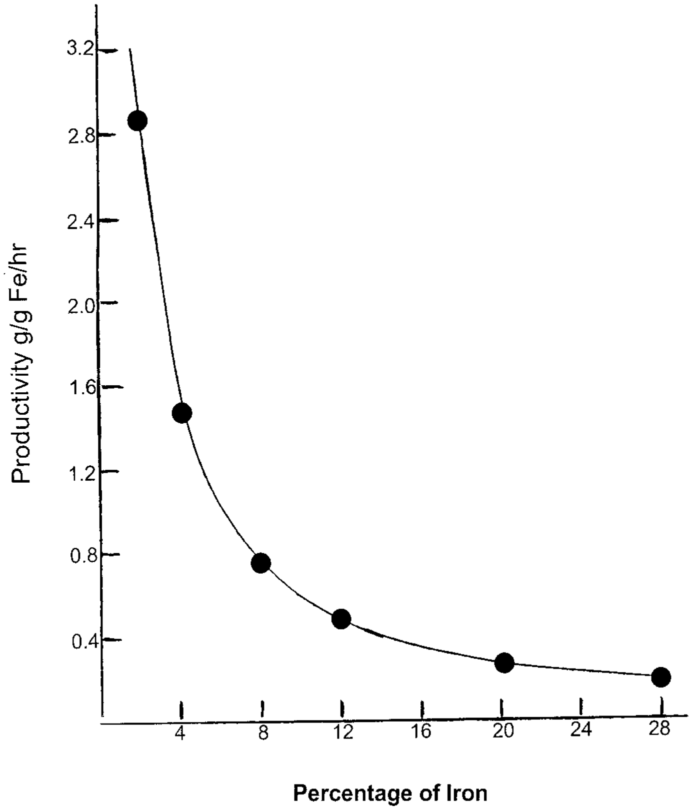

Figure IV.1. Productivity, based upon 2,500 bbl/day and assumed reactor filling, of the Sasol slurry reactor versus percentage of iron in the slurry.

ATTACHMENT V

Productivity - Slurry Phase

I. Iron Catalyst

H. Kölbel, "Chemische Technologie. Band 3: Organische Technologie I, Carl Hansen Verlag, München, 1959, p. 439.

Kg Product/m^3 Reactor/day = 1,000 to 2,000 in the large pilot plant [60 m^3].

0.47 - 0.94 g/g catalyst/hr

Experimental was 0.44 g/g catalyst/hr

Sasol

The reactor is 5 m diameter and 22 m tall. Assuming that only 2/3rd of the total volume is available for synthesis, the reactor volume is about 288 m^3. The productivity is 2,500 bbl/d which is 16,561 L/hr and, assuming a density of 1 g/cm^3 for the product, this corresponds to 16,561 kg/hr. The productivity/reactor volume is then 57.8 kg/hr/m^3. Assuming various iron content per reactor volume produces a productivity of 2.89 g/gFe/hr for 0.02 fraction of iron whereas a loading of 0.2 iron gives a productivity of 0.289 g/gFe/hr (Figure V.1).

II. Cobalt Catalyst

La Porte

Run design for LaPorte Run 3-4

Slurry concentration 24-25 wt.% catalyst, reactor temperature 250-260°C; reactor pressure = 710 psig (48.3 atm), reactor productivity = 150g hc/L/hr. Assume density of slurry is 1.25 kg/L

0.5 g hc/g catalyst/hr

Exxon

R. M. Koros, "Bubble column, tube slurry process and apparatus," U.S. Patent 5,384,336, January 24, 1995.

At 65% CO conversion with H_2/CO = 2.1, 5 cm/s, reaction temperature of 183^{o}C or higher, space velocities of 2800 to 3600 hr^{-1}, the productivities ranged from 450 to 750.

This gives a productivity of 0.28 to 0.47 g hc/cm^3/hr. If the bulk density is 2.7g/cm^3 as given [W.C. Behrmann et al, U.S. Patent5,545,674, August 13, 1996] this corresponds to a productivity of **0.104 to 0.174 g/g catalyst/hr.**

ATTACHMENT VI

Early Slurry Reactors

A unique slurry reactor involved an arrangement of trays, each containing catalysts, that were contained in a cylindrical vertical reactor that was fitted at the top with a reflux condenser and an arrangement for removal of liquid at the bottom of the reactor (figure VI.1) (VI.1,VI.2) Experiments were conducted in a 7-tray reactor, 4.5 cm diameter and 60 cm tall, with up flow of gas.

A tube containing cells, a bundle of tubes, is employed to effect the conversion wherein the catalyst bed is completely submersed in a liquid. An example of one version of this reactor is shown in figure VI.2 (VI.3). Preheated oil is pumped into the outer shell and allowed to descend to the bottom where it is carried, together with the reactant gas, through the reactor tube containing the catalyst. Unconverted gases, the cooling oil and products pass overhead, are cooled and pass to a separator to produce gaseous and liquid product streams as well as recycle cooling oil.

Another reactor is constructed along the lines of a modern multi-tray bubble cap distillation tower. Thus, a reactor is fitted with a number of trays that contain the catalyst with bubble caps arranged to allow vapors, unconverted feed gases and vapor phase products, to be distributed to keep the catalyst in suspension (figures VI.3 and VI.4) (VI.4) Some bubble caps are fitted with downcomers that allow nonvolatile liquid to descent to the bottom of the reactor. In an example, 0.75 lb of catalyst was suspended in one gallon of oil (about 10 % slurry) and charged to a reaction chamber containing 50 bubble trays.

Another variation was provided (figure VI.5 and VI.6) (VI.5). In this version the cooling liquid could be added at several levels in the reactor so as to maintain a better control of the temperature during startup and synthesis.

Benson et al. (VI.6) report that after the preliminary work by F. Duftschmid, E. Linckh and F. Winkler as described above, a pilot plant with a reactor of 0.2 m diameter and 6 m height (about 200 L) was constructed during 1936 and 1937 at pressures of 100 atm and then at 15 to 20 atm. In 1938, a larger plant with a 0.5 m diameter and 6 m tall (1,500 L) was operated.

The U.S. Bureau of Mines constructed and operated a pilot plant that utilized oil-recycle in a reactor with a 3 inch (7.6 cm) and 8 ft. (2.44 m) tall (VI.6). After several runs during 1946-47 with co-current downflow of gas and liquid over cobalt catalysts, a run was made with the cobalt catalyst completely submerged in liquid and co-current upflow of gas and liquid. After it had been demonstrated that the unit could be operated with the cobalt catalyst, the later runs were made with an iron catalyst. The composition of the cobalt catalyst was $Co:ThO_2:MgO$:kieselguhr = 100:7:12:200. The cobalt catalyst was reduced at atmospheric pressure in the reactor. The temperature was raised to 360^oC as rapidly as possible using a hydrogen flow of 10 ft^3/h and then the hydrogen flow was increased to 200 to 400 ft^3/h and the reduction continued for 4 h. Since the catalyst bed occupied about 0.25 ft^3, the GHSV was about 800 to 1600 h^{-1} during the reduction at 360^oC. Following reduction, the hydrogen flow was reduced to 5 ft^3/h and the temperature reduced to 150^oC. Nitrogen replaced hydrogen at this point and the pressure was increased to 40 psig. Oil was then admitted to the reactor. After the oil was added, syngas flow of GHSV = 100 was started. The temperature was slowly increased from 150^oC by increasing the pressure in small increments, which decreased the rate of evaporation of the cooling oil. The temperature was maintained below 175°C, maintaining a gas contraction of less than 50%, during 48 hours. The temperature was increased to 180°C during the next 24 h., after which the induction was considered complete. The conditions were then adjusted as required to obtain maximum productivity.

Kölbel and Ackermann (VI.7, VI.8). obtained patents for an apparatus for carrying out gaseous catalytic reactions in liquid medium. The reactions included Fischer-Tropsch synthesis.

It is stated that the "[Fischer-Tropsch] synthesis according to known processes is feasible without trouble in a reaction space of up to 20 cm [7.9 in] diameter. With increasing horizontal diameter of the reaction space the amount of gas conversion decreases and it is always more difficult to maintain a constant gas conversion. The larger the horizontal diameter of the reaction space, the more the liquid substance leans toward changing from stationary state to a state of vertical rotation. The liquid flows downwardly along the surface of the wall and flows along the bottom to the middle of the reaction space, whereby it is drawn out by the gas bubbles leaving at the middle of the bottom. The compressed central gas stream flows along with the liquid toward the top whereby the firmly compressed gas bubbles combine to form large elongated gas bubbles. Only at the upper reversal point of the liquid, in the vicinity of the surface of the column of liquid, the gas spreads out horizontally across the transverse section and the large gas particles are partially decomposed (Figure VI.7)."

Kölbel and Ackermann illustrated the problem with figure VI.7. As shown, the liquid flows upwardly in the interior of the reactor tube and flows downward along the wall side of the reactor. They indicated several disadvantages accrue from this situation, including:

1. decreased gas conversion,
2. occurrence of secondary reactions,
3. increased catalyst damage, and
4. increased catalyst aging.

These authors state that, for reactions like Fischer-Tropsch synthesis where the gas composition changes with conversion and where the products admix with the unconverted gas, "...the gas conversion should be complete as possible on passing the gas through once..." The authors indicate that, prior to their patent, none of the available operations permit "...maintaining the liquid medium and the suspended catalyst stationary and nevertheless permitting the gas bubbles in uniform size and distribution to pass vertically through the liquid medium at equalized velocity..." The authors indicate that the disadvantages of the liquid and catalyst circulation, as shown in figure VI.7, can be overcome in a cylindrical reactor with a horizontal diameter of more than 30 cm (11.8 in) and up to 3 m or more (9.8 ft or more) and more than 1.5 m (4.9 ft) in height, and a gas headspace above the liquid at least as large as the reactor diameter. To provide within the reaction zone a stationary catalyst and liquid condition, the large reactor shell is subdivided into similar, vertical shafts which are open at top and bottom that have liquid-tight casings and a diameter of at least 5 cm (2 in) (figure VI.8). The shafts should terminate above the expanded liquid level; i.e., in the free gas space. Because of the flows in the bottom of the reactor, it is stated that each of the shafts, in the center as well as at the wall region, receive the same amount gas. While there is circulation of the liquid in the sump (bottom of reactor in figure VI.8), "...there are formed in the shafts extremely stationary liquid columns whose expansion depends on the amount of gas."

The authors indicate that in certain cases, as in the Fischer-Tropsch reaction, it may be an advantage to allow the temperature to rise toward the top of the reactor, and provisions are described which would allow for this to occur. Thus, as the partial pressure of the reactants decrease, the higher temperature will be able to compensate, completely or partially, for the partial pressure decrease.

References

VI.1 F. Duftschmid, E. Linckh and F, Winkler, "Production of valuable hydrocarbons and their derivatives containing oxygen," U.S. Patent 2,159,077, May 23, 1939.

VI.2 F. Duftschmid, E. Linckh and F, Winkler, "Preparation of products containing valuable hydrocarbons or their derivatives, U.S. Patent 2,207,581, July 9, 1940.

VI.3 F. Duftschmid, E. Linckh and F, Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,287,092, June 23, 1942.

VI.4 E. B. Peck, "Method of controlling exothermic reactions, U.S. Patent 2,161,974, June 13, 1939.

VI.5 F. Duftschmid, E. Linckh and F, Winkler, "Synthesis of hydrocarbons," U.S. Patent 2,318,602, May 11, 1943.

VI.6 H. E. Benson, J. H. Field, D. Bienstock, R. R. Nagel, L. W. Brunn, C. O. Hawk, H. H. Crowell and H. H. Storch, "Development of the Fischer-Tropsch Oil-Recycle Process," Bureau of Mines Bulletin 568, 1957.

VI.7 H. Kölbel and P. Ackermann, U.S. Patent 2,853,369, Sept. 23, 1958.

VI.8 H. Kölbel and P. Ackermann, U.S. Patent 2,868,627, Jan. 13, 1959.

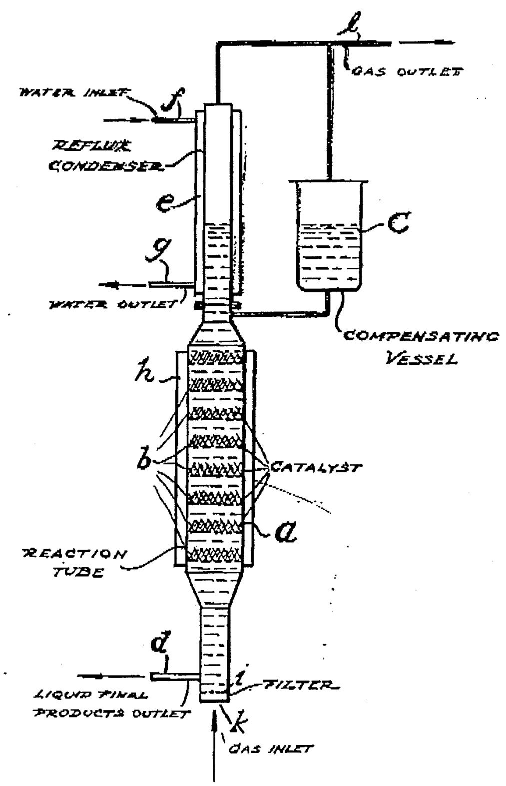

Figure VI.1. Schematic reactor fitted with catalyst trays for the preparation of hydrocarbons from synthesis gas in slurry reactor (from ref. VI.1.).

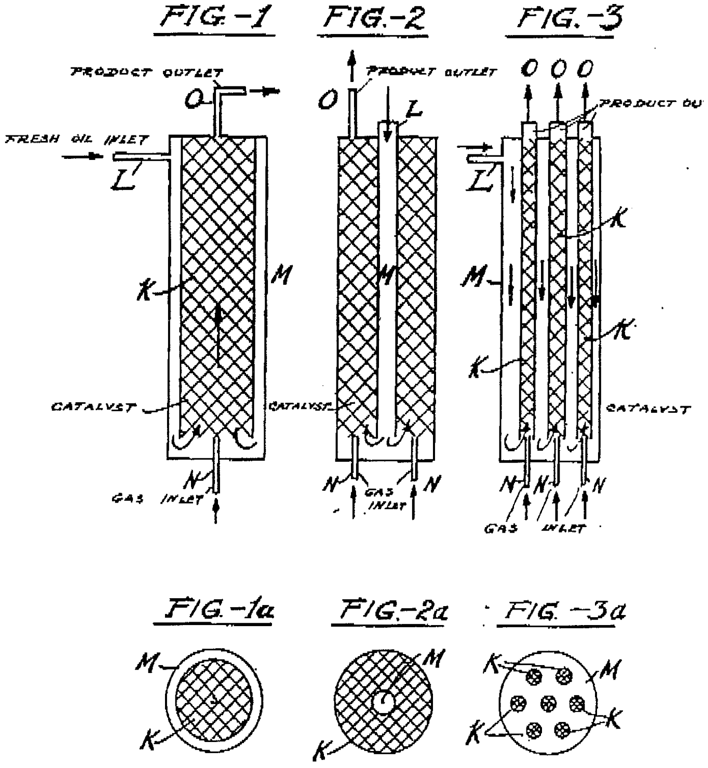

Figure VI.2. Schematic of slurry reactor tube subdivided into cells to modify liquid flow patterns (from ref. VI.3.).

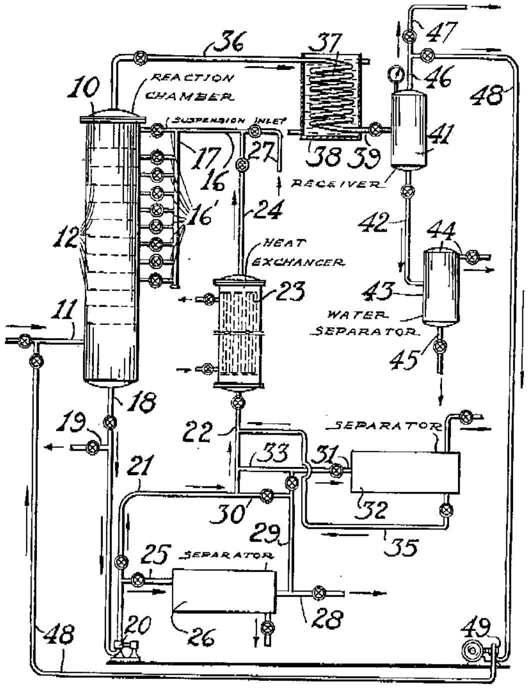

Figure VI.3. Reactor fitted with catalyst trays, each containing bottle caps, to effect slurry phase synthesis of hydrocarbons (from ref. VI.4).

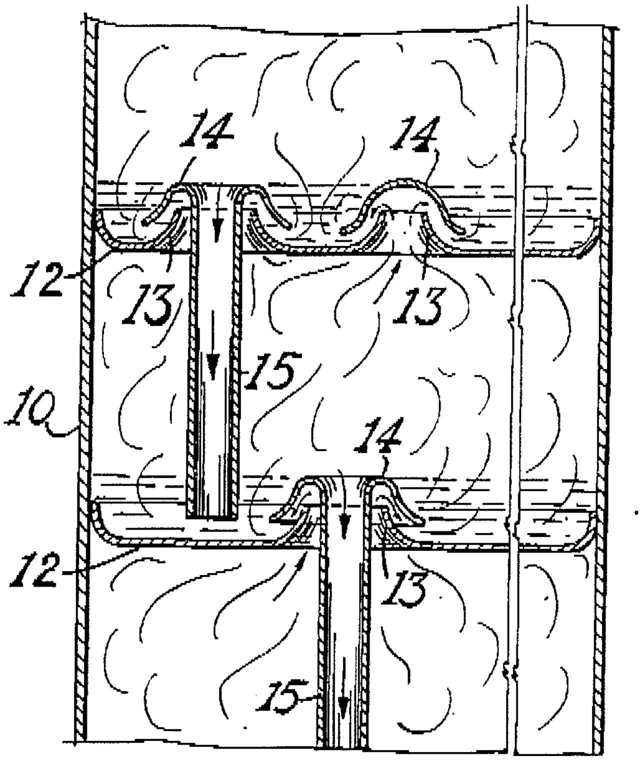

Figure VI.4. Schematic of bubble caps and gas transport columns for trays in reactor shown in figure VI.3 (from ref. VI.4).

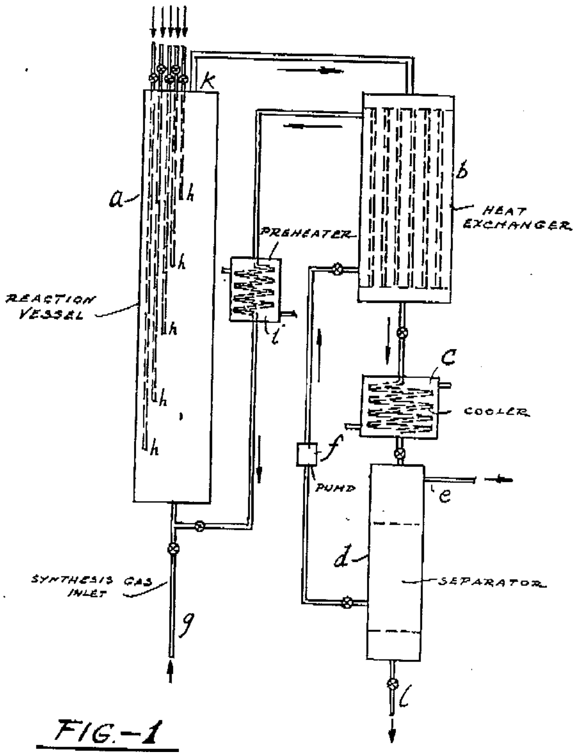

Figure VI.5. Schematic of slurry reactor with capability of adding preheated liquid as several levels within the reactor (from ref. VI.5).

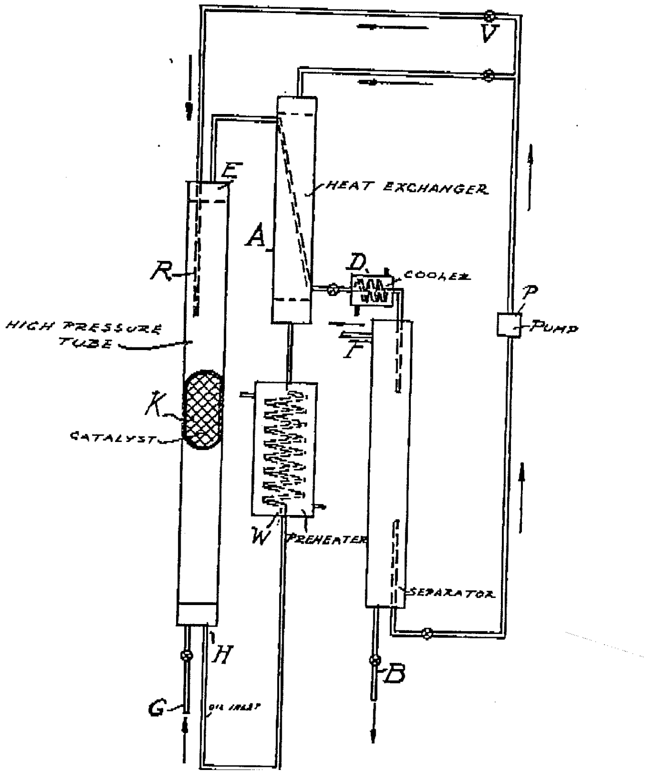

Figure VI.6. Schematic of slurry reactor with recycle of oil to the reactor (from ref. VI.5).

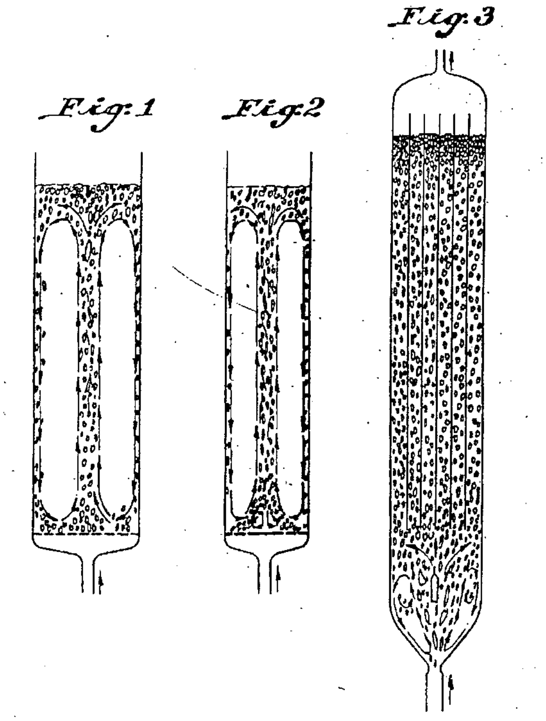

Figure VI.7. Schematic of oil recirculation within slurry reactor (figures VI.1 and VI.2) and the elimination of recirculation by adding shafts (tubes) (figure VI.3) (from ref. VI.7).

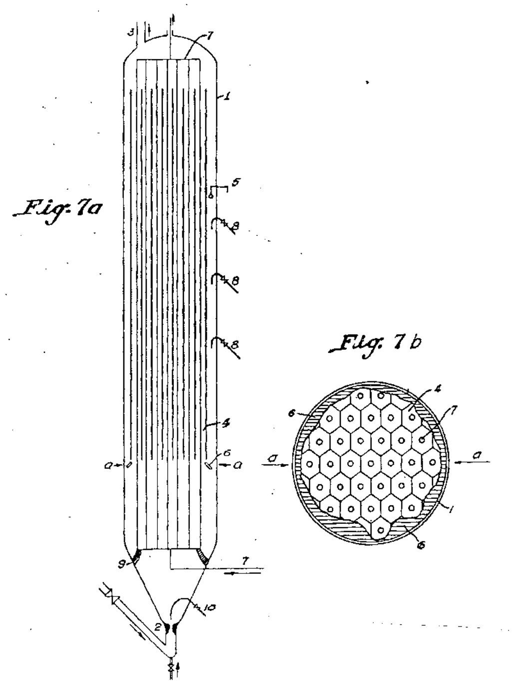

Figure VI.8. Schematic of slurry reactor with shafts (open at top and bottom) to subdivide reactor shell to establish reactor zone with stationary catalyst and liquid condition (from ref. VI.8).

Attachment VII

Tube-in-Shell Fischer-Tropsch Reactor

1. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, **Exxon**, U.S. Patent 5,382,748. The reactor consists of 2-4 inch tubes that are 39.8 ft tall [5.08-10.2 cm x 12.1 m]
2. R. M. Koros, **Exxon**, U.S. Patent 5,384,336; January 24, 1995; filed November 30, 1993. The reactor uses of plurality of reactor tubes (L/D at least 10) in a shell. [Example used 6inch x 50 foot (15.2 cm x 15.2 m) single tube].
3. T. M. Stark, **Exxon**, U.S. 5,409,960; April 25, 1995; filed June 15, 1994. The patent covers the use of pentane rather than steam for heat removal.
4. G. B. Lorentzen, A. Westvik and T. Myrstad; **Statoil**, U.S. Patent 5,520,890; May 28, 1996; filed August 18, 1994. This patent is based on data in U.S. Patent 4,801,573 and presents calculations with no experimental data. The optimum tube diameter is stated to be one which exactly matches heat exchange surface to the synthesis.

ATTACHMENT VIII

Cooling Coils in or outside the Fischer-Tropsch Reactor Shell

1. H. Kölbel, P. Ackermann and Fr. Engelhardt, Erdöl Kohle, 9 (1956) 225; **Rheinpreussen-Koppers**. This report is based on extensive work at Rheinpreussen-Koppers that started in the 1930s. It utilized an iron catalyst and a reactor with dimensions of 1.55 m diameter and 8.6 m height. It used external wax/slurry separation, including filtration, gravity settling and distillation. It also included ex-situ catalyst regeneration.
2. B. Jager and R. Espinoza, Catal. Today, 23 (1995) 17; **Sasol**. The work at Sasol has been scaled from early laboratory work to a 5 m x 22 m reactor that produces 2,500 bbl/day using iron catalyst. Smaller scale work with a 3m diameter pilot plant using a cobalt catalyst has been reported. The commercial plant uses internal separation of wax/slurry.
3. H. Beuther, T. P. Kobylinski, E. E. Kibby and R. B. Pannel, South Africa Patent 855317, July 15, 1985; **Gulf Oil, now Shell**. The work utilized a reactor with external wax-catalyst slurry separation and ex-situ catalyst regeneration. Reactor diameter was not specified - one could reasonably make the assumption that this patent covers **all** reactor diameters. Patent demonstrated the higher productivity of the slurry reactor because of (1) smaller catalyst particle and (2) better temperature control and a lower methane make. The patent also contains data showing the impact of diffusion on the activity, methane selectivity and the C_5+ selectivity when the catalyst is utilized in a fixed-bed reactor.
4. S. J. Hsia, U.S. Patent 5,260,239; November 9, 1993; filed December 18, 1992.

No examples with experimental data. Utilizes downcomer-conduit means of catalyst mixing/transport in reactor and/or ex-situ rejuvenation vessel as means of catalyst rejuvenation on a continuous basis.

5. W. C. Behrmann, C. H. Mauldin and L. E. Pedrick, U.S. Patent 5,382,748; January 17, 1995; filed December 18, 1992.

   Utilizes downcomer(s) to effect liquid recirculation to effect uniform distribution of catalyst in the suspension; a single 3 inch pipe can provide an upward liquid velocity of 2-3 cm/sec in a 4 foot diameter reactor.

6. M. Chang, U.S. Patent 5,332,552;; July 26, 1994; filed December 18, 1992.

   A means of catalyst/slurry recirculation that utilizes concentric shells to provide means for recirculation transport of slurry from the top to bottom of reactor with the additional provision of catalyst rejuvenation on a continuous or at interval basis.

7. C. D. Ackerman, U.S. Patent 5,527,473, June 18, 1996; filed January 9, 1995; **Not Assigned to Company**.

   A slurry reactor with means of internal wax/catalyst slurry separation.

8. E. Rytter, P. Lian, T. Myrstad, P. T. Roterud and A. Solbakken, U.S. Patent 5,422,375; June 6, 1995; February 24, 1993.

   Experimental data using a 4.8 cm x 2 m tube filled with cobalt-alumina catalyst slurry and liquid withdrawn through internal filter during 400 hours of operation. They claim a process using multiphase Fischer-Tropsch synthesis.

9. M. Chang, U.S. Patent 5,242,613; October 12, 1993; filed December 18, 1992.

An improvement of the mixing to improve catalyst distribution by introducing a secondary-suspending liquid, e.g. pentane, above the gas distributor but in the bottom 20% of the column. This is a variation, and may be the same, as used by the Bureau of Mines operation in the 1950s.

10. E. Herbolzheimer and E. Iglesia, U.S. Patent 5,348,982, September 20, 1994; filed May 20, 1993.

    This patent claims a method for optimally operating a large diameter (greater than 15 cm) for Fischer-Tropsch synthesis over a **supported cobalt catalyst** in which particles are fluidized in the liquid phase by bubbles of the gas phase. Derivations are made to define the flows that balance catalyst settling by gravity to catalyst uplift due to the gas bubble velocity. To many, this is a patent based on earlier textbook examples of bubble column operation. It would appear that the region in figure 7 that is considered for optimal performance falls completely, or mostly, within the flows used or described by Kölbel and Ralek.

11. L. E. Pedrick, C. H. Mauldin and W. C. Behrmann, U.S. Patent 5,268,344, December 7, 1993; filed December 18, 1992; **Exxon**.

    One or more vertical draft tubes that are fully immersed in the liquid are used for catalyst mixing and for rejuvenation using pure, or nearly pure, gaseous hydrogen and injecting the rejuvenate catalyst into the top of the reactor.

12. M. W. McEwan and M. B. Teekens, U.S. Patent 4,139,352, February 13, 1979; filed March 14, 1978; **Shell Oil Company**.

    An improved process and apparatus is described for the slurry phase Fischer-Tropsch synthesis. The process utilizes a catalyst but the catalyst is not specified. The slurry reactor separates unconverted gas and gaseous products from the catalyst slurry at the top of the reactor. The catalyst slurry passes through a downcomer fitted with coolers and is returned to the bottom of the reactor. Excess liquid can be removed at the top of the downcomer as can catalyst which requires regeneration.

ATTACHMENT IX

Review of Air Products Fischer-Tropsch Synthesis Work

During the 1980s, Air Products & Chemicals worked on several aspects of the Fischer-Tropsch synthesis. These included the development of novel Fischer-Tropsch slurry catalysts and process concepts, the design of a Fischer-Tropsch pilot plant, the hydrodynamics of bubble column reactors, and the development and operation of the LaPorte Fischer-Tropsch facility (IX.1-IX.7). Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No. [one of two contracts] and is subject to government rights arising therefrom."

The focus of the work was on the use of the low H_2/CO synthesis gas ratios expected from coal gasification. However, a limited number of runs with a H_2/CO ratio that would be typical of the gasification of natural gas were made.

The work on the preparation, characterization and performance of cobalt and ruthenium catalysts focused on the use of carbonyl clusters with the expectation that these would lead to highly dispersed supported metal catalysts. As part of this study a baseline catalyst was prepared by the "normal" procedure using a cobalt nitrate precursor and aqueous impregnation techniques.

The workers utilized a number of catalyst supports. These included: γ-Al_2O_3 (Catapal SB, 217 m^2/g, 45 µm), silica (Davison 952, 339 m^2/g, 70 µm), $MgO \bullet 3.6SiO_2$ (Florisil, 298 m^2/g, 75 µm) and titania (Degussa P-25, 50 m^2/g, 2 µm). These supports were used to prepare the catalysts shown in Table IX.1a and IX.1b.

A common impregnation procedure was used to prepare four batches of a catalyst with a formulation of $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ in which the metal precursor to support ratio was held constant (3.55-3.81 wt.% Co with the Co/Zr ratio 0.55). This base case catalyst, including one larger batch, exhibited similar activity and product selectivity, showing that the preparative method was reproducible.

The catalysts covered in the patents (IX.4-IX.6) are prepared using a decomposable salt or organic compound of cobalt, iron or ruthenium. One claim is (IX.5):

"1. Method of making a catalyst comprising the following steps:

(a) treating an inert, inorganic metal oxide catalyst base material with a nonaqueous solution of a decomposable salt or organic compound of a group IVB metal and removing said nonaqueous solution;

(b) impregnating the product of Step (a) with a nonaqueous solution of a decomposable salt or organic compound of a Fischer-Tropsch metal catalyst from the group consisting of cobalt, iron or ruthenium, and removing remaining said nonaqueous solution; and

(c) exposing the product of Step (b) to a reducing atmosphere; all while maintaining said material and said products under conditions sufficient to avoid hydrolysis, oxidation, and calcination thereof."

A number of catalyst formulations were prepared by the patented technique. Fischer-Tropsch synthesis activity and selectivity were obtained in a fixed-bed reactor (screening test) and for those formulations exhibiting a high activity in a 1-liter continuous stirred tank reactor. The conditions used for the screening studies were 240-280^{o}C, CO/H_2 feed = 0.55 - 2.0, 300 psig (2.0 MPa) and a space velocity of 1.0-2.0 NL/g cat/hr.

The $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (3.5% Co, 6.6% Zr) catalyst was found to be the most active system in the slurry reactor and also gave the best liquid fuel selectivity. The Schulz-Flory pattern was found for the products obtained using this catalyst. The bulk activity ranged from 16 to 54 mole syngas/kg cat/hr. The gasoline range (C_5-C_{11}) products accounted for 20 to 45% of the products and the diesel range (C_{12}-C_{18}) products were 17 to 32%. This catalyst was tested in an extended slurry-phase run that achieved 6 months on stream with a 10% loss in activity.

A comparison was made for 4% cobalt Zr-alumina catalysts in which the dominant difference was the cobalt compound used in the preparation of the catalyst: cobalt carbonyl in an organic solvent and cobalt nitrate in aqueous solution. The specific activity of the nitrate derived catalyst is significantly lower that the one derived from the carbonyl compound when the conversion is effected at 240^{o}C is the CSTR (Table IX.2). However, when the conversions are compared at 260^{o}C, there is less difference between the two conversions; one possibility to account for this is that significantly more sintering of the cobalt occurred for the carbonyl derived catalyst at this higher temperature.

The activity of the $Co_2(CO)_8$-based catalysts decreased with changing supports as follows: $SiO_2 >> TiO_2 > Al_2O_3 > MgO\bullet SiO_2$ (figure IX.1). The Co/TiO_2 catalyst was found to exhibit an unusually high selectivity for C_{3-5} olefins. Zirconium was found to be the better promoter, compared to Ti, for enhancing activity and selectivity, with the optimum Co/Zr ratio being between 0.5 and 1.0.

As the cobalt loading was increased from 4 to 14 wt%, the catalytic activity remained constant and then eventually declined.

The supported Ru catalyst exhibited initially a high activity but the catalyst deactivated rapidly in the slurry reactor. Thus, not much data were obtained with this catalyst.

They found that the following kinetic expression best fitted the data they obtained over a wide range of conversions:

$$-(r_{CO+H_2}) = kC_{H_2}/(1 + k\ C_{H_2O}/C_{CO}C_{H_2}). \qquad [1].$$

However, it was not possible to discriminate with great confidence among the kinetic equations tested during the study.

Catalyst Activation

The activation of supported metal carbonyl catalysts is frequently done by thermal decomposition under vacuum or inert gas atmosphere (IX.8). During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas ($CO/H_2 = 1$) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H_2 or syngas ($CO/H_2 = 1$). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (figure IX.2a,b; Table IX.3).

Catalyst Promoters

The Air Products work included a comparison of the promotional effects of zirconia and titania for both silica and alumina supports. The titania promoted cobalt catalyst on both alumina and silica supports showed lower catalytic activity than a similar zirconia promoted catalyst. The bulk activity at 240°C for the alumina supported cobalt was 20 % lower with the titania promoter; with the silica supported cobalt this was 40% lower. The titania promoter also produced more methane and light hydrocarbons than the zirconia promoted cobalt catalyst. Similar activity trends were obtained in both the fixed-bed and slurry reactors; however, the differences in the selectivity were less noticeable in the slurry reactor.

Cobalt Metal to Promoter Metal Ratio

In this study the cobalt to promoter ratio for the silica support was conducted with precursors which contained the same level of cobalt but with a variable amount of promoter. Four catalysts were prepared and the compositions are shown below:

Weight % Cobalt	Weight % zirconium	Co/Zr
4.0	4.8	1.2
4.4	2.3	0.53
4.6	0.1	0.15
4.2	0.0	0.0

The effect of the Co/Zr ratio in the gas-phase reactor on the bulk and specific activities for this series are shown in figures IX.3 and IX.4. It appears that the optimum ratio for bulk activity occurs at about Co/Zr = 1; however, for the specific activity it occurs at about Co/Zr = 0.5, the base case catalyst ratio. The usage ratio appears to increase as the zirconium content increases. The base case catalyst provided the highest yield of liquid fuel, C_5-C_{18}.

Three of the catalysts, Zr/Co = 0, 0.53 and 1.9, that were evaluated in the fixed-bed reactor were also evaluated in the CSTR (figure IX.5). Just as in the fixed-bed reactor, the optimum activity was obtained for the base case catalyst with a Zr/Co = 0.53 ratio.

Metal Loading

Metal loadings of 3.5, 11.0 and 14.4 wt.% Co on silica were evaluated. For the base case (3.5 wt% Co) the Zr/Co ratio was 0.53 but this ratio was not used for the catalysts with the higher cobalt loadings. One reason for using the higher Zr/Co ratio for the two higher Co loadings was to be able to make a comparison with the Co/Zr/silica catalyst that is used by Shell Oil for their Shell Middle Distillate Synthesis (SMDS). There was little change in the bulk activity in increasing Co content from 3.5 to 11.0; however, at all temperatures there was a significant decline in activity upon further increasing the Co content to 14.4 wt.% (figure IX.6). Selectivity to liquid fuels declined as the Co loading increased.

Significant increases were observed for the bulk density with increasing Co loadings: 0.394 g/cc for 3.5 % Co, 0.564 g/cc for 11.0% Co, and 0.883 g/cc for 14.4% Co. Thus, as the experiments were conducted in the fixed-bed reactors, the amount of catalyst contained in the 10 cc catalyst volume increased significantly and this may have been a major factor in determining the bulk activity shown in figure IX.6.

In the slurry reactor tests of the 3.5 and 11.0% Co catalysts, the activity at both 240 and 260^{o}C declined as the Co content increased in contrast to the fixed-bed reactor runs (figure IX.7).

Product Selectivity

Satterfield et al. (IX.9) reviewed the literature with respect to product distributions for slurry Fischer-Tropsch reactor operation, particularly with iron catalysts. It was concluded that product hydrocarbon selectivities follow a predicted Anderson-

Schulz-Flory (ASF) distribution characterized by the chain growth probability factor, α, and that previously reported deviations are probably due to experimental artifacts. Fixed-bed temperature gradients, insufficient time to reach steady-state, volatilization of certain fractions, and condensation of high molecular weight material are some of the experimental problems that can give misleading selectivity results. These considerations are for deviations which produce chain-limiting Fischer-Tropsch product distributions; most agree that deviations which produce more high-molecular weight products than predicted by ASF are valid (IX.10). Air Products workers sought to avoid the problems previously encountered by their close attention to experimental details, and by determining product distributions over long-term slurry phase operations with good quantitative mass balances (IX.11).

With the fused iron United Catalysts, Inc. C-73 catalyst, a good fit to the ASF distribution was obtained (figure IX.8). However, for slurry catalyst A2 (later shown to be a cobalt-zirconia-silica catalyst) there was an enhanced product deviation from the ASF distribution for the C_{18}-C_{35} region when the catalyst was operated at 2.21 MPa. The effect of pressure in determining this product enhancement can be seen by comparing curves a and b in figure IX.8.

Another catalyst, B, also shows a deviation from ASF (figure IX.9). There was a significant deviation from the ASF distribution for the C_9-C_{25} products when operating with a feed of $H_2/CO = 0.5$. The yield of 67.3 wt% product obtained in the C_9-C_{25} products represents a 25 wt% increase over what was considered to be the limit of 54.1% imposed by the ASF distribution.

An adequate explanation for these deviations obtained early in the experimental program has not been offered. These and similar catalysts usually provided "standard"

ASF distributions based on the data reported. This implies that some experimental operational problem was responsible for this unusual, and highly desirable, deviation from ASF distribution.

Ruthenium Catalyst

A Ru/Zr/alumina ($Co_2(CO)_8$) was a promising catalyst when tested in the fixed-bed reactor. The fixed-bed activity was 26.7 mol syngas/kg cat/hr (comparable to the Co base case catalyst) and a high specific activity of 0.48 mol/mol Ru/min. Methane production was high at about 20%. Slurry phase testing of this catalyst indicated a significantly lower catalytic activity (8 mol syngas/kg cat/hr).

A Ru/Zr/silica catalyst was also tested and it exhibited a much higher activity (70 mol syngas/kg cat/hr; 0.834 mol CO/mole Ru/min at 240^{o}C; 81 mol syngas/kg cat/hr and 1.05 mol Co/mol Ru/min at 260^{o}C) than the similar catalyst using alumina as a support. The Ru catalyst produced higher molecular weight products than a similar Co catalyst. Methane selectivity was low, never exceeding 5.3%.

The performance of the Ru/Zr/silica catalyst was poor in the CSTR. Initially showing a high activity at 240^{o}C (43 moles syngas/kg cat/hr), it had declined to 4 moles syngas/kg cat/hr after only 280 hours on stream.

These preliminary results led the workers to concentrate their further efforts on their cobalt catalysts.

Improving Water-Gas-Shift (WGS) Activity

Since both the Ru and Co catalysts exhibited very low WGS activity, attempts were made to modify the catalyst to increase the WGS activity. A physical mixture of the base case catalyst and a commercial Cu/Zn/alumina low temperature shift catalyst was employed. The addition of the shift catalyst caused a decrease in the Fischer-

Tropsch synthesis without increasing the WGS activity. A Co/Fe/alumina catalyst was prepared using the carbonyl compound of Co and Fe. There was a 53% increase in the usage ratio indicating increased WGS; however, the bulk activity declined by 40%. A Fe/Co/Zr/silica catalyst showed only a slight increase (14%) in usage ratio and a slight decrease in bulk activity. Thus, the exploratory effort to increase the WGS activity failed.

Extended Runs in CSTRs

A run of nearly 6 months was made with a Co/Zr/silica catalyst (4.43% Co, 7.58% Zr) (IX.12). This catalyst displayed remarkable stability. During the first 1012 hours it was utilized at 240^oC, 300 psig, CO/H_2 = 0.5 and space velocity = 1.8 l/g cat/hr, and then from 1012 to 2188 hours at 260^oC, 300 psig, CO/H_2 =1 and space velocity = 2.0 L/g cat/hr. The productivity declined from 52.7 to 46.9 mol syngas/kg cat/hr during 1012 hours (figures IX.10 and IX.11) and then declined slowly during operation from 1012 to 2188 hours (figures IX.12 and IX.13). During the second period the product selectivity remained nearly constant (figure IX.14).

After 2188 hours, a series of changes from the base case conditions, 260^oC, 300 psig, space velocity 2.0 L/g cat/hr and CO/H_2 = 1.0, were made for the CO/H_2 ratio and the space velocity to generate data for kinetic studies. At intervals, the conditions were returned to the base case to obtain data to correct for the slow catalyst aging. A series of tests were made at two feed set of conditions. In one instance, the impeller speed was altered using constant feed conditions and in the other the space velocity was varied by adding a nitrogen flow, maintaining the same partial pressure of hydrogen and carbon monoxide by increasing the total pressure. Both variations show that mass transfer effects can be neglected.

At 3964 hours, the temperature was increased to 280°C to repeat the series of kinetic measurements. At this temperature the methane production was very high (up to 56.4%) and the wax production very low. At the end of the experiment, the reactor contained only solid, indicating that the operations at the higher temperature had caused the reactor to loose essentially all of the liquid through vapor pressure and/or hydrogenolysis effects.

Cobalt Dispersion

Hydrogen chemisorption was measured to obtain a measure of the metal dispersion of the cobalt and ruthenium catalysts. Air Products reports indicate that they were disappointed with the low dispersions that they obtained; however, the 10-12% dispersion values they obtained for 11 and 14% Co on silica are about as high as reported by later workers. In general, the silica supported Co exhibited a higher dispersion than the alumina supported cobalt at a similar metal loading (Table IX.4). The hydrogen chemisorption was considered to decrease along with the catalytic activity as the cobalt loading was increased for the silica supported cobalt catalysts. The dispersions obtained by the Air Products workers agree with those reported by Reul and Bartholomew (IX.13). Chemisorption was measured at higher temperatures because this led to higher surface areas.

Olefin Reincorporation

In a screening study, ethene was added to the syngas feed for runs with the $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ catalyst (5.07% Co; 4.39% Zr). Under the reaction conditions employed, the CO conversion should have been 20% or less. When 10 or 20 volume percent ethene was added to the feed, the major result was the production of ethane. The oxygenate production did increase slightly (from 0.2 to 2.4 wt%) but the majority of this fraction was propanol, the product of hydroformylation. The catalyst underwent significant (20% conversion) deactivation during the addition of ethene. The conclusion is that ethene did not undergo significant incorporation; rather it was hydrogenated to ethane.

Kinetic Study

A program was developed to obtain kinetic data from the experimental data (figure IX.15). Experimental data from two runs were made with a catalyst formulation that was essentially the same as the base case catalyst but a more active $Co_2(CO)_8/Zr/SiO_2$ catalyst (4.9% Co; 9.3% Zr). Henry's Law was assumed to apply and to allow for calculation of vapor partial pressures. Henry's Law data was taken from Peter and Weinert (IX.14) and liquid densities were calculated using correlations proposed by Deckwer (IX.15). Mass transfer from bulk liquid to catalyst surface was considered to negligible, based upon the experimental data.

The authors fit the data to five kinetic expressions (to correlate with equations in reference 13, A=2, B=1, C=3, D=4):

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{CO_2}/C_{CO}) \qquad [2]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{H_2O}/C_{CO}) \qquad [3]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + K_1C_{CO_2}/C_{CO} + K_2C_{H_2O}/C_{CO}) \qquad [4]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{H_2O}/C_{CO}C_{H_2}) \qquad [5]$$

$$-r_{CO+H_2} = kC_{H_2}^{a}C_{CO}^{b}. \qquad [6]$$

For the run with the catalyst similar to the baseline catalyst, the data at high H_2/CO feed ratios and at high space velocities were best described by the first order rate equation:

$$-\ r_{CO+H_2} \ = \ kC_{H_2}^{a}C_{CO}^{b}. \qquad [7]$$

where a = 1.1 and b = 0. For low H_2/CO data, equation 3 fits the data better:

$$-\ r_{CO+H_2} \ = \ k\ C_{H_2}/(1\ +\ KC_{H_2O}/C_{CO}) \qquad [8]$$

where k = 0.349 and K = 0.425. The activation energy was in the range of 33-44 kJ/mole.

For the more active catalyst, none of the five equations were able to be used to fully describe the data. They concluded that equation 3 provided the better fit to the data and transformed the equation to a linear form:

$$C_{H_2}/-r_{CO+H_2} \ = \ (K/k)\ C_{H_2O}/C_{CO}\ +\ (1/k). \qquad [9]$$

The data are plotted using equation 7 and is shown in figure IX.16 for 240, 260 and 280°C. From the intercept, the rate constant, k, is derived with values ranging from 0.328 to 0.775 cc/g cat/sec. This allows K to be determined from the slope and values ranging from 0.466 to 0.302 are obtained. An activation energy of 51 kJ/mole was obtained from the Arrhenius plot.

The authors write that, at that time, relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts have been made (IX.17-IX.22). From the available literature, activation energies for cobalt catalysts are in the range of 67-117 kJ/mole; for iron catalysts they range from 37 to 105 kJ/mole. The activation energies obtained by the Air Products workers for these catalysts are surprisingly low.

The Air Product workers analyzed the kinetic data obtained during run hours 2188 and 3964 in the extended run described above. It was assumed that the deactivation led to a linear decrease in conversion during the kinetic measurements. They concluded that Equation 5, which included water inhibition, fit the data better than the other equations; a plot of the data using the linearized form of Equation 5 is shown in figure IX.17. It had been reported by Huff and Saterfield (IX.23) that this equation describes data with high water concentration quite well. After Equation 5, the data was best fit by equation 6. The rate constant obtained using Equation 5, based upon fresh catalyst activity, are $K = 5.24 \times 10^{9} \exp(-23{,}254/RT)$ cc/g cat/sec and $K = 1.55 \times 10^{-3} \exp(-6{,}250/RT)$ mol/cc. The Arrhenius plot returned an activation energy of 97 kJ/mole, and this value agrees much better with those reported earlier for cobalt catalysts.

Slurry Reactor Hydrodynamics Studies

The final report (IX.24) provides a detailed summary of the literature to that date (about 1983) and experimental data obtained in cold flow simulators of 12.7 and 30.5 cm diameter (1.52 and 4.75 m height, respectively) that was conducted at Air Products. With the simulator, phase holdups, phase dispersion coefficients, and interphase heat and mass transfer coefficients were measured. The measured heat and mass transfer and phase dispersion correlations were found to conform to the literature, while the phase holdup correlations were different from the literature. The product distributions from Air Products' catalyst testing program were combined with the hydrodynamic studies to make predictions of space-time yields of product fuel fractions in large-scale bubble column reactors.

Based upon the study, they concluded:

1. Both hydrodynamic and kinetic effects are important to the proper design of the bubble column reactor.
2. For solid particles below 60 µm, the slurry can be modeled as a pseudo-single phase. Larger size solid particles were distributed in accordance with Cova's sedimentation-diffusion model (IX.25).
3. Of those studied, the most important independent variable affecting the reactor performance was the superficial gas velocity, followed by solid particle loading. The type of liquid had a small effect on the column hydrodynamics. The parameters that had little or no effect in the range studied included the presence of heat transfer internals, solid type, distributor hole size, and superficial slurry velocity.
4. Staging the bubble column system to provide more plug flow behavior of the gas was predicted to result in a 5% increase in conversion rates, assuming the same bubble size, about 0.23 cm, as in the unstaged column. On the other, if the average bubble diameter is decreased to 0.07 cm, the conversion rates are expected to increase by 25%.
5. The gas holdup obtained in the cold flow systems was lower than measured by Deckwer (IX.26) and Mobil (IX.27) but in agreement with results of Satterfield (IX.28) and with the correlations from Air Products' slurry phase methanol project (IX.29).
6. Adding seven, 5.7 cm o.d. x 1.42 m heat transfer internals to the 30.5 cm column had no effect on column hydrodynamics.

7. The heat transfer results agreed with Deckwer's correlation (IX.30) but, unlike Deckwer, the heat transfer rates continued to increase beyond a 10 cm/s superficial gas velocity. Heat transfer tubes would therefore take only a small fraction of the internal volume of a Fischer-Tropsch slurry bubble column reactor.
8. Mass transfer results agreed with Akita and Yoshida (IX.31) and Hikita et al. (IX.30-IX.33).
9. Liquid dispersion results agreed with Kato et al. (IX.34), indicating that above a superficial gas velocity of 3 cm/s, the slurry was well-mixed.

The Air Products workers wrote, "One of the more important aspects of gas flowing through a tubular reactor is its availability at the reaction site. This is ultimately related to the interfacial area between the liquid and gaseous phases. In a two-phase, gas-liquid system, the interfacial area, a, is related to the gas volume fraction, ϵ_G, and mean bubble size, d_{SB}, by

$$a = 6\ \epsilon_G\ /\ d_{SB} \qquad [10]$$

Both the mean bubble size, also known as the Sauter mean diameter, and the volume fraction, which is typically referred to as gas holdup or void fraction, are values which are extremely important to optimum reactor design."

The Air Products work followed three steps:

1. Hydrodynamic data were obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator.
2. Scale hydrodynamic study to 12" ID x 15.5' (30.5 cm ID x 4.75 m) column.
3. Incorporate kinetic data from catalyst studies with hydrodynamic correlations into a computer model and use this to predict the conversion rates and space-time yields that would be obtained in actual Fischer-Tropsch slurry reactor operation.

Using the model, the heat, mass and momentum transfer parameters which most affect the bubble column design were better quantified.

In the slurry reactor, either mass transfer resistance or kinetic resistance is expected to dominate. Gas holdup, average bubble size and mass transfer coefficient are the important dependent variables that impact mass transfer resistance. Two important factors for kinetic resistance are solids dispersion and liquid dispersion, both affecting catalyst loading, and thereby reactor productivity. Heat transfer rate is also important since this will determine the fraction of the reactor volume required for heat exchangers, and not available for production. The Air Products work attempted to quantify the above mentioned parameters (Table IX.5).

The workers reviewed work prior to 1982 concerning gas-liquid-solid systems. They indicate that Kara (IX.35) found that solid particles promote bubble coalescence and hence the onset of the churn-turbulent regime. However, reports of solids decreasing or increasing gas-holdup can be found in the literature. Kurten and Zehner (IX.36) report Sittig's work on bubble breakup caused by solids. It was shown that bubble breakup occurs when the inertia forces of the solid particle exceed the bubble surface tension forces:

$$(\pi/6)(\rho_S/2)\, d_S^3\, u_{SG}^2 > (\pi/4)\, \sigma\, d_S^2 \qquad [11]$$

which, when rearranged, shows that bubble breakup can occur when the Weber number is greater than 3:

$$We = (\rho_S\, d_S\, u_{SG}) / \sigma \geq 3\,. \qquad [12]$$

This indicates that below the critical Weber number the solid will not cause bubble breakup.

Since for a particle of about 4 or about 100 µm, a bubble rise velocity > 0.1 or 0.65 m/sec, respectively, is needed for the particle to induce bubble breakup, it is not anticipated that Fischer-Tropsch slurry column will experience bubble breakup due to the presence of solid catalyst particles. In fact, it is expected that bubble coalescence will occur, decreasing gas holdups.

Deckwer et al. (IX.15) studied gas holdup in 4.1 and 10 cm ID columns in the bubbly flow regime (1 to 4 cm/sec) using a hydrogenated Fischer-Tropsch liquid and up to 16 wt.% of > 5 micron alumina particles and obtained the empirical correlation:

$$\epsilon_G = 0.053\ j_G^{1.1} \qquad [13]$$

where j_G is the superficial velocity of the gas. It was suspected that foaming occurred in the measurements reported by Deckwer et al. (IX.15). Kuo (IX.27) obtained data for the same system showed that with a sintered plate gas distributor he obtained foaming but that no foaming and a much smaller gas holdup was obtained with a distributer with larger openings. Bukur (IX.37) used the same wax as Deckwer and Kuo and obtained a means of eliminating the formation of a foam region. In the absence of a foam region, Bukur obtained a gas holdup that was comparable to those of Pilhofer and Bach (IX.38) and the results obtained by Air Products.

It was concluded that gas holdup was mostly a function of gas velocity and varies to the first power. Slurry density, or weight loading, has the second largest impact on gas holdup. The larger column (30.5 cm) had a lower gas holdup than the 12.7 cm column at the higher gas velocities. It was considered that this was due to more bubble coalescence in the taller column and that the data obtained in the larger diameter column, being more reliable, would be used in the computer simulation of an operating commercial Fischer-Tropsch reactor.

The gas bubble diameter was obtained over a wide range of conditions. The bubble diameter, d_{SB}, relationship with the gas holdup, the gas liquid interfacial area is related to the Sauter mean bubble diameter and gas holdup by

$$a = 6\ \epsilon_G / d_{SB}\ . \qquad [14]$$

The uncorrected bubble chord lengths were in the range from 0.28 to 0.44 cm. The measured values are slightly larger than the true values because the experimental approaches caused bubble acceleration/elongation during the measurement. The corrected bubble diameters ranged from 0.22 to 0.35 cm and the bubble velocity ranged from 26.3 to 32.7 cm/sec, both range over fairly narrow values. Since the bubble size should be smaller in Fischer-Tropsch liquids than in water, they concluded that the Calderbank (IX.39) correlation suggested a Sauter diameter size of 0.23 cm for a Fischer-Tropsch type system and this produces

$$a = 6\ \epsilon_G / 0.23 = 26.09\ \epsilon_G \qquad [15]$$

which was used in the computer model.

The overall mass transfer coefficient, K_La, is the product of the mass transfer rate per unit area, K_L, and the interfacial area, a. Air Products workers measured K_La because of the variation in the reported values. This variation was primarily due to variation in the reported gas holdup and average bubble size; however, there is also variation in the reported values of K_L. They obtained an empirical correlation for K_La:

$$K_La = (0.30\ \epsilon_G^{1.06}\ d_p^{0.05}) / W^{0.08} \qquad [16]$$

where W = weight fraction of solids. Gas velocity was considered to be the primary factor in estimating K_La.

Liquid dispersion relates to how well mixed the liquid phase is and how much solid can be suspended. The Air Products workers discussed this in terms of two extremes:

1. Ideal mixing, continuous stirred tank reactor (CSTR) behavior where any liquid molecule can move to any other part of the column from one instant to the next, and
2. Plug flow reactor (PFR), where any molecule will move in concert with the other neighboring molecules, entering and leaving the column at the same time.

The axial liquid dispersion coefficient, E_z, provides one was to quantify where a particular reactor lies between these two extremes (CSTR and PFR). E_z will be zero for PFR and infinity for CSTR behavior. In practice, when E_z is greater than 10^{-2} m^2/sec, a well-mixed behavior exists. Knowing E_z, one can plot a sample's concentration as a function of time at a fixed point within the column; such a plot is a residence time distribution (RTD) curve.

A model that is used to describe the sample concentration at any time is Fick's Law:

$$dC/dt = E_Z\, d^2C/dZ^2\ . \qquad [17]$$

Using the appropriate boundary conditions, an approximate analytical solution which describes the RTD curve at any point within the column was given by Ohki and Inoue (IX.40):

$$dC/dt = E_L\, d^2C\ /\ dZ^2. \qquad [18]$$

For the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$dC/dt)_{0,T} = dC/dZ)_{L,T} = 0 \qquad [19]$$

where L = extended bed height and

$$C(Z,O) = \begin{array}{l} O,\ O \le Z < Z_1 \\ C_O,\ Z_1 \le Z \le Z_2 \\ O,\ Z_2\ Z \end{array} \qquad [20]$$

$$C/C_e = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L)\exp(-n^2\pi^2 E_L t/L^2)] \qquad [21]$$

Little difference is obtained if the summation is to infinity, the exact solution, or stops at 100.

The experimental program to address the dispersion issue and to obtain the RTD curve utilized the injection of a sodium chloride solution into water, detecting the movement of the sodium chloride, the tracer, by conductivity measurements at various heights in the column.

The energy dispersion is greatest at the gas distributor inlet and least at the gas disengagement zone at the top of the reactor. However, E_Z was not height dependent was not evident since one dispersion coefficient was sufficient to characterize the entire column. The results of the liquid dispersion runs at Air Products were in agreement with the work of Kato and Nishiwaki (IX.41):

$$Pe = (13\ Fr) / (1 + 6.5\ Fr^{0.8}) \qquad [22]$$

where Pe is the Peclet number $((V_G\ d_C) / E_Z)$ and Fr is the Fraud Number $(V_G / g\ d_S)^{1/2}$.

From their experimental work, they obtained data to show that a uniform distribution of 0.5-5 micron sized particles was obtained. With larger particles there was, as expected a distribution of particles along the column height, with more at the bottom than the top. They concluded that nonagglomerating catalyst particles less than 60 microns should be suitable for Fischer-Tropsch bubble column batch operation, as no unsuspended solids were observed.

Heat transfer was studied by placing tubes with heaters in the bubble column. It was noted that the agitation produced by the gas phase within the reactor produces heat transfer coefficients that are higher than those produced by gas or slurry alone. The heat transfer surface needed for internal use is less than required for an external exchanger.

The report ends with an engineering evaluation that utilizes the model proposed by Deckwer et al. (IX.42). The substitution of the Air Products correlations for those in Deckwer's model showed little effect at low gas velocities. At 9 cm/sec the space-time yield was doubled (Tables IX.6 and IX.7). A major reason for this was that the lower gas holdup allowed for more catalyst per unit volume. In the bubble column operation there exists an optimum gas holdup which will maximize column space-time yield. Gas holdups higher than this optimum will be reaction rate-limited while those lower than this will be mass transfer-limited. The optimum gas holdup will be affected by the bubble size (b_{SB}), intrinsic kinetic rate (K_o), catalyst weight loading (W), the rate of mass transfer across the gas-liquid interface (K_L), and the usage ratio (U). The optimum gas holdup is given by the expression:

$$\alpha \text{ opt} = 1 / [1 + (6 K_L(1 + U) / K_o W d_{SB})^{1/2} . \qquad [23]$$

Using this equation allows one to calculate the relative space-time yields for a variety of K_o, W and D_{SB} (Table IX.8).

The Air Products workers compared the space-time yield for a bubble column reactor and for a series of staged reactors. In the first method of calculating the space-time yield, a number of idealized CSTRs are simulated with almost complete recycle of the liquid and catalyst but no recycle of the gas phase. This model would be equivalent to the recirculating cell model used in the literature. In the second method, the extent of backmixing of the gas phase was modeled by applying an axial dispersion model (IX.43).

In this model, a low dispersion coefficient refers to many CSTRs in series, while a high dispersion coefficient refers to very few CSTRs in series. Carberry (IX.44) showed that the two methods are relates so that:

$$N = V_G L/2D \ . \qquad [24]$$

Since the Deckwer computer model incorporates the axial dispersion model for the gas, liquid and catalyst phases, this approach was chosen.

Results of simulating the Rheinpreussen-size column as several stages as having the same total volume as the original single-stage column (figure IX.18) are shown in Table IX.9. Thus, a 5% increase in space-time yield is obtained by using 5 CSTRs but a further increase does not lead to a further increase in yield (figure IX.19).

Design of LaPorte Plant

As part of the work, a design for a pilot plant to be located at La Porte, Texas adjacent to an Air Products plant was completed (IX.45). The bubble Fischer-Tropsch reactor was sized to operate in the churn-turbulent flow regime, in which commercial-scale reactors will operate. The study indicated that this flow regime could be achieved with an effective reactor diameter of five inches. However, it was recognized that the exact diameter of the transition from the quiescent to churn turbulent regime is an unknown function of the slurry viscosity and surface tension. To achieve a 40-50% conversion of the synthesis gas in a single pass at a superficial gas velocity of 0.3 ft/sec would require a 30 foot expanded slurry height.

The reasons for the choice of flow regime were described. Concurrent up-flow bubble columns can operate in any one of three flow regimes (IX.15) and these are illustrated in figure (IX.20) together with an indication of the Air Products cold flow work, the LaPorte design and the Rheinpruessen work. The bubbly flow or quiescent regime occurs at velocities less than typically 0.15 ft/sec. Bubbles are of uniform size and do not interact or coalesce to any substantial degree. At higher velocities, the bubbles do not rise uninfluenced by neighboring bubbles and the churn turbulent regime is entered. Coalescence occurs, yielding larger bubbles and faster rise velocities. Because of coalescence, gas holdup does not increase as quickly with gas flow rate in the churn turbulent regime as in the bubbly flow regime. Where the coalesced bubble would be larger than the diameter of the column, the slug flow regime is reached. Slug flow is undesired because of the low gas/liquid interfacial area and the tendency for the slurry to be lifted out of the reactor along with the gas.

The choice of flow regime was dictated by two economic factors. For a given reactor volume:

1. The highest space time yield or production rate per unit volume is optimal.
2. A tall column is preferred to a short one.

The higher the space-time yield, the smaller the reactor volume required for a given production. The simulations with the Deckwer model and the Air Products hydrodynamic and catalytic data showed that, in every case, the optimum gas velocity for a maximum space-time yield falls within the churn turbulent regime. It was concluded that the value of 9.1 cm/sec (0.3 ft/sec), although slightly below the optimum, would still allow a reasonable conversion for the reactor height chosen.

Air Products workers wrote, "For a commercial plant with multiple trains, it is advantageous to have as few reactor vessels as possible. In the quiescent regime only about 15' of reactor height is required to achieve 90+% conversion of syngas. By increasing the gas velocity into the churn turbulent regime, 90+% conversion of syngas is not achieved until a height of 60'. For equivalent STY's, it is more economical to have N vessels at 60' than to have four times that number of vessels, each with a height of 15'." (IX.45).

The slurry reactor was designed to operate in a fluidized-bed mode. Once charged, the slurry will not be added or removed except for removal of high molecular weight products that form during reactor operation. Gas will flow up the column and exit out the column top.

The design was implemented at the La Porte location and the plant has been modified during the years of operation. To date, four runs, two with an iron catalyst and two with cobalt catalyst, have been conducted.

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Table IX.1a.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an alumina support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
3.6	6.6					0.25
4.4	1.8					0.31
3.4	6.6				1.6	0.31
2.8	4.9					0.48
1.4				0.51		0.40
1.2			0.3	0.4		
4.7[a]						0.25
3.5		8.6				0.23
2.6				0.85		0.34
2.4			0.02	0.79		0.27
3.9	5.0					0.24
5.1[a]	4.4					0.20
4.2[a]	7.1					0.20
4.0	6.4					0.21
10.8	8.5					0.26
3.5	6.6					0.51
3.7	7.3			0.72		0.26

a. Cobalt added as cobalt nitrate.

Table IX.1b.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an silica support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
4.4		4.0				0.24
3.7	7.2					0.23
4.6	7.5					0.43
4.0	3.3					0.83
3.5						0.31
	7.3			2.4		n.d.
4.0	4.8					0.44
4.4	2.3					0.32
4.6	2.3					0.32
4.2						0.14
4.1	6.8					0.31
11.0	7.4					0.15
14.4	10					0.07

Table IX.2

Effect of Co source on activity and selectivity of 4% Co on Zr/alumina catalyst tested in the slurry phase using a CSTR at 300 psig, CO/H_2 = 1.0 and 2.0 NL/g cat-hr. (from reference IX.1)

Cobalt Source	Carbonyl	Carbonyl	Nitrate	Nitrate
	240°C	260°C	240°C	260°C
Bulk activity, mol syngas/kg cat/hr	35.3	38.5	15.8	29.9
Specific activity, mol CO/mol Co/min	0.29	0.32	0.09	0.21
Selectivity, Wt.%				
C_1	7.9	10.4	10.9	16.5
C_{2-4}	13.7	15.0	6.5	11.1
C_{5-11}	37.0	44.5	12.9	26.5
C_{12-18}	23.4	25.8	19.8	23.8
C_{19-23}	8.9	2.0	21.9	10.6
C_{24}+	9.1	2.3	28.0	11.5
TOTAL FUELS, C_{5-23}	69.3	72.3	54.6	60.9

Table IX.3

Effect of syngas vs. hydrogenation activation on the activity and hydrocarbon selectivity using a 4% Co on Zr/Al_2O_3 catalyst in a slurry CSTR (from reference IX.1)

	Syngas	H_2
Space velocity, NL/gcat/hr	1.6	2.0
CO/H_2	1.6	1.5
Pressure, psig	300	300
Temperature, ^{o}C	250	258
Hydrocarbon, wt.%		
C_1	11.5	7.2
C_{2-4}	10.4	10.8
C_{5-11}	29.2	34.1
C_{12-18}	15.3	27.9
C_{19-23}	12.5	8.6
C_{24}+	21.1	11.4
C_{5-23}	57.0	70.6

Table IX.4

Metal dispersion for Co and Ru Catalysts (from reference IX.1)

Catalyst	BET Surface Area, m^2/g	Metal Surface Area, m^2/g	Dispersion, %
3.5%Co/Zr/SiO_2	316	1.9 (a)	6
4.0%Co/Zr/Al_2O_3	209	0.3 (b)	1
4.1%Co/Zr/SiO_2	210	1.9 (a)	7
11.0%Co/Zr/SiO_2	302	8.1 (a)	12
10.8%Co/Zr/Al_2O_3	n.d.	5.4 (a)	7
14.4%Co/Zr/SiO_2	145	9.3 (a)	10
4.0%Ru/Zr/SiO_2	325	1.6 (b)	8

(a) Hydrogen chemisorption performed at 100°C
(b) Hydrogen chemisorption performed at 35°C.

Table IX.5

Slurry Reactor Design Variables Considered in the Air Products Study (reference IX.21)

DEPENDENT VARIABLES	
Gas Hold-Up	Mass Transfer
Bubble Size	Liquid Dispersion
Solids	Heat Transfer
INDEPENDENT VARIABLES	
Slurry Medium: Paraffin, water	
Superficial Gas Velocity: 1.52 - 15.2 cm/sec	
Superficial Slurry Velocity: 0 - 3.0 cm/sec	
Solid: Silica, Iron Oxide	
Solid Size: 1 - 5 µm, 45 - 53 µm, 90 - 106 µm	
Solid Concentration: 0, 10, 20, 30 Wt.%	
Distributor Hole Size: 0.9, 3.2, 12.8 mm	
Heat Transfer Internals: None, Plain	

Table IX.6

Rheinpreussen Simulation using Deckwer Correlations (from reference IX.1)

REGIME	CHURN TURBULENT		
CATALYST	Base Case	Cat. A	Cat. B
Inlet gas velocity, cm/sec	9.00	9.00	9.00
Gas holdup	0.385	0.512	0.526
Interfacial area, cm^2/cm^3	32.66	43.44	44.66
Temperature, ^oC	260.2	259.7	260.2
Rate Constants			
Preexponential factor (sec wt.% in slurry) x 10^5	1.12	90.3	115
Activation energy, kJ/mol	70	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65
Hydrogen conversion, %	80.4	34.9	49.8
Relative mass transfer resistance	0.106	0.021	0.035
Space-time yield, mol CH_2/hr	2937	1065	1022
Constants in Case Study			
Reactor length, ft (cm): 26.25 (800)			
Reactor diameter, in (cm): 59 (150)			
Contraction factor: -0.5			
Particle diameter, µm: 50			
Reactor pressure, psig (bar): 174 (12)			
Weight fraction catalyst in slurry: 0.20			
Specific heat transfer area, cm^2/cm^3: 0.10			

Table IX.7

Rheinpreussen Simulation using Air Products Correlations (from reference IX.1)

REGIME	CHURN TURBULENT			
CATALYST	Base Case*	Cat. A	Cat. B#	Cat. B with Shift
Inlet gas velocity, cm/sec	9.00	9.00	9.00	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm^2/cm^3	32.66	36.06	41.43	35.39
Temperature, ^oC	260.2	260.4	260.4	261.1
Rate Constants				
Preexponential factor (sec wt.% in slurry) x 10^5	1.12	90.3	115	115
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Relative mass transfer resistance	0.106	0.043	0.069	0.048
Space-time yield, mol CH_2/hr	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm): 26.25 (800)				
Reactor diameter, in (cm): 59 (150)				
Contraction factor: -0.5				
Particle diameter, µm: 50				
Reactor pressure, psig (bar): 174 (12)				
Weight fraction catalyst in slurry: 0.20				
Specific heat transfer area, cm^2/cm^3: 0.10				

*Operating conditions at Rheinpreussen
#Cold flow model gas holdup correlation

Table IX.8

Optimum gas holdup, gas velocity*, and space-time yield (STY) (K_L = 0.0205 cm/s; U = 2) (from reference IX.1)

CASE	K_o, sec^{-1} $wt\%^{-1}$	W, %	d_B, cm	α opt, vol %	V_G cm/sec	STY
1	$1.4x10^{-3}$	20	0.07	6.8	2.13	1.00
2	$1.4x10^{-3}$	60	0.07	11.2	12.75	2.72
3	$6.1x10^{-3}$	60	0.07	20.9	36.43	9.42
4	$1.4x10^{-3}$	20	0.30	13.1	5.29	0.87
5	$1.4x10^{-3}$	60	0.30	20.7	36.00	2.17

*Using Air Products cold flow gas holdup correlation

Table IX.9

Rheinpreussen simulation for staged reaction systems (from reference IX.1)

NUMBER OF STAGES	1	20	5	20
DISPERSION COEFF., cm^2/s	72.130	128.8	572.5	143.8
Gas Holdup	0.145	0.148	0.158	0.158
Interfacial area, cm^2/cm^3	4.148	12.717	4.514	4.527
Hydrogen Conv., %	66.1	85.1	69.2	69.2
Rel. Mass Transfer Resistance	0.556	0.310	0.542	0.541
Space-Time Yield, mol CH_2	2,417	3,128	2,529	2,530
Improvement Ratio	1.000	1.294	1.046	1.047

CONSTANTS IN CASE STUDY

Reactor Length, ft (cm): 26.25 (800)

Reactor Diameter, in (cm): 59 (150)

Contraction Factor: -0.5

Particle diameter, m: 50

Reactor Pressure, psig (bar): 174 (12)

Weight Fraction Catalyst in Slurry: 0.20

Specific Heat Transfer Area, cm^2/cm^3: 0.30

Inlet Gas Velocity, cm/sec: 9

Temperature, C: 260.0

Preexponential Factor (see wt% in slurry): 3.45×10^7

Activation Energy, kJ/mol: 94l7

Inlet Ratio, mol CO/mol H_2: 1.98

Usage Ratio, mol CO/mol H_2: 1.98

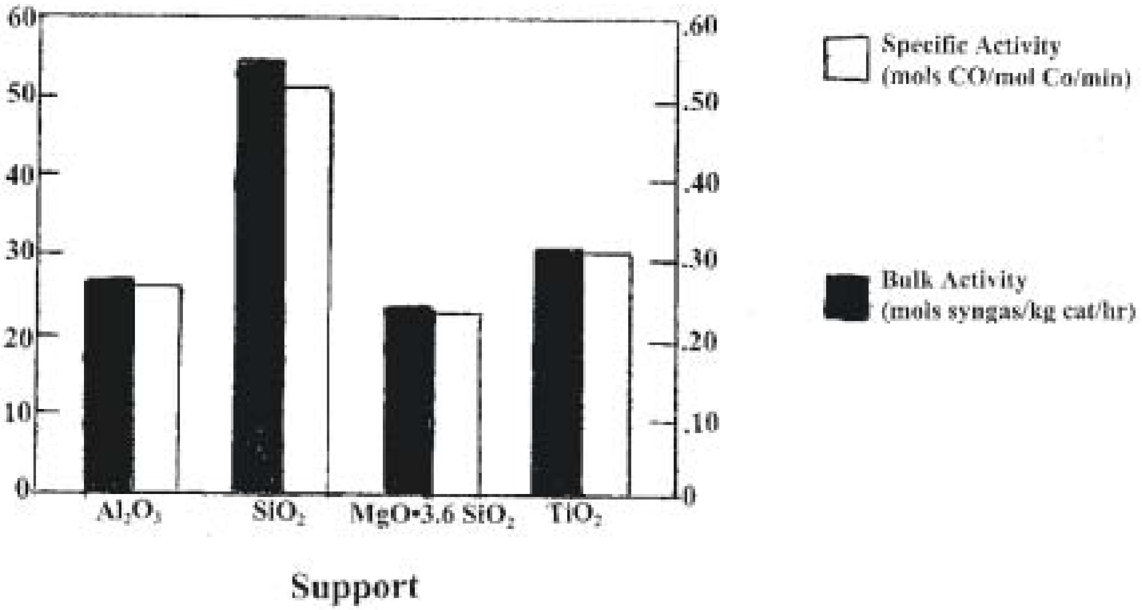


Figure IX.1. Activity of $CO_2(CO)_8$-based catalysts, fixed bed reactor (240°C, CO/H_2 = 1.0, GHSV = 1000 hr^{-1}, 300 psig).

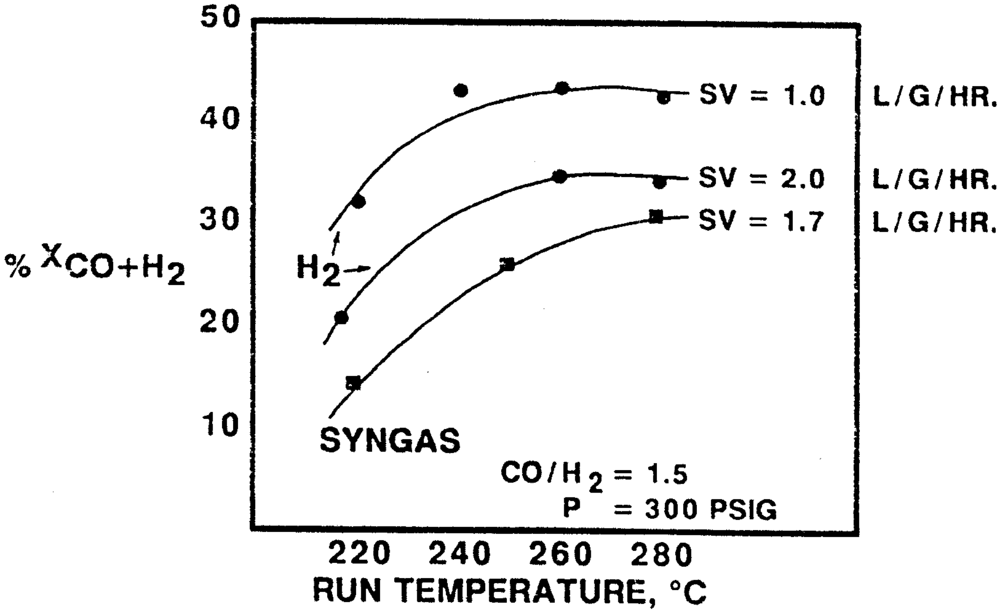


Figure IX.2a. Effect of syngas versus hydrogen activation on conversion.

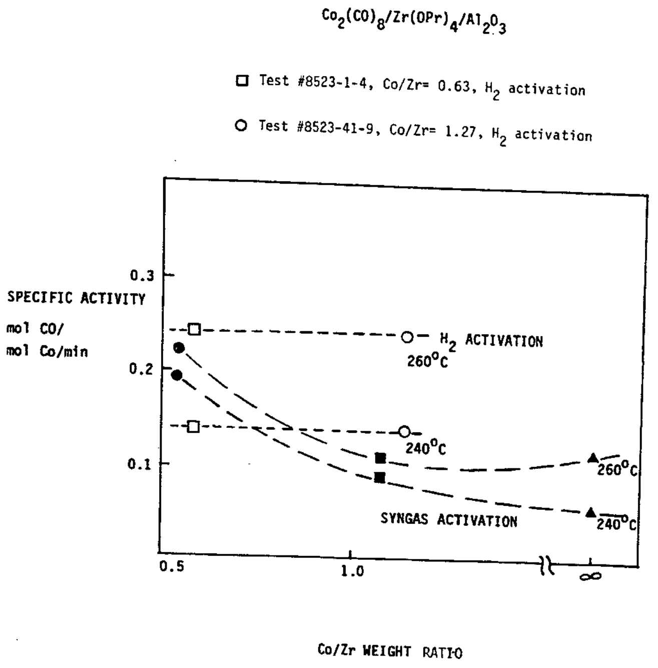


Figure IX. 2b. CO/Zr ratio effect on activity.

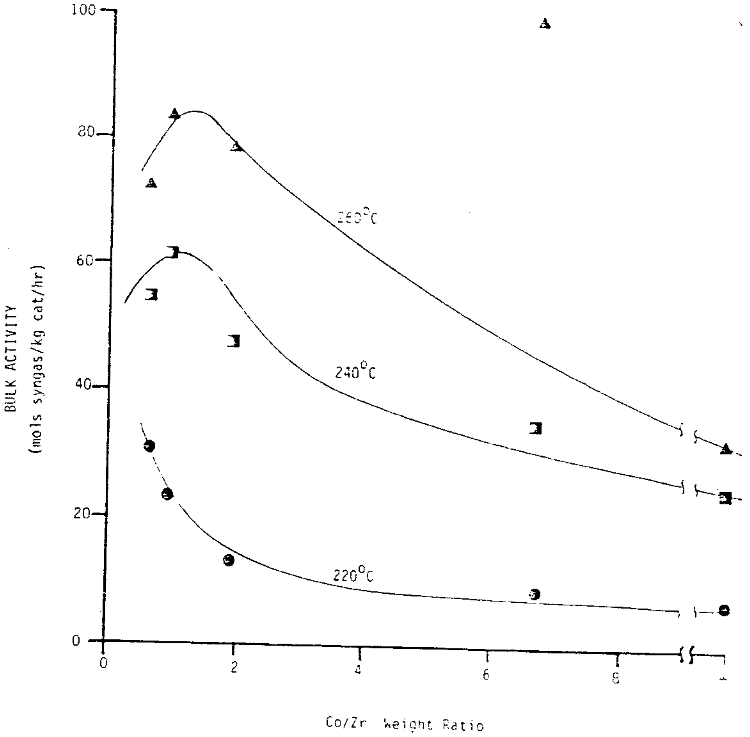


Figure IX.3. Effect of Co/Zr ratio on bulk activity (gas phase, $CO/H_2 = 1$, SV = 1000 hr^{-1}, 300 psig).

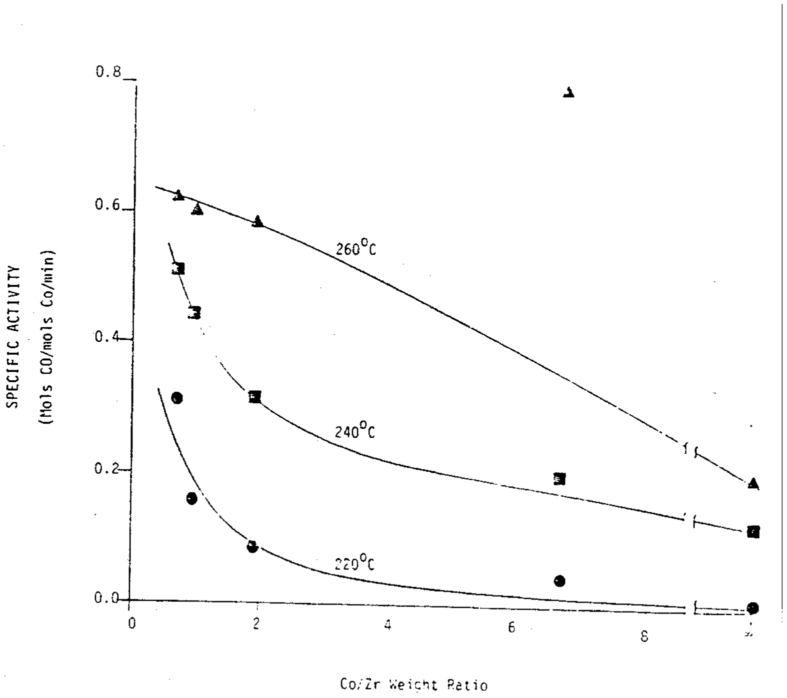


Figure IX.4. Effect of Co/Zr ratio on specific activity (gas phase, CO/H_2 = 1, SV = 1000 hr^{-1}, 300 psig).

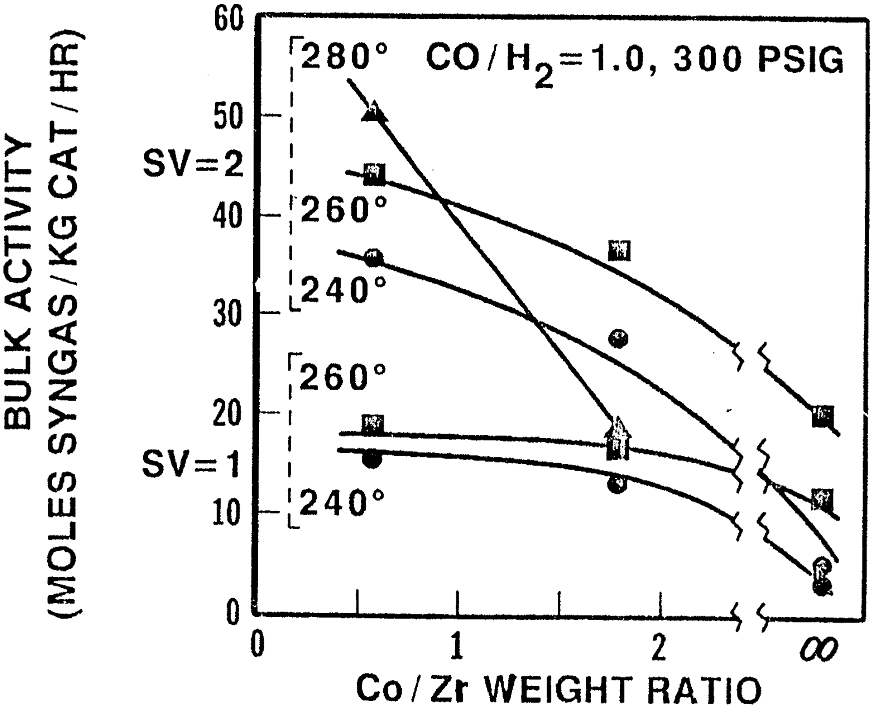


Figure IX.5. Effect of Co/Zr weight ratio on slurry-phase activity of Co/Zr/silica catalysts.

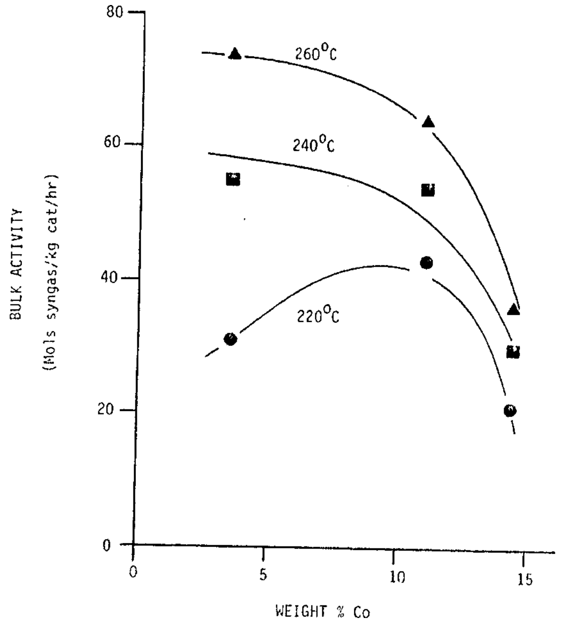


Figure IX.6. Effect of cobalt loading on bulk activity of $Co/Zr/SiO_2$ Catalyst (fixed bed reactor , CO/H_2 = 1, 1000 hr^{-1}, 300 psig).

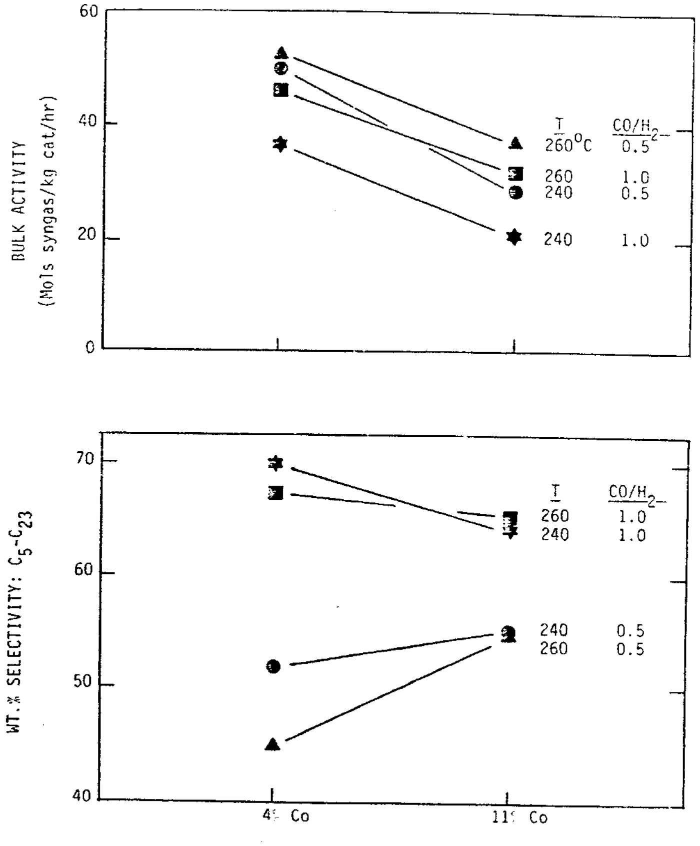


Figure IX.7. Effect of Co loading on $Co/Zr/SiO_2$ performance.

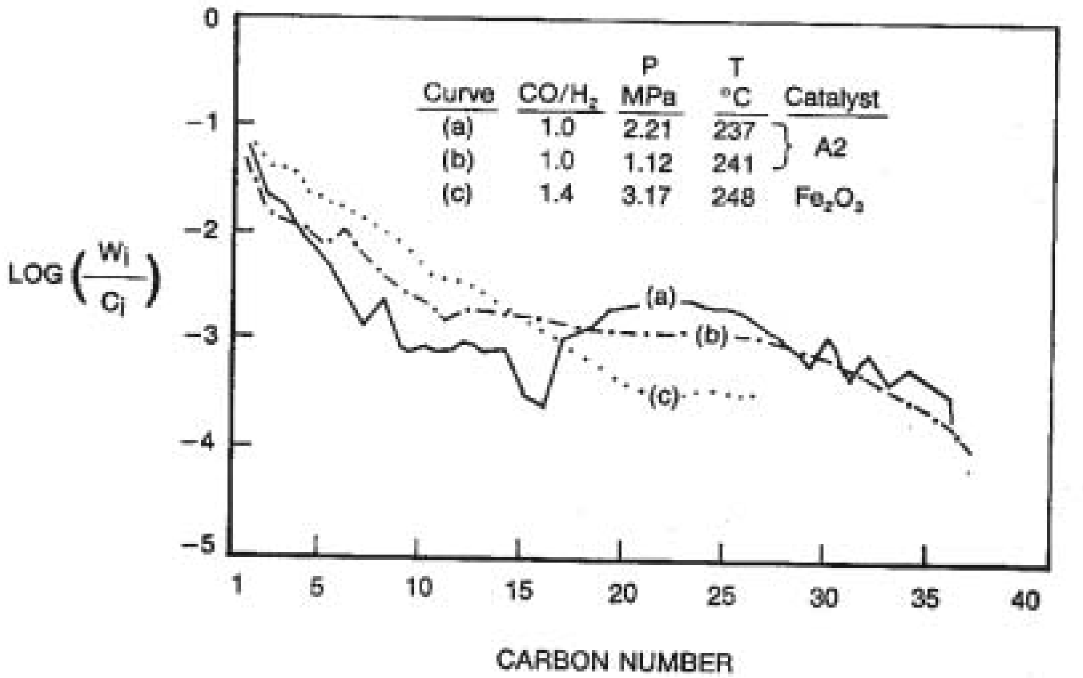


Figure IX.8. Hydrocarbon Schulz-Flory distribution of slurry catalyst A2.

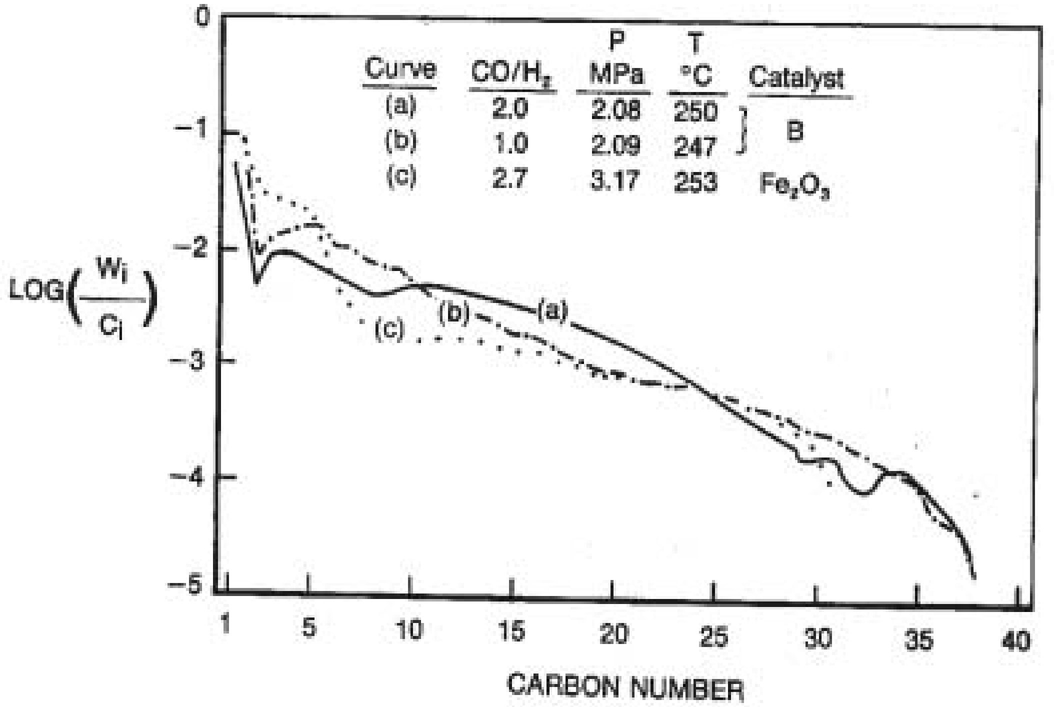


Figure IX.9. Hydrocarbon Schulz-Flory distribution of slurry catalyst B.

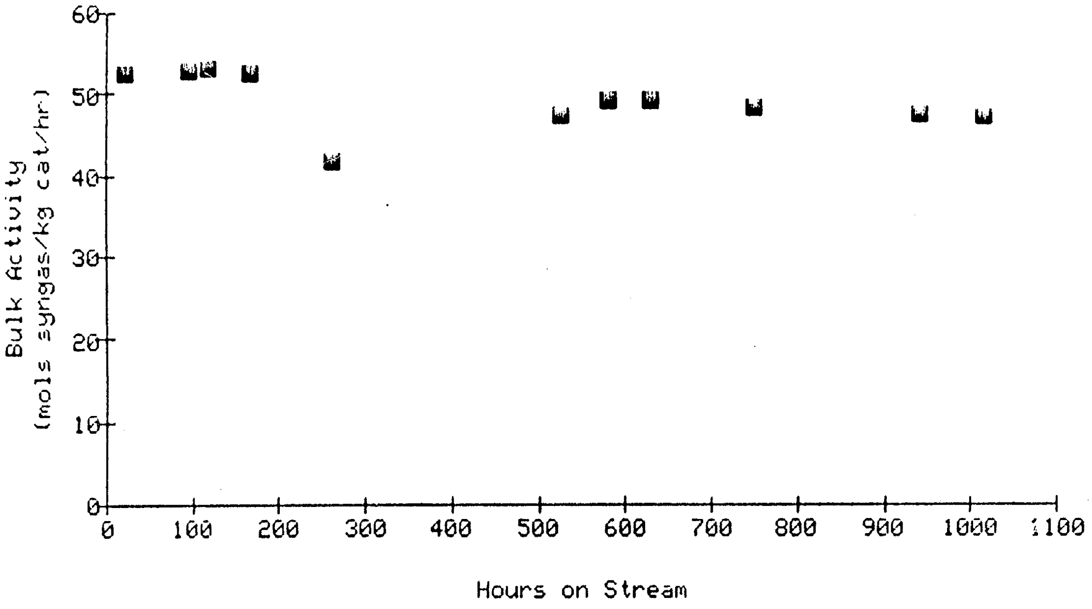


Figure IX.10. Bulk activity maintenance - extended slurry test 8862-1-31 Co/Zr/SiO$_2$, 240°C, CO/H$_2$ = 0.5, 1.8 L/g/hr, 300 psig.

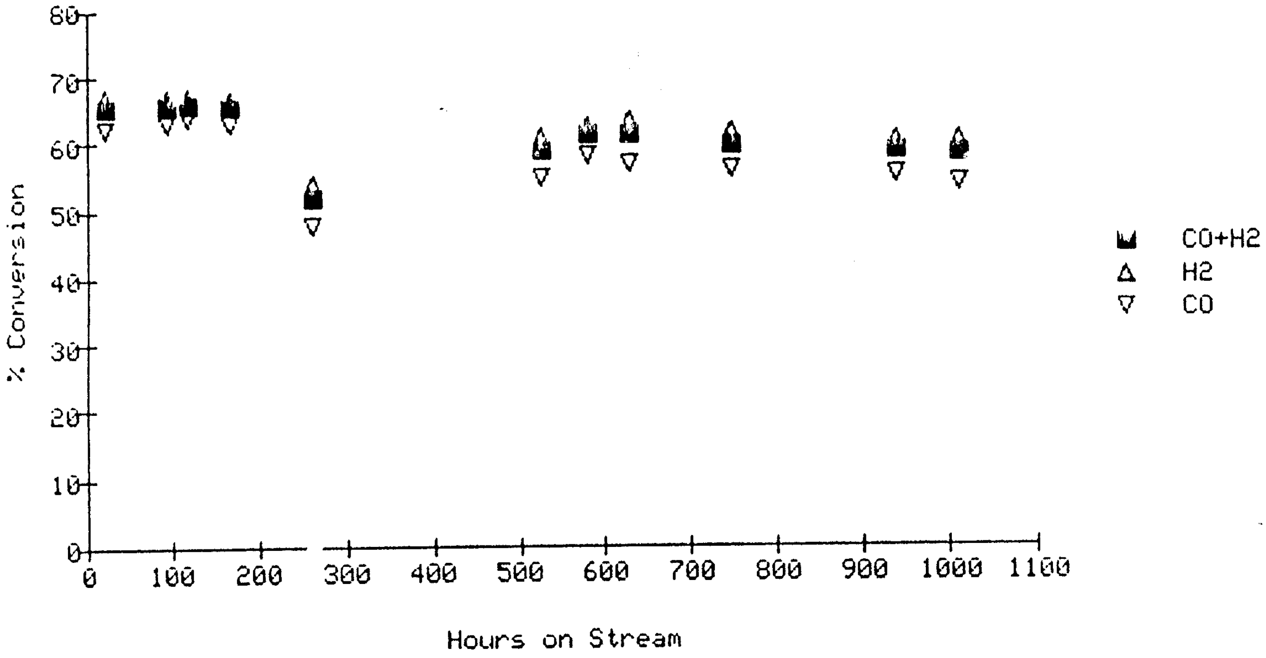


Figure IX.11. Conversion maintenance - extended slurry test 8862-1-31 Co/Zr/SiO$_2$, 240°C, CO/H$_2$ = 0.5, 1.8 L/g/hr, 300 psig.

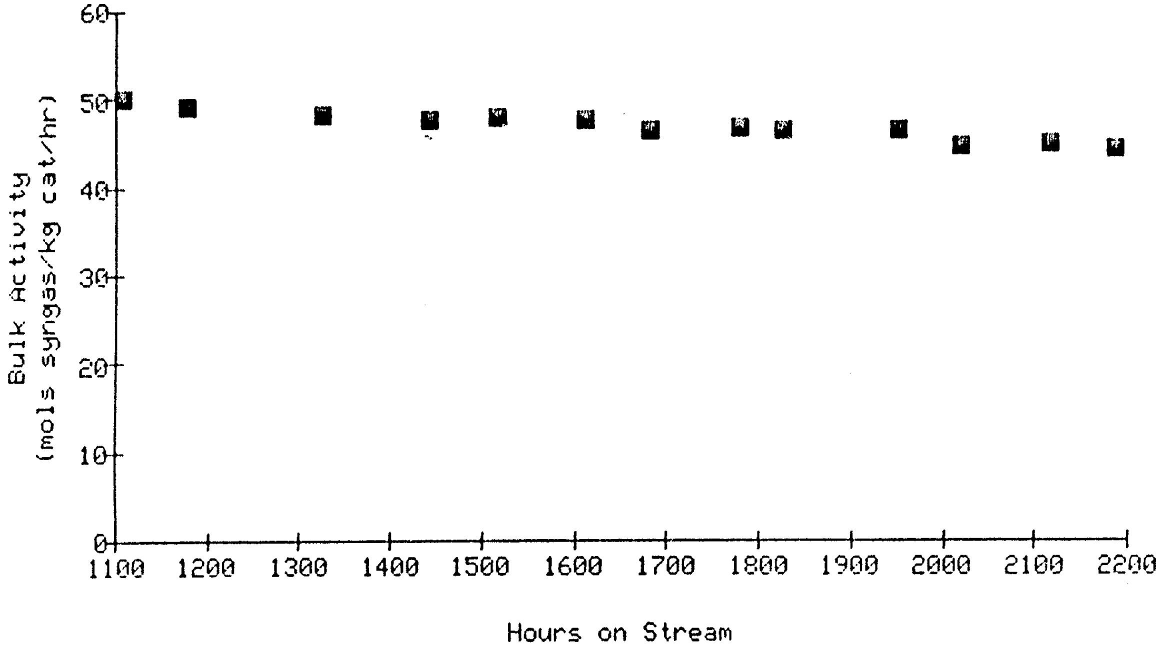


Figure IX.12. Bulk activity maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

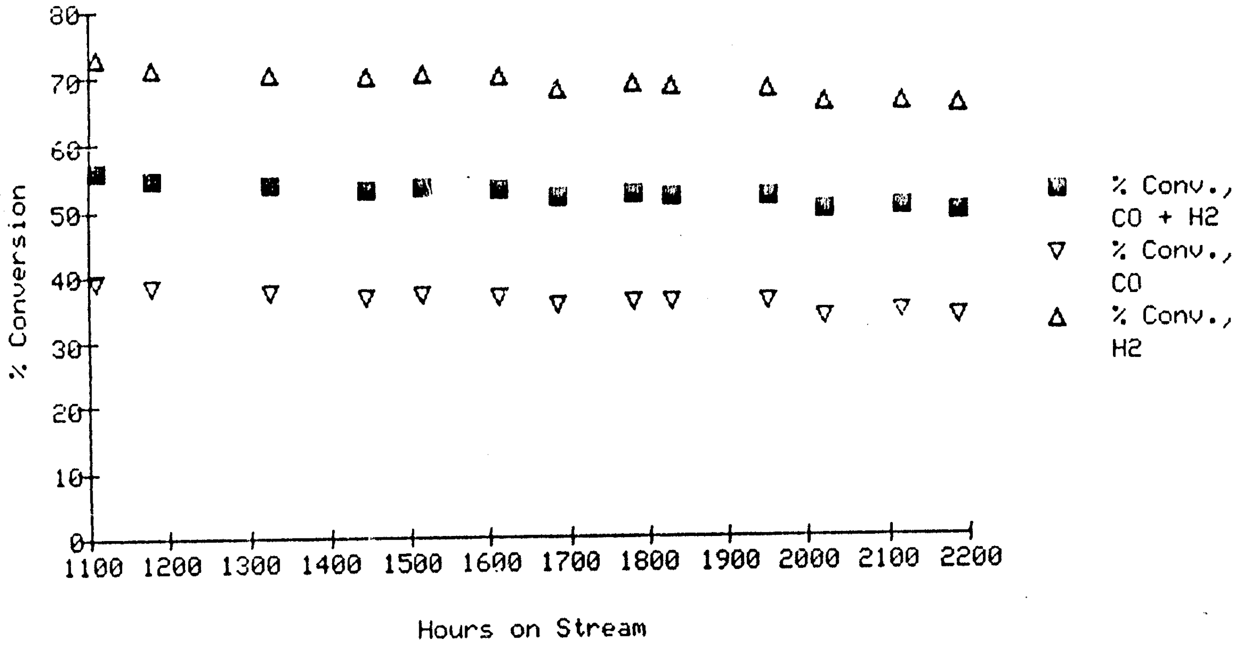


Figure IX.13. Conversion maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

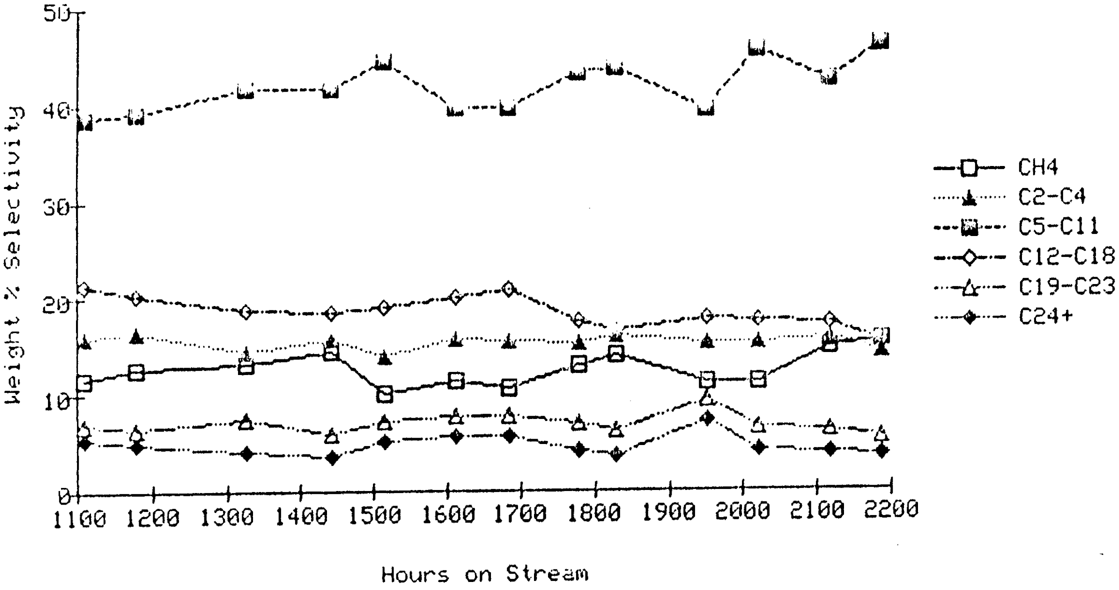
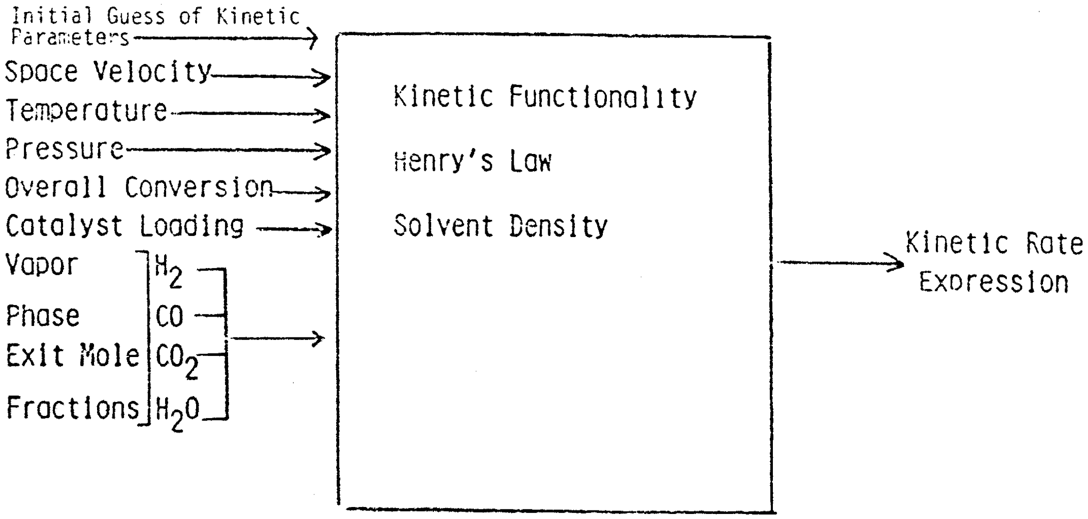
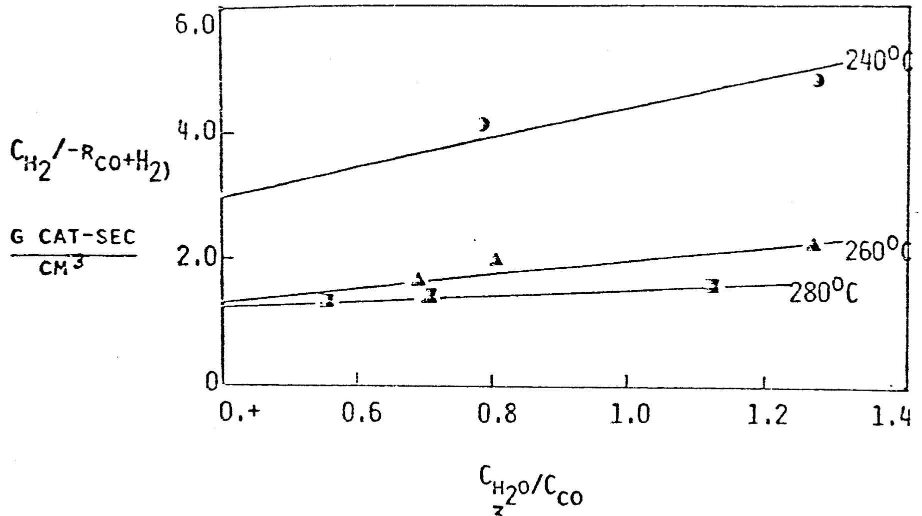


Figure IX.14. Hydrocarbon selectivity — extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

Figure IX.15. Kinetic data analysis program (ρ = 0.758-0.555•(T_k-373) (ref. 12);



He_{H_2} = 34.162 •exp (739.485/T_k)•14.23 psia/mol/kg oil (ref. 11); He_{CO} = 44.583/T_k)•exp (433.391/T_k)•14.23; He_{CO_2} = 119.925•exp (-438.926/T_k)•14.23; He_{H_2O} = 275.113 • exp (-1122.92/T_k) • 14.23.



	K, CM³/G CAT.SEC.	K
240	0.328	0.466
260	0.709	0.439
280	0.775	0.302

Figure IX.16. Fitting $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ data.

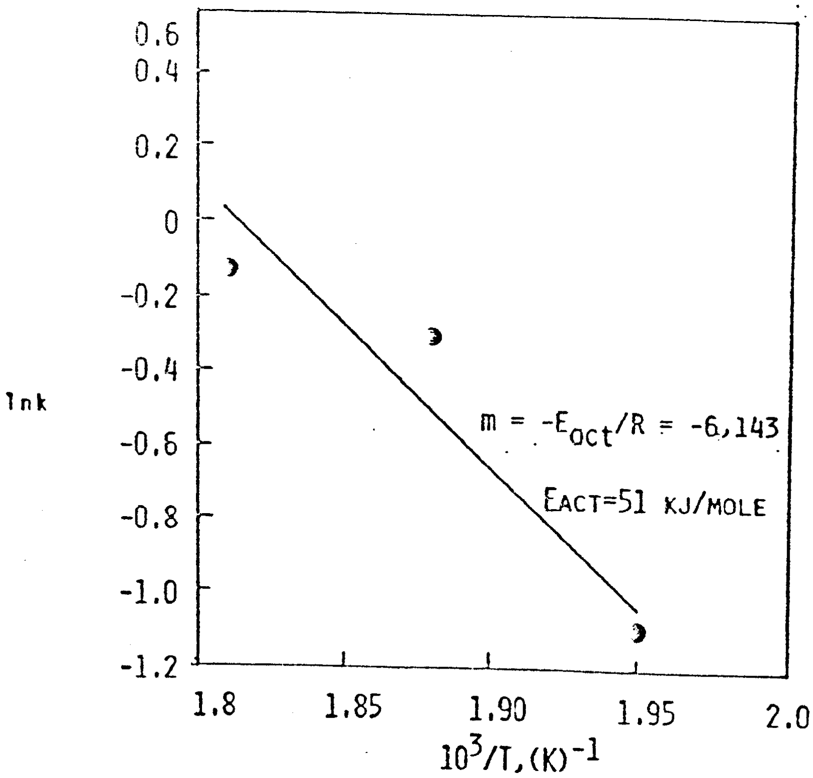


Figure IX.17. $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ activation energy.

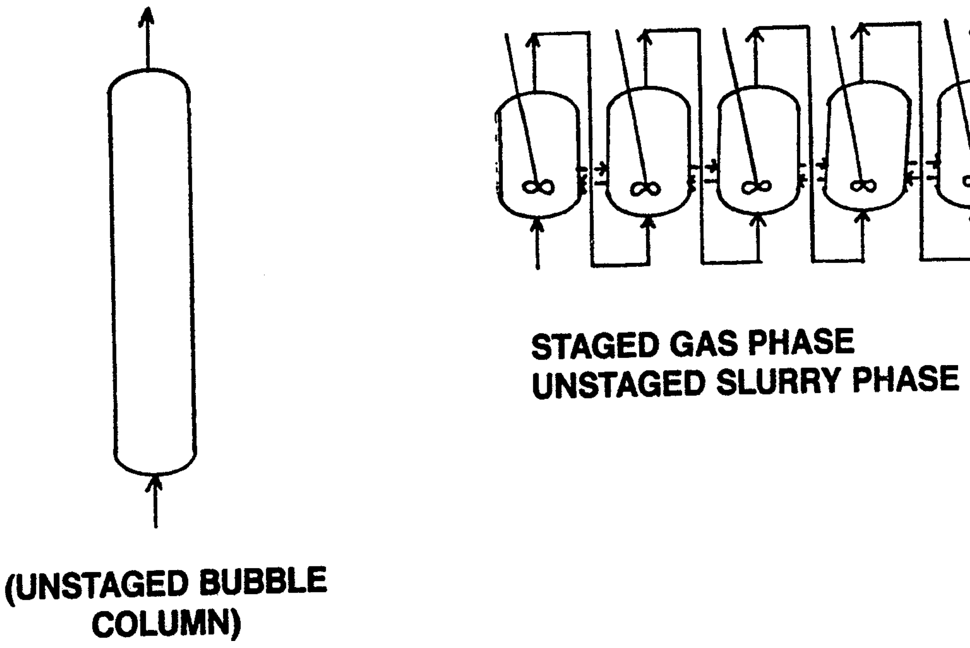


Figure IX.18. Staged reaction systems.

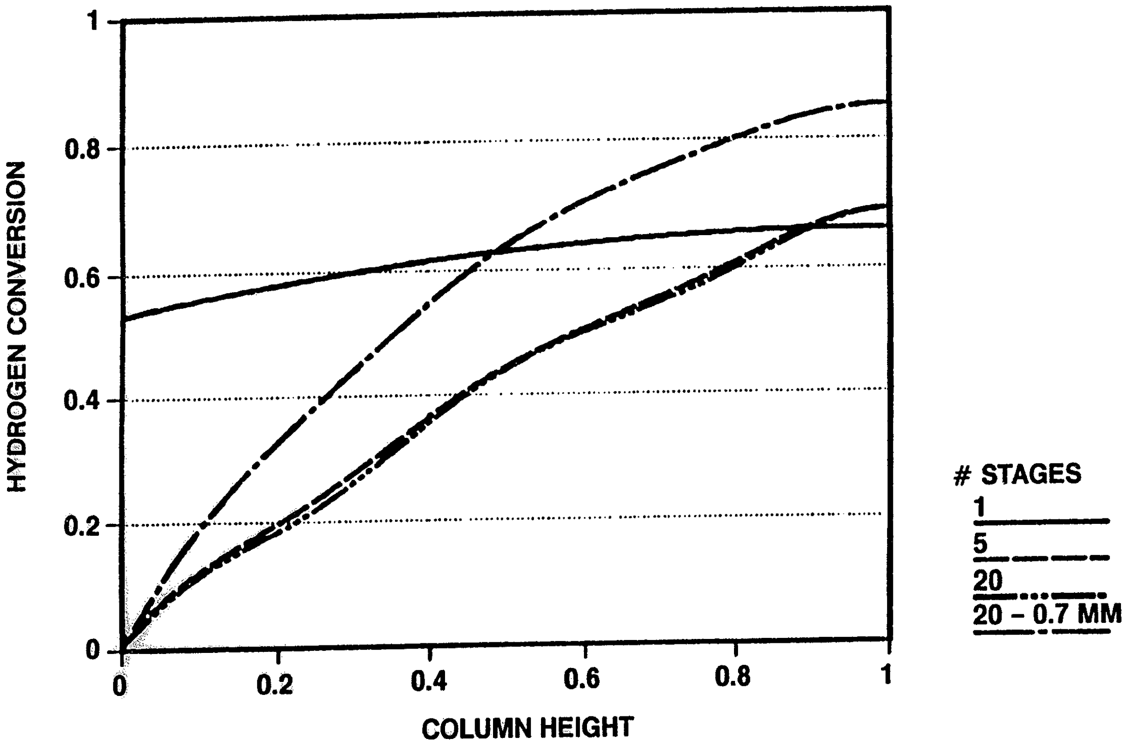


Figure IX.19. Hydrogen conversion vs. column height.

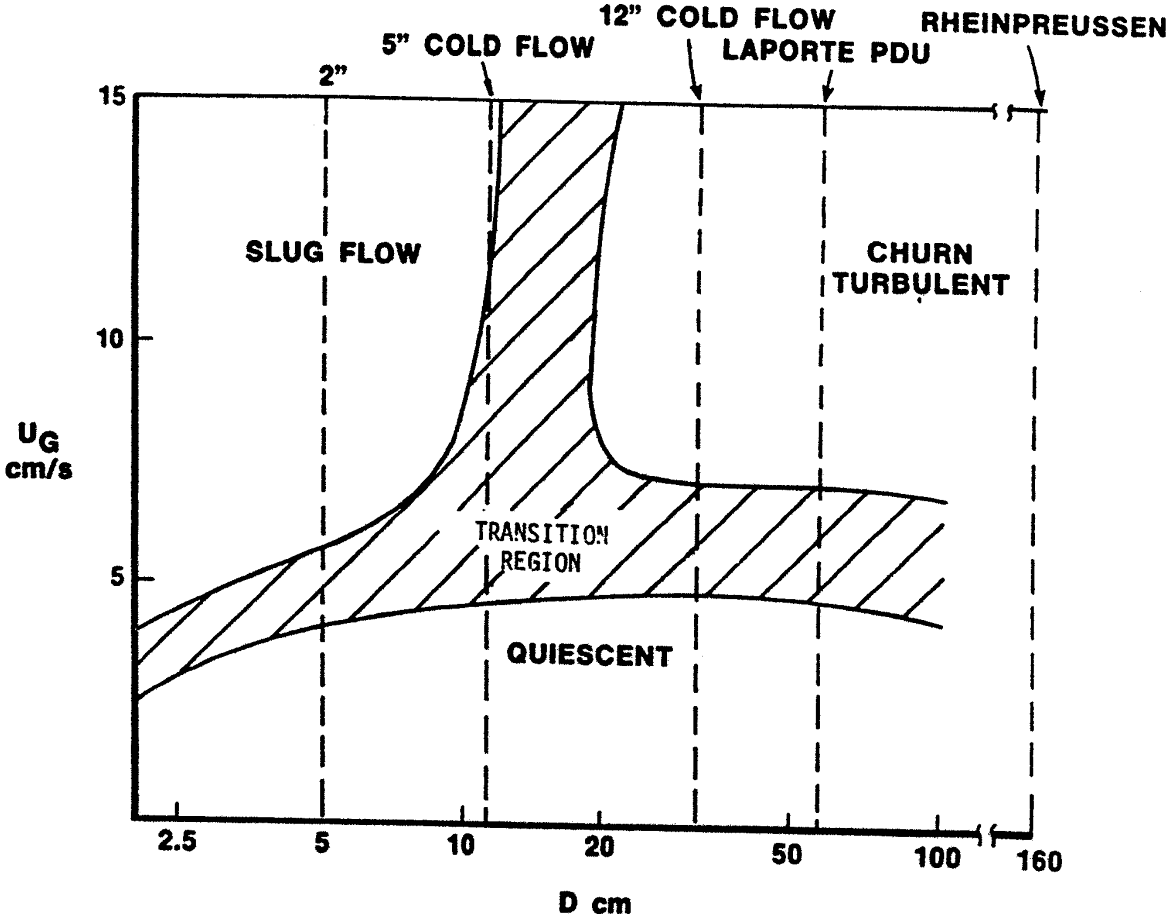


Figure IX.20. Bubble column flow regimes.

ATTACHMENT X

Review of Exxon Patents

Edwin N. Givens

and

Burtron H. Davis

ATTACHMENT X

Review of Exxon Patents

INTRODUCTION

It is quite apparent from searching the patent literature that Exxon has been actively involved in conducting research on conversion of synthesis gas to fuels and chemical products for many years. They have used CO as a chemical reactant for producing olefins and alcohols in addition to preparing liquid fuels. Since the mid 1970s the number of patents that have been assigned to Exxon and the types of examples contained in those patents reflect an increasing interest in converting synthesis gas to hydrocarbons. The earlier patents that were obtained during this period contain numerous examples of synthesis gas conversion at ambient pressures that gave very small CO conversions, typically less than 10%. More recently, the data reflect a more sophisticated evaluation of catalysts and the beginning of a string of patents that relate to improvements in equipment and operation. The latter are a result of the operation of a sizable pilot facility at their Baton Rouge Laboratory. These patents have addressed many of the finer points of reactor design.

The search was focused on synthesis gas conversion, i.e. the Fischer-Tropsch reaction, and limited to U. S. patents that were assigned to Exxon that were abstracted by Derwent through mid-1995. There are apparently numerous other patents that were issued to Exxon that relate to CO conversion which are not included, such as those related to conversion of CO to hydrocarbons or alcohols. Exxon's approach to developing a patent portfolio in this technology area is unlike most of their competitors, in that they have obtained an extensive number of composition of matter patents. Supplementing these patents are a large number of process related patents that apply to either methods for preparing these materials or the use of these compositions in the conversion of synthesis gas. In some of the composition of matter patents that are of interest for synthesis gas conversion, the claimed materials are used for hydrocarbon conversion without mention of their use as catalysts for the FT reaction. Based upon the addresses of the inventors in these various patents, it is clear that significant work on the FT reaction has been going on at Exxon's New Jersey and Baton Rouge laboratories. Although there is overlap in the type of work that was being done in these laboratories, it appears from the timing of the patents that the approaches that were being taken were quite independent. Those differences were apparent from the discussion in the patents regarding various elements of catalyst composition and the claims that are made regarding those compositions.

The Exxon patent portfolio includes a large number of patents on iron and iron-containing catalysts. The majority of these cases relate to compositions that have spinel structures that are isostructural with Fe_3O_4 but contain one or two additional metal atoms, with iron usually being the dominant metal. In these patents, the spinel structures are expressed interchangeably either as $M_xN_{3-x}O_4$ or as $M_{3-x}N_xO_4$, where M is almost exclusively Fe. For consistency, the first format is used exclusively throughout this discussion. Other iron-related catalysts are also covered including catalysts in which the iron, as the oxide, is used as a substrate, and others in which the iron is deposited on other substrates.

There is extensive coverage for catalysts in which titania and titania containing materials are used as metal supports. These include combinations of titania with vanadium, tantalum and niobium oxides (Group Vb) which are used either as intimate mixtures or as coatings on the surface of titania. All of these supports apparently give rise to unique metal-support interactions that had not hitherto been reported. Other coverage was obtained for titanias that are coated with silica. Some of these patents specify titanias having rutile as the dominant crystalline phase which is favored at high temperatures. One case claims an anatase based catalyst that was stabilized though addition of silicon, zirconium and tantalum. In many of these cases, the catalyst is formed by impregnating the oxides with metals from Group VIII, of which cobalt or ruthenium are the most common. In other cases, addition of rhenium, thorium, cerium, copper, hafnium, zirconium, and uranium is claimed. Although many of the catalysts that are covered in these patents fall into one of the above categories, they have also obtained coverage in several related areas. Catalysts comprising ruthenium or combinations of several Group VIII metals on manganese oxide are covered as are cobalt-manganese spinels. Coverage of catalysts comprising Group VIII metals supported on various oxide supports was obtained which specifically apply to FT type processes.

In almost all of these cases the use of an alkali promoter is also covered, either in the main claim or a dependent claim. Almost without exception, potassium is specified as the alkali metal of choice, although in a few rubidium has been specifically mentioned. Most of the patents specify that the catalysts can be used in either a fixed-bed or a slurry type process, although in some cases they can be applied to both. Generally, powder catalysts are specified for slurry operations while sintered spinel type catalysts apply to fixed-bed type operations. There are, however, cases which claim that the catalysts are useful for either slurry or fixed-bed type operations.

The third area of significant coverage includes various process improvement patents that relate to process equipment or operation, most of which have been obtained in recent years. These include 2-stage processes, modified feeds, modified reactor designs, methods of reactor operation and methods of catalyst pretreatment. Many of these patents contain data that were taken from highly sophisticated pilot plant operations, some of which were quite large in size.

Iron

A number of patents were issued to Exxon related to the use of iron in FT synthesis. Most apply to catalysts in which the iron is in combination with other metals. However, two patents were issued that apply to the use of iron alone. These were catalysts that were prepared using a laser technique in which volatile iron compounds were thermally decomposed to form iron carbides having particle diameters of less than 0.1 μm. Most of the iron containing catalysts that are covered in these patents relate to spinels in which Fe is combined with different metals in the spinel structure, including cobalt, manganese, zinc, and titanium. Various promoters are also added, including cerium, copper and potassium. Two patents covered catalysts in which thallium was deposited on an iron support, while others covered catalysts prepared by depositing Fe salts onto supports. One covers an Fe/TiO_2 catalyst that was prepared by converting an impregnated Fe salt to the carbided form. Another covered catalyst prepared by decomposing Fe and Co carbonyl compounds in the presence of CO which deposited them onto finely divided supports which were then reduced in H_2.

Particulate Iron Catalysts

A patent issued to Rice et al. (X.1) claims compositions comprising finely divided particles of iron and carbon in absence of Si produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron reactants, and pressure sufficient to give non-pyrophoric particles having diameters from 1-100 nm. The iron reactants are selected from iron carbonyls, iron acetylacetonate and ferrocene. A related patent issued to Rice et al. (X.2) claims the same compositions which are subsequently impregnated with $\geq$2% of a promoter selected from a group of salts and oxides of alkali and alkaline earth metals. These patents specify these compositions can be used in either slurry or fixed bed FT reactions. Data were presented in the examples for a fixed-bed catalyst in which the claimed composition was deposited on a refractory MgO support. Laser generated Fe carbide, either with or without K, was found to be considerably more active than Fe carbides generated from either Fe_3O_4 or from mixtures of $Fe(CO)_5$ and C_2H_4 in the presence of $SiH_2(CH_3)_2$ (see Table X.1). The Fe_3O_4 and silane generated carbides have lower CO conversions and higher methane yields while the catalysts of these inventions produce more olefins in the C_2-C_4 fraction.

A catalyst was illustrated which was prepared by reacting Fe_3O_4 until all of the iron was converted to a carbide phase which was predominantly Fe_5C_2 and Fe_3C. The iron carbide phase was dispersed in a matrix of 40 to 70 wt.% of amorphous carbon. The comparison of the activated Fe_3O_4 catalyst and the laser generated catalyst is for activity for CO conversion on a volume of gas/volume of catalyst basis. The laser generated sample contained 5-15 wt.% of amorphous carbon phase. If we take into account (1) the difference in density of amorphous carbon and iron carbide (factor of 2) and (2) the difference in the amount of amorphous carbon (factor of about 5-8), we calculate that the material produced by the laser technique will contain 10 to 20 times as much iron as the material prepared from Fe_3O_4. Thus, while the material prepared using the laser technique is about two times as active as the material derived from Fe_3O_4 when the comparison is based on volume of catalyst, it is estimated by us to be 5 to 10 times less active on the basis of the iron content. Furthermore, it has been shown that, under reaction conditions utilized for slurry phase synthesis, a significant fraction of the iron carbide is gradually converted to Fe_3O_4 (X.3) during synthesis. Thus, the relative advantage of the catalyst generated by the laser technique depends upon how it is compared to the precipitated catalyst.

Spinels Containing Fe

The first patents assigned to Exxon that apply to the use of spinel or spinel-derived compositions for converting synthesis gas appeared in 1985. These materials were generally prepared by one of two methods and they had distinctly different morphological features. In one case, high surface area materials were prepared by co-precipitation of salts coupled with moderate heating. These materials have been used directly as slurry catalysts. The second method of preparation involves sintering of metal/metal oxide mixtures at much higher temperatures to give low-surface-area, fused materials, which after grinding and sizing are used directly in fixed bed applications. Hydrogen reduction of either of these products at temperatures of 400^{o}C leads to alloys, which when treated with CO, give high surface area carbides containing considerable carbon inclusion. The reduced and carbided spinels are then used as catalysts in either slurry or fixed-bed applications.

A number of different combination of metal spinels have been patented in this series, all of which, except one, contain iron. In all the Fe cases, the claims cover spinel compositions that allow the use of high concentrations of Fe. From an economical standpoint, this is favorable since the cost of co-metals is generally greater than for Fe. The different Fe-containing combinations that are covered, most of which are promoted with potassium, are:

- Fe-Co, either with or without added Cu,
- Fe-Mn containing Cu,
- Fe-Zn containing Ce or Cu,
- Fe-Zn-Ti and/or Mn with Ce and
- Co-Mn with Cu.

The only non-Fe containing spinel that was covered was a Co-Mn spinel that is promoted with Cu. This catalyst is discussed with the manganese supported catalysts.

Fe-Co Spinels. Both high and low surface area spinels are covered. High surface area spinel compositions and reduced and carbided iron-cobalt alloy compositions derived from the spinels that are isostructural with Fe_3C and chi-Fe_5C_2 are covered in a patent issued to Soled and Fiato (X.4). Because of their fine particle size, the preferred use of these materials is in a slurry process which is covered in a patent issued to Soled and Fiato (X.5). High surface area copper promoted Fe-Co spinel compositions are covered in a patent issued to Soled and Fiato (X.6) while their use as a catalyst in a slurry process is covered in Soled and Fiato (X.7). Low-surface area Fe-Co spinel compositions are claimed by Fiato et al. (X.8) and their use as catalysts in a fixed-bed process is claimed by Fiato et al. (X.9). The use of the carbided and reduced form of these low-surface area Fe-Co spinels in a slurry phase process is claimed by Fiato and Soled (X.10). No patents were found that contain claims related to low-surface area Cu-promoted Fe-Co spinels.

Fe-Mn Spinels. High surface area K and Cu promoted Fe-Mn spinels are covered in a patent issued to Fiato and Soled (X.11). The use of this spinel as catalyst in a slurry process is covered in Fiato and Soled (X.12) and in a fixed-bed process in Iglesia et al. (X.13). The corresponding low surface area spinels derived from sintering mixed oxides was covered in a prior patent issued to McGrath and Rubin (X.14) and assigned to Kellogg. An alternative method for forming Fe-Mn alloys directly at low temperature without going through the spinel is covered by Soled et al. (X.15).

Fe-Zn Spinels. Two patents comprising compositions of Fe and Zn using different promoters were issued. In one patent compositions comprising sintered combinations of metal oxides of Fe and Zn promoted with Ce and K are covered in Gates and Fiato (X.16). In the other, compositions containing Fe and Zn promoted with Cu and K are covered in Soled et al. (X.17).

Fe-Zn Spinels with Ti and/or Mn. Compositions comprising sintered combinations of metal oxides of Fe, Zn, Ti, and/or Mn promoted with K and Ce are claimed in Fiato et al. (X.18).

Fe-Co Spinels

Seven patents assigned to Exxon relate to Fe-Co spinels, five of which were issued either from applications filed on December 14, 1983, or were continuations-in-part of applications filed on that day. Cross reference was also made to applications which apparently never issued as patents. The series of seven patents that did issue fit into three different groups with at least two patents being in each group. One of the groups relates to Cu promoted Fe-Co spinels while the other two groups relate to Fe-Co spinels that are prepared by two different methods. In one group the spinels are prepared by sintering mixtures of metal-metal oxides while in the other, spinels are prepared by precipitating metal oxides from the respective metal salt solutions. In each of these three groups, two of the patent specifications are identical differing only in their claims. In the one group that includes a third patent, the specification differs only slightly from the other two. For each of the three groups, one patent is a composition of matter case for a specific Fe-Co containing spinel and the other(s) claims either a fixed-bed or slurry process that employees the claimed catalyst composition.

The empirical formula of the spinels claimed in these cases can be written as $Fe_xCo_{3-x}O_4$ where compositions having x-values $\geq$2.4 or 2.7 are claimed. Prior art existed for structures having x values of 2, i.e. Fe_2CoO_4 (X.19). Among the various spinel compositions that were patented, there appears to be a pattern of obtaining coverage for both slurry and fixed-bed type FT processes. In the case of the Fe-Co spinels, specific claims are made to fixed-bed processes using catalysts derived from spinels prepared by sintering metal-metal oxide mixtures. These are classified as having low surface areas (less than 5 m^2/g). For slurry processes, patents were issued that claim use of catalysts derived from both low surface area spinels as well as those prepared by precipitating metal oxides from the respective metal salt solutions. This latter group is classified as high surface area spinels having surface areas greater than 5 m^2/g. In these Fe-Co spinel cases, patents were not found that claim the use of high surface area spinels in a fixed-bed process, although such claims were obtained for Fe-Mn spinels, which are discussed below.

High surface area spinel compositions are covered in a patent issued to Soled and Fiato (X.4) that claims Group 1A or IIA promoted high surface area spinels having compositions $Fe_xCo_{3-x}O_4$ with x-values $\geq$2.4 and BET surface areas >5 m^2/g. A second composition in this same patent, given in claim 20, comprises reduced and carbided iron-cobalt alloy that is isostructural with Fe_3C and has a BET surface area >5 m^2/g. A third independent claim covers compositions that are isostructural with chi-Fe_5C_2 having surface areas >5 m^2/g that are produced by carbiding iron-cobalt alloy which is isostructural with alpha Fe and has a BET surface area >5 m^2/g, which is produced by reducing the high surface area spinel composition. Therefore, compositions are claimed that include the spinel, the reduced alloy and the resulting carbided alloy. The specification is even broader in that it anticipates the application of the spinel, the alloy and the reduced-carbided spinel in either a fixed-bed or slurry-type process. The corresponding process related patent issued to Soled and Fiato (X.5) claims a slurry process that uses the catalyst that is claimed by Soled and Fiato (X.4). The two specifications are identical except for the claims. Although there is a slight difference in the spinel compositions that are claimed in these two cases, in that Soled and Fiato (X.4) claim spinels having Fe/Co ratios $\geq$4/1 while Soled and Fiato (X.5) claims Fe/Co ratios $\geq$7/1, this would not likely have any real impact on the application of the invention.

Low surface area Fe-Co spinel compositions are covered in a patent issued to Fiato et al. (X.8) that claims hydrocarbon synthesis catalyst compositions comprising an unsupported, Group Ia or IIa metal salt promoted low-surface area iron-cobalt spinel, an initial empirical formula $Fe_xCo_{3-x}O_4$, where x is $\geq$2.625, a powder X-ray diffraction pattern isostructural with Fe_3O_4 and having an initial BET surface area <5 m^2/g. Various dependent claims are included such as the use of diluents like silicas, aluminas, titanias, oxides of La, Ce, Cr, and Mn and mixtures including zeolites, glasses, etc. K_2CO_3 is claimed as a promoter and potassium promoted compositions are claimed that are substantially carbided by contact with CO/H_2 at elevated temperatures. Two process patents were issued that are related to use of low-surface area spinel compositions in synthesis gas conversion reactions. One patent, issued to Fiato et al. (X.9), claims a process for synthesizing hydrocarbons containing C_2-C_6 olefins by contacting a fixed-bed of catalyst, having the initial spinel composition specified in Fiato et al. (X.8), with synthesis gas. The specifications of Fiato et al. (X.8) and Fiato et al. (X.9) are identical, except for different claims. The second process patent issued to Fiato and Soled (X.10) claims a slurry process utilizing the carbided and reduced unsupported spinel of Fiato et al. (X.8), which reflects the need to *ex situ* pretreat the spinel before placing it in the slurry reactor.

Catalyst preparation

The following method was used to illustrate the preparation of several of the high surface area spinels. A solution containing Fe and Co nitrate salts and an ammonium α-hydroxy carboxylic (glycolic) acid was evaporated and the recovered solid was heated at 350°C for 2 hours and then impregnated with K_2CO_3 and dried. The material, prior to impregnation with potassium, had a very small particle size, an x-ray diffraction pattern isostructural with Fe_3O_4, and surface area >100 m^2/g. The specification refers to prior art for the preparing of Fe_2CoO_4[19] that involved evaporating aqueous solutions of metal glycolates, lactates, and tartarates to dryness. The prior art apparently limited claims to Fe/Co ratios > 4.

The invention was illustrated for various low-surface area spinels prepared by sintering mixtures of metal oxides and metals in combinations having the stoichiometric composition necessary to provide the correct empirical formula. Sintering is done first in an inert or vacuum atmosphere at temperatures preferably from about 800 to 900°C for about 8 to 24 hours. The material is then exposed to air and heated an additional 24 hours until the x-ray diffraction pattern of the material is isostructural with Fe_3O_4. Sintered pellets are crushed, sieved and then impregnated with aqueous potassium carbonate to a 1% K loading providing a material having a surface area of 0.25-0.30 m^2/g.

Reduced and carbided slurry catalysts are prepared starting with both high and low-surface area spinels. The preparation starting with low-surface area spinel is described in Fiato and Soled (X.10) and the preparation from high-surface area spinel is described in Soled and Fiato (X.4). In both cases, the respective spinel powders were reduced at 400°C in H_2 for 4 hours to produce an alloy, which was passivated with dilute oxygen. These materials had surface areas of 3 and 8 m^2/g and x-ray diffraction patterns isostructural with alpha iron. The active catalyst was produced by carbiding the alloys in dilute synthesis gas and passivating with dilute oxygen to give products having x-ray diffraction patterns isostructural with chi Fe_5C_2 and BET nitrogen surface areas of 118 and 173 m^2/g. The resulting catalysts contained 60-70% carbon and had the composition $Fe_{2.85}Co_{0.15}O_4$/1 wt.% K.

The form of the active catalyst generated by these two different preparative methods was not differentiated from each other. Both, after reducing and carbiding, give materials that are isostructural with chi-Fe_5C_2 or Fe_3C, apparently contain sizable amounts of carbon, and have surface areas >100 m^2/g.

Slurry Catalysts. A number of examples were provided in the five cases which illustrate the use of catalysts derived from spinels for converting synthesis gas. Catalysts to be used in slurry reactors were pretreated in various ways before being placed in the slurry reactor and exposing them to synthesis gas at reaction condition. The methods of pretreatment included:

- Adding the spinel to the slurry reactor and reducing in H_2 before exposure to synthesis gas;
- Reducing and carbiding the spinel *ex situ* before introducing into the reactor;

! Reducing the spinel in H_2 to form the alloy before introducing into the reactor.

Conversion and product distribution data were provided for each of the respective catalysts and compared with data obtained on a high surface area Fe_3O_4/1%K catalyst that was prepared in the same manner as the high surface area spinel.

There was a big difference in the activities of the *in situ* treated spinel slurry catalysts. The high surface area Fe-Co spinel oxide that was reduced in situ with flowing H_2 (1 atm) for 1 hour at 200^{o}C gave 60% CO conversion, whereas both the high surface area Fe spinel and the low-surface area Fe-Co spinel that were pretreated in the same way were inoperable. They gave CO conversions of only 8 and <4%, respectively (see Table X.2). *Ex situ* treatment had little effect on CO conversion of the high surface area spinel derived catalyst which gave essentially the same CO conversion as the *in situ* treated spinel, namely 64 and 60%, respectively. By contrast, *ex situ* treatment of both the low-surface area Fe-Co spinel and Fe spinel catalysts improved their activity, giving 42 and 65% CO conversion, respectively. Apparently insufficient carbided catalyst was formed in the *in situ* pretreatment of the low-surface area spinel, whereas the *ex situ* treatment was sufficiently severe to convert the low-surface area spinel to the carbided form. In the comparisons that were provided, the Fe-Co spinels produced more C_5+ hydrocarbons and less C_2-C_4 olefins than the Fe spinel catalysts. Although data with a 2/1 H_2/CO synthesis gas mixture in Table X.2 on *ex situ* treated catalysts indicate a difference between the CO conversion of the reduced-carbided low- and high-surface-area Fe-Co spinel derived catalysts, i.e. 42 and 64% conversion, respectively, other data with a 1/1 H_2/CO synthesis gas mixture showed no difference in activity (see Table X.3). The latter data indicate that the *ex situ* reduced and carbided high- and low-surface-area Fe-Co spinel derived catalysts, as well as the activity of the *ex situ* reduced and carbided high-surface-area Fe spinel catalysts, have essentially the same activity. The activity of the *ex situ* low-surface-area Fe-Co spinel and the lack of activity for the *in situ* treated low-surface-area spinel appears to be one reason why Fiato and Soled (X.10) claim a slurry process utilizing only the carbided and reduced low-surface area spinel.

Alloys active for CO conversion are formed by reducing the high-surface-area Fe-Co spinel *ex situ* with H_2 at 350°C for 12 hrs followed by further reduction with H_2 at 400°C for 24 hrs. CO conversions with either 1/1 and 2/1 H_2/CO synthesis gas mixtures were higher than the correspondingly reduced Fe-only spinel, as shown in Table X.4. Although the correspondingly reduced high surface area Fe-only spinel was not quite as active as the Fe-Co alloy, its selectivity for CO_2 production was much smaller. The hydrocarbon selectivity of the Fe-Co spinel was greater and its methane and C_5+ selectivities were less than for the Fe-only spinel. In this series of patents, no claims were made nor information provided on alloys produced from reduced low-surface area Fe-Co spinels.

Fixed-Bed Catalysts. Only catalysts prepared from low surface area Fe-Co spinels were used as fixed-bed catalysts. Although high-surface area spinel derived catalysts were anticipated for use in fixed-bed reactors, no claims nor examples were found that relate to such usage. An example was provided in which low-surface area $Fe_{2.85}Co_{0.15}O_4$ spinel was reduced at 500°C with a mixture of 90% H_2 in N_2 at 100 psig for 5-7 hrs before exposing to synthesis gas. It was more active for CO conversion than a comparably prepared and treated Fe_3O_4/1%K spinel, as shown in Table X.5. At a run temperature that was 35°C lower than the control sample, the Fe-Co conversion of

CO was higher than for the Fe-only catalyst at the same space velocity. Both CO_2, hydrocarbon yields and olefin content in the C_2-C_4 fraction were higher for the Fe-Co catalyst while the C_5+ and C_6+ products were greater for the control.

In all the Fe-Co spinel patents, there was only one example of a spinel having an Fe-Co concentration that did not fall within the claimed limits. That spinel, having an x value of 2.20, falls below the 2.4 value specified in the claims. The CO conversions and hydrocarbon yields were essentially the same for this catalyst as for those that fell within the claimed limits, i.e. x values either $\geq$2.4 or >2.625, both of which were used in different patents (see Table X.6). Regardless, all of these catalysts had Fe/Co ratios that were greater than 2 (x value 2.0), which was consistent with the prior art value discussed above.

In almost all of the patents regarding the FT reaction that are assigned to Exxon, only a few discuss the exotherm that is observed in any of the experimental reactors. In one of the patents, assigned to Fiato et al. (X.8) claiming Fe-Co spinel derived materials as catalysts for fixed-bed FT reactors, the exotherms observed in those reactors are discussed. Actual maximum bed temperatures are given for runs in which furnace temperatures were from 225 to 290^oC. In these runs made with a cobalt spinel having an x value of 2.625 ($Fe_{2.625}Co_{0.375}O_4$/1 wt.% K), exotherms of 8 to 44^oC were observed at 240^oC and 290^oC, respectively (see Table X.7). Over this range the corresponding CO conversion increased from 31% to 97%. The CO conversion follows the same trend as does the difference between the furnace and bed temperatures. At the higher temperature, the hydrocarbon selectivity deteriorated resulting in increased conversion to methane, whereas at the lower temperature the olefin selectivity was higher, i.e. 55.3% versus 37.1%, and the C_6+ yield was also higher. The effect of furnace temperature at 235 and 270°C for a $Fe_{2.85}Co_{0.15}O_4$/1 wt.% K spinel, where x = 2.85, is also shown in Table X.7. In this case the actual bed temperatures were not reported but can be assumed to be about the same as for runs made at the same temperature. The CO conversion and CO_2 and hydrocarbon yields for the x = 2.85 spinel were essentially the same as for the x = 2.625 spinel. At high conversion, hydrocarbon selectivity of the x = 2.85 spinel was better giving less methane, more C_6+, and more C_2-C_5 olefin yields. This provides further evidence that lower cobalt concentration provides better yields.

Copper promoted Fe-Co spinels. Two patents claim Cu promoted Fe-Co spinels as slurry phase catalysts. A patent issued to Soled and Fiato (X.6) claims compositions comprising a reduced-carbided Cu-promoted Fe-Co alloy, produced by contacting a Cu-promoted Fe-Co alloy with a carbiding atmosphere, which was prepared by reduction of a Group Ia or Group IIa metal salt promoted Fe-Co spinel possessing a BET surface area greater than 5 m^2/gm. The spinels correspond to high surface area spinels prepared by precipitating the Fe and Co nitrate salts, as presented in Soled and Fiato (X.4). A corresponding patent issued to Soled and Fiato (X.7) which, except for the claims, is identical to Soled and Fiato (X.6) claims a slurry process using a catalyst comprising an unsupported Cu-promoted Fe-Co spinel having an initial BET surface area >5 m^2/g and a Fe/Co ratio $\geq$4/1.

Copper promoted spinels are prepared by impregnating Fe-Co spinel with an aqueous solution of cupric nitrate, drying, and then impregnating with an aqueous solution of K_2CO_3 followed by a final drying to give a composition of $Fe_{2.85}Co_{0.15}O_4$/(1 wt.% K, 1 wt% Cu). *Ex situ* carbided catalysts were prepared by reducing the spinel in a 40% H_2, 20% CO and 40% He containing stream at 400°C for 24 hrs. After cooling to room temperature, the oxygen (1%) passivated sample gave an X-ray diffraction pattern isostructural with Fe_5C_2, had a BET surface area of 150 m^2/g, and contained 40-50% carbon. Corresponding Co-free and carbided spinels were also prepared by the same method.

Examples were included which illustrate the use of these spinels as catalysts in a slurry reactor both in *in situ* unreduced as well as *ex situ* carbided forms. CO conversion for the *in situ* reduced catalysts followed the sequence Cu/K-promoted Fe-Co spinel > K-promoted Fe-Co spinel > Cu-free Fe spinel (see Table X.8). However, data were not provided that showed relative selectivities for hydrocarbon versus CO_2 formation. The CO conversion activities of the *ex situ* carbided-reduced Fe and Fe-Co spinels were quite similar as were the methane and C_2-C_4 olefin selectivities. The olefin concentrations (52-59%) in the C_{10} fractions from these catalysts were quite high.

Iron - Manganese Spinels

A composition of matter and three process related patents assigned to Exxon cover iron-manganese spinels. Two cases that were originally filed on December 20, 1983 were abandoned and refiled in December 1985. Both applications resulted in patents that issued in 1986. Apparently at some time during the application process, claims for a fixed-bed process were split from the slurry bed process application and refiled as a separate application. The latter fixed-bed application was subsequently abandoned, refiled and again abandoned before being refiled in 1990, which apparently resulted in a patent covering a fixed-bed process. Unlike the Fe-Co spinel cases, only high-surface-area Fe-Mn spinels were covered, since prior art appears to preclude coverage for Fe-Mn spinels prepared by sintering mixtures of iron oxide and manganese oxide.

The first patent in this series, issued to Fiato and Soled (X.11), claims compositions comprising an unsupported Group Ia or Group IIa metal and copper promoted Fe-Mn spinel having a BET surface area >30 m^2/g, an Fe/Mn ratio >2, and an empirical formula of $Fe_xMn_{3-x}O_4$, where x is >2. The second patent issued to Fiato and Soled (X.12) is identical to Fiato and Soled (X.11), except for the claims, and claims a slurry FT process using a catalyst comprising the composition of Fiato and Soled (X.11). The third patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the composition of Fiato and Soled (X.11) in a pelletized form.

In the examples, a high-surface area Cu-K promoted $Fe_{2.25}Mn_{0.75}O_4$ spinel was prepared by combining Fe and Mn nitrate, in a molar ratio of 3/1, with a solution of ammonium glycolate having a pH of 6.5 in a ratio to give a total metal ion to glycolate ion ratio of 1/1. Water was removed at room temperature and the solid was air calcined at 175°C for 2 hours to produce the spinel having a surface area >50 m^2/g. Promoter was added by impregnating the spinel with 2 atomic % K and 1 atomic % Cu. Interestingly, a paper that appeared in 1985 by Maiti et al., (X.20) at about the same time that the final application was filed, also reported preparing Fe-Mn spinels by base precipitation of Fe and Mn nitrate salt solutions. The reduced and carbided form of the resulting solids, none of which contained promoters, was active for FT synthesis gas conversion. Even though the Maiti paper disclosed materials related to the claimed compositions, it apparently did not preclude the issuing of a patent for these compositions.

Under slurry conditions, the high surface area K-Cu dual-promoted Fe-Mn spinel gave higher CO conversions than either the comparable K or Cu promoted spinels, as shown in X.Table 9. At half the catalyst loading, CO conversion for the Cu promoted catalyst was higher at 69% than the 34% and 36% conversion for the K-promoted catalyst. The methane selectivity was also favorable in that it was lower for the dual promoted catalyst. The effect of Fe-Mn ratio is shown in Table X.10. CO conversions for Cu-K promoted spinels having Mn concentrations with x values >2, as claimed in this patent, were higher than for two spinels having x values of 0.25 and 1.5, which were below the Mn concentrations in the compositions claimed in this patent.

Unlike patent coverage for the Fe-Co spinels, which claimed both high and low-surface area compositions, none of the patents assigned to Exxon claimed compositions or processes comprising low-surface area Fe-Mn spinels as catalysts or precursors to catalysts for synthesis gas reactions. Such catalysts are apparently covered by a previous patent issued to McGrath and Rubin (X.14), and assigned to Kellogg, which claims a process for converting synthesis gas using a catalyst comprising elementary Fe with manganese oxide and alkali compound as promoters. Fiato and Soled (X.11) showed that a reduced low-surface area Fe-Mn composition reported by McGrath and Rubin (X.14) was inactive for CO conversion in the slurry process. This composition had an empirical formula of $Fe_{2.86}Mn_{0.14}O_4$/0.7 atomic % K and was prepared by sintering a paste of $Mn(NO_3)_2$ and Fe_3O_4 containing K_2CO_3 at 1400°C for 6 hrs and reducing with H_2 at 371°C for 48 hrs. For comparison, two low-surface area (<5 m^2/g) K and K-Cu promoted Fe-Mn spinels were evaluated. They were prepared by fusing a mixture of Fe_2O_3, Fe and Mn_3O_4 at 800-1000°C for 48-72 hours and impregnating with K or with K and Cu to give spinels having a composition of $Fe_{2.25}Mn_{0.75}O_4$ and containing 2 atom % K or 2 atom % K/1 atom % Cu. Both of these materials were inactive for CO conversion in the slurry process (see Table X.9). However, based upon the fact that reduced and carbided low-surface area Fe-Co spinels are quite active for CO conversion in the slurry process (see Table X.3), similarly pretreated Fe-Mn spinels may also be active; however, such information was not provided.

The use of glycolate in the production of the $Fe_xMn_{3-x}O_4$ spinel is covered in an independent claim that specifies the use of α-hydroxy aliphatic carboxylic acid. The spinel prepared in the examples using glycolate, as the carboxylic acid, was more active than spinel prepared by precipitating a solution of the salts using ammonium hydroxide. The latter spinel was prepared by calcining at 500°C. The CO conversion for the glycolate spinel was 68.9% versus 20.5% for the ammonium hydroxide prepared spinel.

Another related patent issued to Soled et al. (X.15) claims a process for producing powdered metal-based iron alloys which are structurally the same as prepared by reducing $Fe_{2.25}Mn_{0.75}O_4$. This method comprises heating a mixture of powdered mixed metal oxide with a stoichiometric amount of calcium metal in an inert atmosphere at 850°C for 72 hours, leaching out the Ca and calcium products with an aqueous acid and recovering the metal-based alloy. The other method used by Fiato and Soled (X.11) involves sintering the metal oxides at 1000°C to form the alloy.

The patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the Cu-K-promoted Fe-Mn spinel composition in a pelletized form. Comparison between a fixed bed and slurry operation for this catalyst indicates the slurry catalyst gives higher conversion, similar CO_2 selectivity, and lower methane and higher C_5+ olefin yields (see Table X.11).

Fe - Zn Spinels

A patent issued to Gates and Fiato (X.16) claims a sintered combination of metal oxides having the following components (preferred metals) from Group VIII (Fe), Group

IIB (Zn), Group IA (K), and the Lanthanum Group (Ce). Although there are no limits on the claimed composition, the only catalyst prepared in the examples had an empirical formula of $Fe_{2.81}Zn_{0.19}O_4 \cdot Ce_{0.08}K_{0.08}$ (atom ratio of 1.0/0.065/0.03/0.03). This corresponds to an Fe_2O_3 concentration of 87 wt.%, which, surprisingly, falls outside the 5-80 wt.% range specified in the independent claim 7. The spinel catalyst was prepared by sintering a mixture of Fe_2O_3, ZnO, and CeO_2 at ~1050°C in air for 24 hours. It had a BET surface area <2 m^2/g and XRD indicated it was a highly crystalline mixture of mixed spinels and iron oxides in a CeO_2 phase. The composition is very similar to the Fe/Zn/Ti-Mn spinels that are discussed below. The spinels were reduced in H_2 at 500°C for 7 hours, after which they were pacified by exposure to oxygen at 25°C. The reduced form still contained unreduced metal oxides as shown by X-ray diffraction analysis. The passivated reduced catalysts, after preheating in H_2 in a fixed bed reactor at 500°C, gave the same level of CO conversion as a Zn and Ce-free 1% K/Fe_2O_3 that was prepared in the same way. The Zn-Ce containing catalyst gave lower methane and higher C_7+ liquid selectivity in addition to producing a higher yield of CO_2, as shown in Table X.12.

Another patent issued to Soled et al. (X.17) claims compositions comprising Fe, Zn, and Cu and one member chosen from the group of K, Rb, or Cs wherein the Fe/Zn atomic ratio is ≥ 5 and the alkali metal/Cu atomic ratio is ≥ 2. The claim specifies spinel compositions having empirical formulas of $Fe_xZn_{1-x}O_4$ with x values ≥ 2.5. Although compositions having single phase spinel structures are preferred, the compositions claimed in the patent are not limited to a method of preparation, specific structures or any morphological feature. A corresponding patent, having an identical specification, issued to Soled et al. (X.21) claims a FT process utilizing these catalyst compositions.

Only methods that generate high surface area materials were used in the examples to demonstrate the preparation of three different spinel compositions, i.e. $Fe_{2.8}Zn_{0.2}O_4$, $Fe_{2.45}Zn_{0.55}O_4$ and $Fe_{2.3}Zn_{0.7}O_4$. Only the first catalyst, which was prepared by two different methods, fell within the range specified in the claims. All three catalysts were prepared by mixing a solution of iron nitrate and zinc nitrate with an ammonium glycolate solution having a pH of 6.5, forming a precipitate, and drying and heating in air at $350^{o}C$/1 hr. The resulting spinels were impregnated with K_2CO_3 and $Cu(NO_3)_2$ and dried in a similar fashion. The second $Fe_{2.8}Zn_{0.2}O_4$ spinel was prepared by adding ammonium hydroxide to a solution of iron nitrate and zinc nitrate to a final pH of 9. The washing, drying and impregnation steps were the same.

Although the catalysts were claimed to be useful in either fixed-bed or slurry FT reactors, the examples included only slurry reactor applications. The effect of promoter on synthesis gas conversion of Cu, K and Cu-K promoted $Fe_{2.8}Zn_{0.2}O_4$ showed that the K/Cu promoted catalyst gave higher CO conversion and methane selectivity, as shown in Table X.13. Surprisingly, the highest CO conversion was observed for a spinel having a Fe/Zn ratio less than 5 which falls outside the claimed composition range. It is not clear why this composition was not included in the claimed range of compositions.

Comparative performance tests of the zinc ferrite based catalysts were conducted with 2g samples of catalyst and 72g of octacosane in a 300 cc Parr CSTR. The synthesis gas (H_2:CO = 2:1) feed rate was 180 cc/min at 75 psig and $270^{o}C$. Activation was accomplished by heating up to and at $270^{o}C$ in synthesis gas. Nitrogen (20 cc/min) was added as an internal standard. The superficial space-velocity (V/V/hr) based on an initial catalyst density of 1.8 g/cc was approximately 15,000 V/V/hr. CO conversions in excess of 60% were maintained during initial 80 hr test. Methane selectivity of 4.5% (CO_2 free) was obtained. C_{5+} selectivities were >75% on a CO_2 free basis. On this basis, the space velocity (including 20% inert gas) was about 6 NL/hr-g catalyst (Table X.14); this compares favorably with the activity of cobalt catalysts discussed later. The Exxon workers report that the pressure useful in the process will range between 150 and 450 psig and preferably 250 and 400 psig. They state that higher pressures can be used but these can lead to high levels of condensed water which can retard activity. This statement implies that the catalyst either has low water-gas shift activity or is being operated under conditions where the fraction of CO converted to hydrocarbons, and not CO_2, is very high.

Fe-Zn-Ti and Fe-Zn-Mn Spinels

A patent issued to Fiato et al. (X.18) claims compositions comprising sintered combinations of metal oxides taken from Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn), Group Ia (K), and the Lanthanum Group (Ce) such that the sintered combinations comprise a series of spinels of Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn) and a Group Ia metal oxide in a lanthanum group oxide matrix. The preferred metals are shown in parenthesis. There were specific limits on concentration of the metal oxides in the mixture which are quite similar to the sintered combination in Gates and Fiato (X.16) which included Fe, Zn, Ce and K. In that case, the only limits on concentrations of the metals were in a subordinate claim. The sintered catalysts are red-brown or red-purple, have BET surface areas ≤ 2 m^2/g and are highly crystalline. The crystalline phase comprise hematite, magnetite, ilmenite, a series of mixed spinels and CeO_2. A corresponding identical patent issued to Fiato et al. (X.22) claims a FT process utilizing this catalyst.

The catalysts are prepared, as in Gates and Fiato (X.16) by sintering a mixture of oxides having the correct atomic ratio and reducing in H_2 at 500°C for 6 hrs. The K, Ce, and K/Ce catalysts in a fixed-bed reactor configuration had CO conversion activities that varied with the promoter following the order K/Ce > Ce > K, as shown in Table X.15. At a reasonable CO conversion level the C_2-C_3 olefin selectivity was high and the methane selectivity was lower for the K/Ce spinel. Data were also given at higher reactor temperature, i.e. 305°C, as well as at lower space velocity, which resulted in excess of 80% CO conversion with high olefin concentrations in the C_2-C_4 fraction plus a sizable yield of C_5+ product.

K, Ce and K/Ce catalysts having compositions in which Ti was replaced with Mn were also included. The atomic ratio of the metallic components in the catalyst containing both K and Ce was 1.0 Fe/1.0 Mn/0.07 Zn/0.05 K/0.04 Ce. On a weight basis, this composition (43.6% Fe_2O_3/48.2% MnO_2/3.1% ZnO/1.2% K/3.8% Ce) is excluded from being a covered composition since it fell outside the specified composition in the main claim. Specifically, the MnO_2 composition of 48.2 wt.% of the total oxides is excluded, unless there is an error in the composition as stated in Example 6, since the claims specify a range for MnO_2 of 10 to 40 wt.% of the combination. The performance of the K, Ce and K/Ce promoted Fe/Mn/Zn spinels in a fixed-bed reactor configuration are shown in Table X.16. The K/Ce dual promoted spinel provides high activity, low methane selectivity and high C_2-C_3 olefin selectivity.

Thallium Impregnated Iron Supports

Two patents were issued regarding thallium and iron catalysts. One is a composition of matter case issued to Wright (X.23) and the second, a process patent issued to Wright et al. (X.24). Both cases involved several filings and abandonments;

there is also a difference in the inventors for the two cases. Overall, the texts in these two are very similar, though not identical. The main claims cover all Fe-Tl compositions wherein the thallium compound, being supported or unsupported, is substantially deposited on the surface of the iron compound, with the iron compound in the trivalent state. Included in a dependent claim is incorporation of promoters including Co, Zn, Cr, Mn, Ba and Group I metals.

The main claim appears confusing since it states that the thallium may be both supported and unsupported but is also substantially supported on the surface of the iron. The examples contain numerous examples in which the thallium was impregnated onto the surface of the iron, however one catalyst was prepared by impregnating a melt of ferric nitrate and thallium nitrate onto a magnesium-alumina spinel. This presumably is a supported example. Also, there is nothing in the claims regarding pretreatment of the catalyst to reduce the Tl and Fe to the metallic or carbided forms, although a number of different methods for preparing the catalysts are included in the examples.

Several techniques for preparing Fe/Tl catalysts were presented in the examples. Several Fe-Tl catalysts were produced having Fe/Tl ratios from 10/1 to 2.5/1 by precipitating solutions of ferric nitrate with ammonium carbonate and impregnating the washed and dried solids (110^{o}C for 12 hrs in air) by an incipient wetness method with solutions of thallium nitrate or thallium chloride. Examples were also given for preparation of other Fe/Tl catalysts supported on alumina, cesium-doped and magnesia-doped aluminas, and commercially available iron oxide. Examples explaining the preparation of several fluoride impregnated catalysts were also provided. Test results were provided on only a limited number of these preparations.

All of the Fe-Tl catalysts that were prepared in the examples were run under FT conditions that gave CO conversions up to 97%. The product contained large concentrations of liquid hydrocarbons in the C_5-C_{11} range that was rich in olefins and contained a lesser amount of aromatics. Data for a 10 Fe/1 Tl catalyst prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate and reducing at 270^{o}C/18 hrs are shown in Table X.17. Over a range of temperatures from 270 to 350^{o}C, the maximum C_6+ yield at CO conversions >90% was ~20% with methane yields ranging between 6 and 15%. CO conversion is very dependent on space velocity, however, methane, C_5-C_{11} liquid, C_1-C_4 gas, alpha-olefin and aromatic selectivities are only weakly dependent on space velocity. It was suggested that the aromatics yield is probably related to conversion of olefins. None of the examples provided any data on CO_2 yields.

The performance of two Fe-Tl catalysts in the FT reaction was compared with an Fe/K and a commercial ammonia synthesis catalyst. Two Fe-Tl catalysts, having Fe/Tl ratios of 10/1 and 5/1, were prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate. The method for preparing the Fe/K catalyst that contained 4% K is not clear and no further description of the commercial ammonia synthesis catalyst was given. Selected results from runs presented in Example 9 in the patent are shown in Table X.18. In the patent, in several instances, differing sets of results are given for the same run condition without any explanation. For example, included in Table X.18 are two sets of data that were both taken at 350^{o}C and 300 GHSV for the 10 Fe/1 Tl catalyst. Due to the lack of clarity in the presentation of the data, it is difficult to draw any conclusions regarding the CO conversion activities of these various catalysts. However, the product selectivities in these runs are quite similar. The discussion in Example 9 of the patent states that CO conversions were initially in the 80-98% range. Whereas the Fe/0.4K catalyst appeared to lose activity after about 18 hours on stream, conversion for the Fe/Tl catalyst decreased to only 40-60% after several days on stream. The selectivity for the 10 Fe/1 Tl catalyst appears to be maximum at 270°C at a CO conversion of 46.8%.

Iron - Cobalt Impregnated Slurry Catalysts

A patent issued to Fiato et al. (X.25) claims a process for preparing a slurry FT catalyst system in which an Fe-Co catalyst is formed (in situ) in the absence of air. A corresponding identical patent, except for references and claims, issued to Fiato et al. (X.26), claims a FT process utilizing this catalyst system. The catalyst is prepared by adding Fe and Co carbonyl compounds, or Fe and Co compounds which are capable of forming carbonyl complexes, in a CO atmosphere, along with a powdered support, to a hydrocarbon liquid. The iron and cobalt compounds are present in a ratio of from 35:1 to 1:10. This combination is decomposed in the presence of CO such that the cobalt complex is decomposed to the metal at a lower temperature followed by decomposition of the Fe complex at a higher temperature. The slurry is heated in H_2 to reduce the metals and their decomposition products. Representative complexes are $Fe_3(CO)_{12}$, bis(dicarbonylcyclopentadienyliron), $[CpFe(CO)_2]_2$, and $Co_2(CO)_8$. Potassium carbonate, that promotes olefin formation in the reaction and decreases the formation of methane, may be added to the mixture in the first step.

In the examples in the patent, $[CpFe(CO)_2]_2$ and $Co_2(CO)_8$ were added to the reactor either alone or in the presence of a support. In each case shown in Table X.19, the absolute amount of Fe and Co in the reactor was the same except for the run in which Fe_2O_3/1% K was added as the support. In runs with a 1:1 H_2/CO synthesis gas mixture, CO conversions were 20-30% with the C_2-C_4 fraction being predominantly olefinic. After 96 hours on stream, conversion had increased from ~21 to 27%. In a comparative run, an *ex situ* catalyst, $Fe_{2.85}Co_{0.15}O_4$/1%K, gave <5% CO conversion. For this run, the preparation of the catalyst nor its concentration in the reactor were not given.

TITANIA AND TRANSITION METAL OXIDE SUPPORTS

An extensive number of patents were obtained related to the use of titania containing catalysts in various applications, including the FT reaction. Early patents in this area disclosed the unique features of titania containing supports but did not refer to any FT type of application. However, these cases were fundamental to many of the subsequent patents that were issued for FT application. A patent issued to Tauster et al. (X.27) disclosed compositions comprising Group VIII metals supported on bulk oxides of titanium, vanadium, niobium, tantalum, zirconium titanate and barium titanate which were reduced in H_2 before use. A corresponding approach of coating a support with titania and adding a Group VIII metal is disclosed in a related patent issued shortly thereafter to Wheelock (X.28). Numerous patents have subsequently been issued using these approaches.

Tauster et al. (X.27) claimed that H_2 reduced Group VIII metals supported on Group IVb and Group Vb oxides are distinctly different from the same metals deposited on common carriers such as alumina, silica, carbon, magnesia, and silica alumina. These metals deposited on common carriers are found to retain their capacity for H_2 chemisorption, whereas the same metals when supported on various Group IVb and Group Vb oxides exhibit a marked suppression of this capacity. This change is attributed to the chemical nature of a strong metal-support interaction (SMSI) that consists essentially of covalent bond formation between metal atoms of the supported phase and metal cations of the oxide support at the surface.

Such an interaction between the supported metal and the support is highly unusual. Typically, the role of the support is simply a geometrical one which exerts the major influence in the preparation of a well dispersed supported-metal catalyst. Thus chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided that they are employed in their high surface area form, e.g. >100 m^2/g. In these situations no strong chemical interaction between the support and the metallic phase is required to bring about good dispersion. If surface interaction occurred, the results observed for temperature-programmed-desorption of H_2 from Pt/alumina and Pt/silica catalysts, which are very similar, would be expected to be quite different.

The patent argues that although covalently-bonded species are observed in the hexagonal barium titanates and Lewis acid-base intermetallic compounds, which are representative of cation to cation and metal-atom to metal-atom types of bonding, respectively, the metal-atom to cation bonding in the SMSI are unique to the structures of this invention. In a Lewis acid-base intermetallic type of bonding structure, the titanium would be present as zero-valent. By photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), zero valent titanium was not found in a composition of this invention, i.e. a 2% Rh/TiO_2 catalyst that had been reduced in H_2 at 550°C.

In the broadest sense, the catalyst composition consists of a catalytic metal component selected from the group consisting of Group VIII metals, and mixtures thereof, supported on a transition metal oxide selected from the group Ti, V, Nb, Ta, alkaline earth titanates, and mixtures thereof. These SMSI oxides can be used either in the pure state or, alternatively, in combination with additional oxides such as alumina, silica, magnesia, zirconia, hafnia, thoria, ceria, etc. They may be prepared by coprecipitation from solutions containing precursor salts of the respective oxides or by deposition of the precursor salt of the SMSI oxide on a carrier. The latter compositions, comprising titania deposited on the surface of an inorganic oxide support to which Group VIII metals are added, were disclosed by Wheelock (X.28) who anticipated a stabilizing interaction between Group VIII metals and Group IVb metal oxides.

The key characteristic of the SMSI oxides is that after the critical temperature for reduction is reached, the supported metal is no longer able to absorb H_2 and CO at room temperature. However, the supported metal particles are still in a high state of dispersion and retain their ability to chemisorb oxygen resulting in high ratios of adsorbed oxygen to metal atoms. Since the SMSI effect is a chemical interaction between the supported metal and the carrier, it is necessary for the metal to be well dispersed in order to provide sufficient interfacial contact between metal and support. Thus large metal crystallites are incapable of significantly affecting the properties of the surface metal atoms in contact with the gas phase. Therefore, the particle size of the supported metal should be preferably 50 Å or less. There also is a difference in the temperature of H_2-activation needed to confer SMSI properties on the Group VIII metal, which varies primarily with the particular SMSI support. A SMSI state is achieved when a composition, e.g. Group VIII metal supported on the oxide of Ti, V, Nb, Ta, a mixture thereof, or a Zr or Ba titanate, is subjected, as a final preparative step, to reduction in a reducing atmosphere at a temperature sufficient to cause the composition to exhibit the suppression of H_2 and CO chemisorption.

Properties of Titania Supports. Tauster et al. (X.27) did not address the question of surface area and how it relates to the development of the SMSI state, although they used the argument that chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided they are employed in their high surface area form, e.g. >100 m^2/g. Based upon data contained in a subsequent patent issued to Arcuri et al. (X.29) the titania supported catalysts prepared by Tauster et al. (X.27) probably had only moderate surface areas. Arcuri et al. (X.29) showed that the rutile to anatase ratio increased with higher air calcination temperatures which caused a corresponding decrease in surface area (see Table X.20). They also found reduction of a calcined sample with H_2 at 450°C did not prevent further decrease in surface area upon further calcination in air at 500°C. These data suggest that the surface areas of the titania used by Tauster et al. (X.27) was initially about 60 m^2/g and because of the thermal transformation of anatase to the rutile form, the final surface areas were probably somewhat less than the starting material and somewhat enriched in the rutile form. In a still later patent issued to Mauldin and Riley (X.30), additional data were reported showing increases in rutile concentration with calcination temperature (see Table X.21).

Vannice and Garten (X.31) described the titania that was probably used in many of these patents as being prepared by flame hydrolysis of $TiCl_4$ and having a surface area of ~60 m^2/g after thermal treatment at temperatures ≤500°C. A number of the cases referred to a material of this type that was designated as Degussa P-25 and was described as having a BET surface area of 50 m^2/g and contained 65% anatase and 35% rutile titania in Wachs and Yang (X.32). Although a number of these patents contained claims that specified limits on the concentrations of the crystalline forms in the titania phase, several actually contained these limits in either the main claim or another independent claim. This, of course, provides an unalterable requirement for the catalyst of the invention and was peculiar to a series of five patents, four of which claim titanias having high rutile contents while the fifth claims a stabilized titania having a high anatase content. Interestingly, the four high rutile cases, that originated from work presumably done at the Baton Rouge laboratories, were filed on the same day, June 29, 1984, and no subsequent patents had such a restriction in their main claim, although several continued to claim such materials in dependent claims. The level of rutile specified in the claims is >40%.

An alternative to using bulk titania is supports in which titania would be coated onto common, inorganic oxides. Such compositions were covered in a patent issued to Wheelock (X.28) which disclosed compositions comprising Group VIII noble metals and titania deposited onto inorganic oxides. Interestingly, that patent actually specified in its main claim that the titania existed on the surface as clusters. Whether such speculation regarding the morphological form of the catalyst, which was based upon ion scattering experiments, limits the compositions claimed by the invention is not clear. Assuming that it does not, Exxon then has rights to all compositions comprising Group VIII noble metals on titania coated inorganic oxides, of which platinum was specifically mentioned.

Ruthenium on Titania and Transition Metal Oxide Supports

The earliest Ru on titania Exxon patent that was found related to application in NO_x reduction. A composition of matter patent issued to DeLuca et al. (X.33) claimed a composition comprising ruthenium in combination with zirconium titanate or zirconium titanate in admixture with titanium dioxide, but not with TiO_2 alone. Ruthenium on titania compositions had been disclosed in previous patents, one of which was issued to

Kobylinski and Taylor (X.34), and assigned to Gulf, which claimed a process for reducing the content of nitrogen oxides in the exhaust gases from internal combustion engines. Such patents probably precluded claiming such compositions.

A problem with Ru/TiO_2 catalysts is the loss of Ru oxide upon treatment at temperatures around 840^{o}C. DeLuca et al. (X.33) claimed decreased volatility of Ru oxide from compositions comprising Ru on zirconium titanate, either with or without additional titania being present. Tauster et al. (X.27) claimed the use of these materials in hydrocarbon conversion reactions but not in a FT type application. Various combinations of these supports, either alone or in combination with supported metals, are claimed in subsequent composition of matter patents or as catalysts in various FT process application patents. Several patents were issued regarding ruthenium on titania type supports. The claims in all these cases included not only titania but numerous combinations with silica, alumina, carbon, Group Vb metal oxides, and various alkali, alkaline earth and rare earth oxides. Exxon came close to claiming the composition Ru on TiO_2 in a patent issued to Arcuri et al. (X.29) which claimed catalyst compositions comprising ruthenium with rhenium on titania. A companion process patent that utilized this catalyst, which was essentially identical except for the claims, was issued to Arcuri (X.35). The titania support in these compositions were specified as having rutile concentrations >40%. The examples in these patents showed in extended runs with synthesis gas that Ru/TiO_2 that contained rhenium had a longer half-life at a level of 97% CO conversion than rhenium-free catalyst (see Table X.22). The interactive effects of these two metals on catalysts containing 0.5-1.0% Re with ruthenium concentrations from 0.1-1.0% indicate that the highest CO conversions were obtained for catalysts containing 0.5% Re and 1.0% Ru (Table X.23). The effect of the ratio of rutile to anatase in the catalyst is shown in Table X.24 in which the catalyst containing 67% rutile in the titania had the slowest deactivation rate when operating at the 90% CO conversion level. Also, methane selectivities were much lower for the catalysts containing higher levels of rutile.

Several of the ruthenium-titania patents that were issued relate to processes that use Ru on titania. Vannice and Garten (X.31) claimed the use of a reduced Ru on titania, which they prepared by impregnating $RuCl_3$ onto titania and reducing in H_2 for 1 hr at 450°C. The Ru/TiO_2 catalyst gave higher olefin yields than a related Ru on η-Al_2O_3 (see Table X.25), albeit at a CO conversion level of 10% or less in both cases. Mauldin (X.36) claims a process for converting methanol in the presence of H_2 using a catalyst comprising ruthenium composited with titania. At a 4/1 methanol to H_2 ratio, conversion to hydrocarbon product was 76% after 35 hrs on stream (see Table X.26). Either in the absence of H_2 or the presence of added CO, conversions dropped significantly. CO was presumed to adsorb preferentially on the catalyst preventing reaction of the methanol.

Vannice and Tauster (X.37) claimed a FT process using a catalyst comprising Ru deposited on V, Nb and Ta oxides either alone or in combination with silica, alumina, or carbon type supports. Titania was not included in the claims. Preparation of the catalysts was by methods as presented in Tauster et al. (X.27) which was incorporated by reference. Higher olefin yields were obtained with the catalysts of the invention under conditions that the CO conversions were less than 18% (see Table X.27).

Madon (X.38) also claimed a FT process using a catalyst comprising Ru deposited on the same supports claimed by Tauster et al. (X.27), i.e., Ti, V, Nb and Ta oxides. In an improvement over Vannice and Tauster (X.37), this case claimed a process which employed a reduced catalyst which was contacted with a mixture of H_2 and CO for at least 10 hours, after which continued contact with H_2/CO gave a C_5-C_{40} hydrocarbon product having a paraffin to olefin ratio in the C_5-C_{20} fraction of $\geq$1.5. With a 0.76% Ru on TiO_2 catalyst, in excess of 80% CO from a 1.39 H_2/CO synthesis gas mixture was converted to liquid products under conditions shown in Table X.28. All of these catalysts were shown to be more active than Ru supported on conventional SiO_2 or Al_2O_3 (see Table X.29).

A patent issued to Wachs and Yang (X.39) claims a catalyst comprising Ru supported on a surface modified titania support wherein the support comprises an oxide of a metal selected from the group Nb, V, and Ta supported on the titania. In a corresponding patent, Wachs and Yang (X.32) claim a method for preparing this catalyst composition by depositing noncrystalline metal oxides of V, Nb, and/or Ta on a titania support having a 50 m^2/g surface area. In a related patent, Wachs and Chersich (X.40) claim a simple Ta_2O_3/TiO_2 composition prepared in this manner. No related patents claiming V and Nb oxide modified titania surface compositions were found. In Wachs and Yang (X.39) the modified support was impregnated with a solution of the Ru precursor which was reduced to the metal form. In the examples, all of the catalysts contained 1% Ru loadings. The activity of the catalysts containing various concentrations of the oxide promoters were compared with an impregnated physical mixture of TiO_2 and Ta_2O_5 in a fixed bed reactor (see Table X.30). Although the patent states that the data clearly show the difference between the catalysts of this invention and prior art Ru/TiO_2 catalysts, it is a challenge to recognize any differences.

A patent issued to Fiato and Miseo (X.41) claims slurry catalyst compositions consisting of titania, the decomposition product of $Ru_3(CO)_{12}$ formed in the presence of

H_2, and an inert alkane hydrocarbon. Fiato and Miseo (X.42) claim a process for preparing the *in situ* Ru/TiO_2 slurry catalyst. Preparation includes adding TiO_2, a Ru carbonyl complex, and an inert alkane hydrocarbon to a slurry reactor and increasing the temperature of the reactor to 230-270°C and pressure from 4 to 20 atm for 2-6 hr while adding a gas mixture of N_2:H_2 to cause the decomposition of the Ru carbonyl complex to form a slurry catalyst composition. In the example, a TiO_2 that had been pretreated with H_2 for several hours was added to the reactor with the Ru carbonyl complex and then subjected to the carbonyl decomposition step. The catalyst was highly active and selective for production of liquid hydrocarbons giving 40 to 60% CO conversion at 240°C with an alpha of 0.80. When TiO_2 was not present in the reactor, the Ru carbonyl complex was incompletely reduced and gave only 15% CO conversion (see Table X.31). The performance of the slurry catalyst was compared with a particulate Ru/TiO_2 and a Ru supported on ceria and alumina. The Ru - TiO_2 slurry catalyst had the highest CO conversion (55%) with a selectivity very similar to the particulate Ru/TiO_2 catalyst.

A patent issued to Mauldin (X.43) claims a process wherein the Ru on titania catalyst is pretreated with steam or steam and H_2 at 200 to 550°C to mildly agglomerate the ruthenium. By this procedure, Ru particles are generated having the same size as obtained after start-up with synthesis gas. The same effect occurs upon treating in air at 500°C where the crystallite size of the Ru grows from 12 to 30 Å. In the examples, a Ru/TiO_2 was prepared by impregnating a titania having a rutile content of 73% with ruthenium nitrate in acetone solution. One portion of this material was calcined in air at 500°C for 4 hours. Another was contacted with mixtures of steam with H_2 or N_2 at elevated temperature, as shown in Table X.32. The oxygen chemisorption decreased while the Ru crystallite size increased. The performance of the Ru/TiO_2 that had been treated in air at 500°C for 3 hrs was compared with an untreated sample. Results after several times on stream, as shown in Table X.33, indicate that the selectivity to methane was higher and to C_2+ hydrocarbons was generally lower than for the untreated catalyst. The catalyst treatments that were presented in the patent, including air or steam with H_2 or a carrier gas, provide an advantage over a non-treated catalyst, as determined by Ru crystallite size, oxygen chemisorption or synthesis gas conversion and selectivity.

A patent issued to Pruett and Bradley (X.44) claims compositions comprising bimetallic cluster compounds containing Ru with Tl, In or Ga. A cluster having the formula $[(C_2H_5)_4N][(Ru_6C(CO)_{16})_2Tl]$ deposited onto an alumina surface was reduced in H_2 at 200°C and used for conversion of 1.5/1 H_2/CO mixture at 7 MPa and 275°C. The product contained a mixture of linear hydrocarbons and alcohols.

Rhodium on Titania

A patent issued to Vannice and Garten (X.45) claims a process in which synthesis gas is passed over a catalyst comprising Rh on a titanium-containing oxide support. The activity of this catalyst, reduced at 450°C and 100 kPa, though quite low, was higher than for a Rh on alumina catalyst (Table X.34). The product was largely methane.

Cobalt on Titania and Transition Metal Oxide Supports

There has been a considerable amount of activity by Exxon regarding cobalt on titania catalysts with a number of patents being issued that parallel the ruthenium cases discussed above. Included in the series were three filed on June 29, 1984 from the Baton Rouge laboratory that relate to titanias having rutile concentrations $\geq$40%. Very broad coverage was obtained in a patent issued to Payne and Mauldin (X.46) which claims catalyst compositions comprising cobalt on high-rutile titania which are useful for both synthesis gas and methanol conversion. A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of titania to an average depth of 0.02 to 0.20 mm with a cobalt loading, on a total bulk basis, from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. A related patent issued to Iglesia et al. (X.48) claims a method for preparing supported cobalt catalyst on which the Co is deposited to a depth of less than about 200 µm on the rim of the catalyst particles. Other patents issued to Payne and Mauldin (X.49) and Behrmann et al. (X.50) claim processes that utilize these catalysts for conversion of synthesis gas. The addition of rhenium as a promoter to this family of catalysts, i.e. rhenium with cobalt on titania, was also covered. Catalysts in which the Co and Re were concentrated at the surface of the spherical particle was claimed by Behrmann et al. (X.47). Rhenium is claimed to improve activity for CO conversion for cobalt as it does for ruthenium. Bulk Co/TiO_2 catalysts, either with or without thoria, were claimed in a patent issued to Mauldin (X.51) with addition of thoria being claimed to be especially beneficial for conversion of methanol. Since the main claim in this case specified an inorganic oxide support, with titania being mentioned in a dependent claim, compositions that were covered were actually broader than titania itself, although titania supports were the only ones used in the examples.

Of the nine examples on Co/TiO_2 in the Payne and Mauldin (X.46) case, the first six relate to conversion of methanol and the last three to conversion of synthesis gas. The latter examples with synthesis gas are repeated in Payne and Mauldin (X.49) while the first six, which are related to methanol conversion, were probably included in

Application Number 626,026, which was filed on the same day, as noted in Payne and Mauldin (X.49), but apparently never resulted in an issued patent. A process patent issued to Mauldin (X.52) used the Mauldin (X.51) catalyst comprising rhenium and cobalt on titania.

The examples of bulk titania catalysts in Payne and Mauldin (X.46) were prepared from calcined Degussa TiO_2, which was impregnated with Co nitrate and/or perrhenic acid. The addition of perrhenic acid to the substrate is a puzzle, since none of the catalysts contain Re, nor do any of the claims refer to catalysts containing Re. At any rate, the impregnated materials were then calcined in air at 250 or 500°C and reduced in H_2 at 450°C. Thoria containing catalysts were prepared by impregnating the support with a thorium compound or salt in a similar manner to give thorium concentration up to 10%. Actually, the specific thorium compounds or salts that were used to impregnate the substrate were not mentioned anywhere in the specification. Another set of cobalt-titania catalysts were also prepared having both high and low rutile concentrations. The low rutile concentration catalyst was prepared by impregnating cobalt carbonyl onto uncalcined Degussa P-25 titania that had a rutile concentration of 28% while the high-rutile catalyst was prepared from Degussa P-25 that had been calcined at 600°C. The impregnated cobalt carbonyl was decomposed either by heating at 257°C in vacuo for 1 hr, or by calcining at elevated temperatures. Catalysts were tested in a fixed bed reactor either with synthesis gas or with methanol after reducing in H_2.

A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of spherical titania with an average thickness of 0.02 to 0.20 mm. A corresponding patent issued to Behrmann et al. (X.50) claims use of these compositions in a FT process. The cobalt loading in these catalysts, on a total bulk basis, was from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. Special techniques for depositing the cobalt along with Re as a promoter were used wherein the metals were concentrated at the surface of the spherical titania particles having diameters of approximately 1 mm. The activity of rhenium promoted Co/TiO$_2$ catalysts, in which the metals are deposited on the surface of spherical titania substrate, is related to the thickness of the metal layer. With these catalysts that were prepared from spherical titania, the methane concentrations in the hydrocarbon product, relative to the converted CO, was lower than for Co-Re/TiO$_2$ in which the metals were uniformly distributed onto powdered substrate (see Figure X.1). The metals were deposited onto the surface of the spheres by either spraying a metal-containing solution onto the titania spheres and quickly removing the solvent or treating spheres that had been saturated with one solvent with a metal-containing immiscible solvent which would not penetrate into the particle.

Another method to prepare rim-type supported cobalt catalysts is covered in a patent issued to Iglesia et al. (X.48) who claim that contacting a support particle with a molten cobalt salt results in deposit of the cobalt to a depth of less than about 200 µm on the rim of the support. After reduction in H$_2$, these catalysts are more active than incipient wetness impregnated catalysts where the Co is evenly distributed throughout the particle, as shown in Table X.35, where a lower GHSV is necessary to achieve the same level of CO conversion. Each of the rim-impregnated silica based catalysts have a higher volume of CO conversion per volume of catalyst per hour. Crushing the 2.2 mm spheres provided a slight increase in CO conversion which denotes some additional diffusional effect in the rim catalysts even though the Co is located primarily at the surface of the particle. There is also an advantage of having higher Co concentrations on higher surface area supports, as shown in Table X.35.

The advantage of incorporating a binder into titania was covered in patents issued to Mauldin and Riley (X.30) which claim support compositions comprising titania in which up to 20% alumina or zirconia is incorporated. A corresponding essentially identical patent issued to Mauldin and Riley (X.53) claims a FT process utilizing these catalysts. Their data show that incorporating a small amount of alumina increases the volume of CO converted per gram of cobalt/hr, as shown in Figure X.2. This increased activity is attributed to an increase in cobalt dispersion due to the increase in pore volume of the binder. Hydrocarbon synthesis activity suffers at higher alumina concentrations, however, because the Co oxide is only partially reduced on the alumina, as compared to titania where complete reduction occurs. This is reflected in the higher turnover numbers for the titania and the steady decline as incorporation of alumina increases (see Figure X.3). Thus, incorporation of small amounts of alumina results in an increase in activity. Higher dilutions, however, result in a decline in activity. An example is also presented that shows that catalysts prepared by spraying Co salts onto titania substrate containing 3.5% alumina binder using the method of Behrmann et al. (X.47) were more active than spherical titania without the binder.

A method for impregnating cobalt onto supports was covered in a patent issued to Mauldin and Riley (X.54) which claims a process for preparing a FT catalyst in which a catalytically effective amount of Co is impregnated and dispersed as a film or layer on the peripheral outer surface of a particulate porous inorganic oxide support, wherein the catalysts are prepared by spraying a bed of the fluidized particulate support particles with a liquid containing a dispersed or dissolved Co metal compound. The operation is performed at specified operating conditions of 0.6 g liquid/ft^3 fluidizing gas. Titania was one of the supports specified in a dependent claim. In the examples, solutions of cobalt nitrate and perrhenic acid were sprayed onto particulate material and reduced at 450^{o}C for 1 hr. Conversion of a 2/1 H_2/CO feed at 200^{o}C, 280 psig and 1000 GHSV after 20 hrs on stream was 79% with product selectivities for CH_4 of 6.0%, CO_2 of 6.0% and C_2+ of 93.6%.

Synthesis Gas Reactions. Co/TiO_2 catalyst has a higher activity toward synthesis gas conversion, as shown in Table X.36, than conventional cobalt on silica or alumina or Co-Mg-thoria on kieselguhr, which was prepared following a published procedure (X.55). The 0.91 Schulz-Flory alpha value for the titania catalyst was higher than for conventional catalysts and was reflected in a C_{10}+ hydrocarbon yield that was $\rangle$75%. Higher CO conversions in these Co/TiO_2 catalyst appear related to higher rutile concentrations and higher O_2 chemisorption values of the starting catalysts as shown in Table X.37. The pseudo first-order CO conversion rate constants calculated by Equation 1 correlate directly with the oxygen chemisorption values for these four catalysts, as shown in Figure X.4.

$$k = \frac{GHSV}{P} \ell n \frac{1}{(1-X)} \qquad \textbf{(15)}$$

where:

x = fraction CO conversion,

P = reactor pressure in atm, and

GHSV = space velocity at ambient temperature and pressure in hr^{-1}.

Similar results were obtained with catalysts prepared by impregnating cobalt carbonyl onto 28% and 100% rutile titanias where the carbonyl was decomposed by heating in vacuum. Synthesis gas conversion over these catalysts shows that the high rutile catalyst gave much higher CO conversion (see Table X.38). Cobalt catalysts prepared either from the nitrate or the carbonyl gave essentially the same results.

Incorporation of 0.5 to 3% Re in the Co/TiO_2 catalyst further improved both oxygen chemisorption and CO conversion, as shown in Table X.37. The improvement resulting from addition of Re is probably through improving the reduction of the Co in the pretreatment step (X.56). Results from a 200 hr extended run, presented in (Figure X. show that CO conversion dropped from about ~98% to ~80%. Comparison with a Ru/TiO_2 catalyst with the Co-Re catalyst under the same conditions (Figure X.6) indicate the Co-Re catalyst was significantly more active than the Ru catalyst while both had similar selectivities for methane and CO_2 (Figure X.7).

<u>Methanol Reaction</u>. Examples of methanol conversions were given for a number of cobalt catalysts including Co/TiO_2, $Co\text{-}Re/TiO_2$, $Co/ThO_2/TiO_2$, and $Co\text{-}Re/ThO_2/TiO_2$. The effect of rutile concentration on methanol conversion was observed for catalysts containing 12% cobalt on titania. The 100% rutile catalyst completely converted the methanol while the 55% rutile titania support gave only 66% conversion (see Table X.39). The selectivities were also quite different with the catalyst having the lower rutile content being more selective for producing C_2+ hydrocarbon product and less CO_2.

Experimental data showing the effect of adding thoria on the conversion of methanol is provided in Payne and Mauldin (X.46). In these cases the rutile contents of the catalysts were not specified (see Table X.40). Assuming that the titania components in these catalysts had the same rutile concentration, the data show that addition of thoria to the catalyst increases methanol conversion, decreases methane yield, and gives nearly the same Schulz-Flory alpha values. Comparisons with other state-of-the-art catalysts showed that conventional FT 100 Co/5 ThO_2/8 MgO/200 Kieselguhr catalyst gave higher methanol conversion but poorer C_2+ hydrocarbon selectivity under the run conditions. Compared to Co on silica or alumina, both Co-titania catalysts, with or without thoria, gave better C_2+ selectivity at comparable or higher methanol conversion levels. The liquid product was highly paraffinic as reflected in the 78.2% straight chain paraffinic content of the C_8 fraction from the thoria containing catalyst. Even over the Co/alumina catalyst, where methanol conversion was 64%, the yield of dimethyl ether was only 2.4%, indicating the non-acidic nature of the alumina support. At the low methanol conversion levels, dimethyl ether formation was quite small.

The presence of rhenium with cobalt in 56% rutile titania catalysts, either with and without added thoria, increased MeOH conversion (see Table X.41). Addition of 0.5 wt.% Re to Co/ThO_2/TiO_2 increased methanol conversion quite sharply from 49% to 100%. Conversion to CO_2 increased sharply while C_2+ yields decreased from 74% to 56%. The effect of Re/TiO_2 on methanol conversion was not provided.

Hydrogen partial pressure has a strong effect on methanol conversion and product selectivity. Payne and Mauldin (X.46) showed that increasing the H_2 partial pressure at constant methanol space velocity increased conversion from 38% to 83% (see Table X.42), decreased the yields of CO+CO_2, and sharply increased methane selectivity. The C_2+ yield appears to go through a maximum at a H_2 partial pressure of 17 psi. At low methanol pressures over a 12% Co/2% ThO_2/TiO_2 catalyst, the products are almost exclusively CO and H_2, except for a very small amount of methane.

A patent issued to Mauldin et al. (X.57) claims cobalt-titania catalyst to which is added small amounts of hafnium, zirconium, cerium or uranium to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatment. The concentration of promoter to cobalt was specified as a weight ratio greater than 0.01 to 1 and typically between 0.04-0.25 to 1. Although there were no limits placed on the catalyst composition, the catalysts presented in the examples were prepared by impregnating high rutile titania either sequentially with Zr, Hf, Ce or U compounds followed by Co nitrate or simultaneously with the promoter metals and cobalt nitrate. In the preparation of these catalysts when the metals were added sequentially, the catalysts were calcined between metal additions. The final catalysts were then calcined at 400, 500 or 600°C to simulate catalyst regeneration and tested for synthesis gas reactions. CO conversions for the promoted catalysts were higher than for the non-promoted catalysts at all air treat temperatures >150°C, as shown in Figure X.8. The 500°C catalyst regeneration data plotted in Figure X.9 show that addition of approximately 0.5 wt.% promoter provides optimal thermal stabilization giving CO conversions of 70-80%. The examples also showed that addition of 0.06 wt.% Hf and 0.3 wt.% Zr, both of which fell within the limits of the claimed compositions, was not adequate to stabilize the Co/titania, although higher concentrations did stabilize the catalysts.

Synthesis gas conversion data were provided for a 2/1 H_2/CO mixture that was passed over a Co-Hf-TiO_2 catalyst at 1000 GHSV and 204°C at 280 psig to give 89% CO conversion with a 91% C_5+ hydrocarbon product selectivity. No other synthesis gas data were provided. Comparative runs with methanol, however, are reported for each of the metal promoters (see Table X.43). All of the promoted catalysts gave higher MeOH conversion than the unpromoted catalysts with about the same selectivities for higher hydrocarbon product.

Silica Promoted Co/TiO_2

A patent issued to Iglesia et al. (X.58) claims compositions of cobalt on an inorganic refractory support comprised of a major portion of titania to which up to 15 wt.% silica has been added. This catalyst is utilized in another process related patent issued to Iglesia et al. (X.59). These two cases are identical except for the claims. The patent specifies that the Co may be incorporated onto the inorganic refractory titania support either before or after adding the silica or silica precursor. Incorporation of rhenium in the catalyst is covered in a subordinate claim. Although the main claim does not specify Re in the catalyst, the examples include only Re-containing catalysts.

In the examples, a series of catalysts, as described in Table X.44 were prepared starting with a CoRe/TiO_2 (Catalyst A) that was prepared by depositing Co and Re components from an acetone solution onto a 97% rutile titania and calcining at 250°C for 3 hrs. Two silica containing catalysts (Catalysts B and C) were prepared by impregnating Catalyst A with tetraethoxysilane (TEOS), treating with a stream of H_2O (40 Torr) in He while heating at 400°C for 13 hrs after which it was reduced at 250-400°C for 2-14 hrs. A catalyst that was free of silica but exposed to the same H_2O treatment (Catalyst D) was prepared by treating Catalyst A with H_2O (40 Torr)/He while heating at 400°C/13 hrs, after which it was reduced at 250-400°C for 2 to 14 hrs. The activities of the catalysts were determined at run times up to almost 200 hrs under conditions to give ~60% CO conversion. There was little difference in hydrocarbon selectivity observed by incorporating silica into the samples. Although the CO_2 yield was in every case quite small, it dropped to an almost imperceptible level with silica.

The increased stability of the silica containing catalysts was observed in reduced carbon buildup at low temperatures on the surface of the catalyst in the presence of CO. The "effect of SiO_2 during carburization suggests that it may prevent short term deactivation during the first few hours in H_2/CO environments; the effect is to increase the apparent site activity by maintaining surface cobalt atoms available during hydrocarbon synthesis."

Anatase Titania Supported Cobalt Catalysts

A patent issued to Soled et al. (X.60) claims both a composition of matter and a method for preparing a catalyst containing anatase titania. What appears to be the omnibus claim is claim 13 which claims a catalyst composition comprising Co composited with a ternary metal oxide support of titania having the general formula $Co/Ti_{1-x}M_xO_2$ where x is 0.01-0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum and wherein the titania is an anatase polymorph stable under oxidative regeneration at temperatures of 400-750 ^oC. Claim 1, on the other hand, claims a method for preparing this catalyst which comprises contacting a titanium alkoxide or titanium chloride, such as $TiCl_4$, with a metal alkoxide or metal chloride, respectively, to form a solution; adding water to the mixture of alkoxides or an aqueous base to the mixture of chlorides to form a co-precipitate; separating the co-precipitate; calcining the dried co-precipitate to form a ternary metal oxide; depositing a cobalt metal compound solution onto the surface of the ternary metal oxide to form a composite; and activating the composite to form a catalyst. Activating the composite includes drying and calcining followed by reduction of the Co. Depending on the precedence of claims 1 and 13, the coverage may be broad as defined in claim 13 or it may be very narrow being confined to the composition prepared by the method disclosed in claim #1.

Neither the claims nor the specification in this case discuss the coexistence of mixtures of rutile and anatase forms in the titania. Likewise, the concentration of the anatase phase in the titania prepared by the method of this invention was also not revealed. If the composition of the claimed catalyst is limited to the material prepared according to the method in claim 1, then the question of anatase concentration is mute. However, if the patent covers all Co/$Ti_{1-x}M_xO_2$ compositions per claim 13 where M is silicon, zirconium, and tantalum and where titania is in an anatase form, the limits on anatase concentration covers only titania compositions that contain, at most, very small amounts of rutile. Regardless, this case is likely an improvement over Iglesia et al. (X.58) which claims cobalt on silica-modified titania wherein no limitation on the form of the titania is made. It also must be an improvement over Mauldin et al. (X.57) which claims catalysts comprising zirconium added to titania to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatments. In the main claim, there are no limitations on the form of the titania. These three cases, however, provide Exxon with coverage for cobalt impregnated anatase to complement their many cases on rutile-rich titanias.

Apparently the reason why the anatase phase is stabilized at high temperatures is related to substitution of Si, Ta, and Zr cations into the anatase structure of the catalyst which apparently retards the formation of $CoTiO_3$ preventing the entrapment of the cobalt and preserving its specific surface area. Once cobalt titanates form, a higher temperature is required to reduce them to the metal. Through addition of Si, Ta, and Zr, the amount of the $CoTiO_3$ is decreased. For a Si incorporated polymorph, the concentration of the $CoTiO_3$ is decreased, as determined by XRD, and its concentration is a function of calcination temperature, as shown in Figure X.10. Silica incorporation has no affect on the thermal properties of the catalyst but increases by approximately 100 centigrade degrees the temperature for onset of carburization in a synthesis gas stream, as shown in Figure X.11.

Catalysts incorporating each of the promoters were prepared and their stability to calcination was reported in the examples. Anatase titania was prepared by first hydrolyzing $Ti(t\text{-}buO)_4$ and calcining at 430°C. Co as Co nitrate was then impregnated onto the substrate and calcined at 430-700°C. Calcining at 430°C gives anatase having a surface area of 120 m^2/g while calcining at 700°C transforms the anatase to rutile having a surface area of 2 m^2/g. Silicon promoted titanate was prepared by adding the silicon alkoxide, tetramethylorthosilicate (TMOS), to $Ti(t\text{-}BuO)_4$ following the above procedure. Surface areas containing various levels of silicon substitution were obtained upon calcination at 700°C:

Si, %	m^2/g
1%	52
3%	76
5%	119
14%	133

Zirconium promoted titanate was prepared by adding zirconium n-propoxide to $Ti(t\text{-}BuO)_4$ following the above procedure. A catalyst containing 3% Zr had a surface area of 36 m^2/g while a 14% Zr catalyst had a surface area of 56 m^2/g, both of which stabilized the anatase. A tantalum promoted titanate was prepared by adding tantalum ethoxide to $Ti(t\text{-}BuO)_4$ following the above procedure. A catalyst containing 14% tantalum had a surface area of 71 m^2/g. No FT data were provided in the patent.

Cobalt-Ruthenium on Titania

A patent issued to Iglesia et al. (X.61) claims a catalyst prepared by a process comprising impregnating titania with solutions of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the metals with an oxygen containing stream to form the oxides and reducing the oxides. A corresponding patent issued to Iglesia et al. (X.62) claims a process that utilizes this catalyst. The intimate contact of the Co and Ru in the catalyst lowers the temperature at which the cobalt is reduced to the metallic form. This results in a decrease in the amount of carbon deposited upon heating in synthesis gas at temperatures up to 500°C. Intimate contact is obtained by reducing the metals on the surface, calcining in air to reform the oxides and then reducing to the metal form. Unlike many of the other composition of matter patents, a corresponding process patent was not found.

TGA and DTA data provided in the patent showed that the carbon deposited more slowly on calcined Co-Ru/TiO_2 when subjected to a 1:1 H_2/CO synthesis gas mixture than on either Co/TiO_2 or uncalcined Co-Ru/TiO_2. The patent states that the advantage of the Co-Ru combination relative to other catalysts is that "a combination of increased cobalt oxide reducibility and inhibited catalyst poisoning by carbon are believed to account for the increased number of active sites observed on calcined CoRu/TiO_2 catalysts."

Energy dispersive X-ray (EDX) analysis of uncalcined versus calcined CoRu/TiO_2 catalysts that had been aged in process runs for 700 hrs showed that both aged catalysts were identical. Apparently Ru in fresh uncalcined CoRu/TiO_2 catalyst cannot be detected since its concentration over the surface is below detection limits. However, in calcined CoRu/TiO_2 catalyst that has been reduced, Ru can be detected in the cobalt particles where it concentrates sufficiently to be detected by EDX. Apparently, Ru also concentrates in aged uncalcined CoRu/TiO_2 catalysts since the EDX analysis was the same as the calcined sample.

In the examples, three titania catalysts were prepared starting with a sample containing 70% rutile. The first catalyst, Co/TiO_2, was impregnated with cobalt, calcined at 400°C for 4 hrs in air and reduced in H_2 at 400°C for 16 hrs (Catalyst A). Ruthenium was then impregnated onto this catalyst and reduced to give reduced-Co-Ru/TiO_2 (Catalyst B). A portion of this material was calcined in air at 300°C/4 hrs and reduced in H_2 to give the calcined-reduced Co-Ru/TiO_2 composition of this invention (Catalyst C). A Co/SiO_2 catalyst was prepared for comparison by impregnating silica with a cobalt salt (Catalyst D). In synthesis gas runs in which the space velocity was adjusted to attain comparable conversion levels (see Table X.45), the cobalt time yields of the calcined-reduced Co/Ru/TiO_2 catalyst was higher than for the other three catalysts. This appears to be similar to Gulf patents where reduced-oxidized-reduced catalysts had a higher activity than the reduced catalyst (X.63). The methane and C_5+ selectivities of reduced-Co/Ru/TiO_2 and the oxidized-reduced Co/Ru/TiO_2 were very nearly the same, but slightly better than Co/TiO_2 or Co/SiO_2 catalysts.

Data were provided that showed that hydrogen regeneration of oxidized-reduced Co/Ru/TiO_2, catalysts that had been aged from 10-30 days, was more complete than for the untreated Co/Ru/TiO_2 catalyst (see Table X.46). CO conversions and methane and C_5+ selectivities were higher for both the fresh and regenerated oxidized-reduced Co/Ru/TiO_2 catalyst than for the untreated reduced Co/Ru/TiO_2 catalyst and the ruthenium free Co/TiO_2 catalyst.

Iron on Titania

A series of three patents were issued to Fiato and Kugler which are identical except for the claims. Fiato and Kugler (X.64) claim a composition consisting of a mixture of iron carbide and ilmenite, either with or without an alkali metal promoter, having an Fe_2O_3 concentration of 2-25 mg/cm^2, wherein the catalyst is formed by depositing an iron salt onto titania, calcining, treating with H_2 free of CO at 300-500^oC until the composite is reduced and then contacting with CO at a temperature that is 100-200^oC lower than the H_2 reduction temperature. In this preparation, the iron precursor deposited on the titania is calcined to form the iron oxide which is reduced in H_2 to form Fe metal which then reacts with CO to form carbide. X-ray diffraction showed that the calcined material contained anatase and rutile forms of TiO_2, $FeTiO_3$ (ilmenite), and metallic Fe. Xray diffraction of the sample after CO treatment showed that the TiO_2 and ilmenite were unchanged, metallic Fe disappeared, and Fe_5C_2 was formed.

In one of the other cases, Fiato and Kugler (X.65) claim a process for producing hydrocarbons from synthesis gas using this catalyst composition. In the other, Fiato and Kugler (X.66) claim a process for improving the activity of this catalyst in a FT reaction by cycling the temperature in the reaction zone, by increasing the temperature by 50-150^oC above the FT reaction temperature in the absence of H_2 for from 1-6 hours and then returning to reaction temperature and reestablishing the H_2 content of the feed stream. None of the examples actually illustrated the effectiveness of this procedure.

The activity of a series of catalysts indicated that the Fe concentration in these catalysts must be $\geq$2 mg Fe_2O_3/m^2 of titania (see Figure X.12). The activity of an Fe supported titania catalyst of this invention that had been both reduced and subsequently carbided, with an Fe concentration of 0.002 g Fe/m^2 TiO_2, was higher than a corresponding material that had not been carbided, i.e. 27 versus 60% CO conversion, respectively. The hydrocarbon selectivities for the carbided catalyst was lower for methane and higher for C_5+.

A patent issued to Wachs et al. (X.67) claims catalysts comprising an iron carbide on a modified titania support comprising at least 25% of an oxide of Nb, V, and Ta in a noncrystalline form and containing at least 2 mg Fe, as Fe_2O_3, per m^2 support surface. A corresponding process patent, which was essentially identical, issued to Wachs et al. (X.68) claims a process for producing hydrocarbons using this catalyst. These cases relate to an application by Wachs and Chersich (X.40), that was filed on the same day, that claims compositions of tantalum oxide on titania support that were used as catalyst supports. The background on this case was that the Fe/Group Vb oxide/TiO_2 combination was anticipated in the specification by Tauster et al. (X.27) but not actually claimed as compositions of that invention. The Wachs et al. patent (X.67) differs in that the titania surface was modified by addition of limited amounts of Nb, V, and Ta to modify the TiO_2.

The catalysts used in the example were prepared by slurrying Degussa P-25 titania with an ethanol solution containing either $Nb(C_2H_5O)_5$ or $VO(C_2H_5O)_3$. The solvent was removed, the V or Nb ethoxides were oxided, and the resulting powders calcined in pure O_2 at 575^{o}C for 2 hours. The resulting supports contained 10% Nb_2O_5 or V_2O_5 on TiO_2. The Fe precursor was impregnated onto the support, reduced in H_2 at 500^{o}C for 5 hrs, and carbided by exposure to synthesis gas. Results from runs with synthesis gas (see Table X.47) show that at similar CO conversions levels, i.e. 47-49% or 60-70%, the vanadia and niobia catalysts gave lower methane and higher olefin selectivities than a Fe/TiO_2 catalyst. At the same run temperature, i.e. 270°C, the methane yields were lower for the catalysts of the invention.

Nickel on Titania

Two patents related to nickel-titania catalysts were issued; in one, Ni as a promoter of titania based catalysts was claimed while in the second, titania promoted bulk Ni catalysts were claimed. The first patent issued to Vannice and Garten (X.69) claims a FT process that uses a catalyst comprising nickel on a titanium-containing oxide support with a Ni concentration up to 75% by weight. The second patent issued to Kugler and Garten (X.70) claims a FT process using a catalyst comprising bulk nickel promoted with up to 10% titania. These two patents pretty well cover the use of all possible combinations of Ni and titania catalysts in the FT reaction.

In the first patent, Vannice and Garten (X.69) claim that nickel on titania exhibits higher activity, improved selectivity to higher hydrocarbons, improved life and tolerance to sulfur, and resistance to Ni carbonyl formation. The catalysts were prepared by impregnating nickel salts onto the titania support and reducing in H_2 at temperatures >400°C. Synthesis gas conversion at 1 atm over these Ni/TiO_2 catalysts was higher than with bulk nickel or Ni on silica, alumina, and graphite. C_2+ paraffin selectivity versus CO conversion is shown in Figure X.13. In these runs, the Ni/TiO_2 catalysts had higher CO conversions per gram Ni, and lower methane and higher C_2+ hydrocarbon selectivities. Still, the methanation reaction was quite high for the Ni/TiO_2 catalyst. An experiment was described in which the volatility of the Ni was shown to be lower over the TiO_2 catalyst than a Ni/SiO_2 catalyst (see Figure X.14).

In the second patent, Kugler and Garten (X.70) claim the addition of titania to bulk nickel shifts hydrocarbon selectivity from methane to C_2-C_6 hydrocarbons, along with trace quantities of C_7 product. The influence of increasing titania concentration up to 8.4%, as shown in Table X.48, was to increase the CO conversion while the selectivity to higher hydrocarbons increased. Since the relative rates for CO conversion and CH_4 formation both increased, the changed product distribution reflected the much higher increase in the rate of CO conversion versus the smaller increase in methanation rate. The selectivity of the 8.4% TiO_2 on Ni catalyst is very similar to the selectivity of 10% Ni on TiO_2.

A physical mixture of 1/1 Ni powder and TiO_2 behaved very similarly to Ni powder indicating that for such a physical mixture a synergistic interaction did not occur upon activation in H_2. The effect that was observed with the catalysts prepared by addition of solutions of the Ti oxide precursor to bulk Ni indicates a chemical interaction between the titania and the Ni, since a change in activity and selectivity occurs. Evidence for a chemical interaction was observed in ESCA that showed that Ti exists on the catalyst surface before reduction as Ti^{+4}. After reduction in H_2 at 250°C, some of the Ti is in a lower oxidation state but not reduced to the metallic form. The titanium promoter changes the surface area and chemisorption properties of the bulk nickel. Small quantities of Ti additive increases the surface area while creating an oxide layer, as observed by ESCA. Concomitantly, H_2 chemisorption was reduced due to physical blockage of the sites. The highest CO conversion level was observed at the lowest H_2 chemisorption level for the Ti promoted samples.

MANGANESE OXIDE SUPPORTS

Exxon has been assigned 2 patents which claim compositions, or use thereof, comprising the five Group VIII metal oxides of iron, cobalt, nickel, iridium and ruthenium on manganese oxide supports which are reduced at a temperature sufficient to suppress hydrogen chemisorption. These cases parallel Tauster et al. (X.27) who claim catalyst compositions comprising Group VIII metals on Group IVb and Group Vb metal oxides that are reduced at a temperature to suppress hydrogen chemisorption. Since manganese falls in Group VIIb, it falls outside of Tauster et al. (X.27). There are other manganese patents assigned to Exxon which involve the use of manganese in spinels which are discussed elsewhere in this review.

Ruthenium

A patent issued to Kugler et al. (X.71) claims a FT process that provides improved yields of C_2-C_4 olefins that uses a catalyst comprising ruthenium on a manganese containing support which has been reduced at a temperature sufficient to suppress hydrogen chemisorption. Manganese can be used in its pure form or combined with alumina, carbon, silica, or oxides of Groups IVb and Vb. A 1% Ru/MnO catalyst was prepared by impregnating MnO with $RuCl_3$ and reducing with H_2 at 450°C. Synthesis gas mixtures, having H_2/CO ratios from 1.6 to 3, were passed over the catalyst at 300°C and at 1 atm pressure to give CO conversions less than 10%. Under those conditions Ru/MnO catalyst gave higher yields of C_2-C_3 olefins and lower yields of CH_4 relative to a Ru/Al_2O_3 catalyst.

Iron, Cobalt, Nickel, Iridium

A composition of matter patent issued to Tauster and Fung (X.72) claims compositions comprising iron, nickel, cobalt and iridium supported on a manganese containing oxide support, the improvement comprising contacting said composition with a reducing atmosphere at temperatures $\geq$300°C, except for iridium which requires a temperature $\geq$250°C, to produce a catalyst composition which exhibits suppressed hydrogen chemisorption. Under these conditions, the reduced materials would, therefore, be in the SMSI state as defined by Tauster et al. (X.27). Two different 2% Ir/MnO catalysts were prepared by impregnating the metal onto two different MnO substrates. The two MnO substrates prepared by reducing battery grade MnO_2 in H_2 at 540 and 740^oC had surface areas of 21.7 and 7.8 m^2/g, respectively. Less than 0.01 atoms of hydrogen were adsorbed per atom of Ir for each of these catalysts that had been reduced in H_2 at 500^oC versus values of 0.46-1.08 for samples reduced at 200^oC. A sample (prepared at 740^oC) reduced at 350^oC adsorbed less H_2 (0.041 atoms per atom Ir) indicating it was in the SMSI state.

Cobalt - Manganese Spinel

A patent issued to Soled et al. (X.73) claims compositions comprising a copper promoted Co-Mn spinel having a formula $Co_{3-x}Mn_xO_4$ where x is 0.5-1.2. Subordinate claims specify a Cu concentration from 0.1 to 5 g-atom percent based on the total amount of Co and Mn in the catalyst and a surface area >5 m^2/g. A corresponding patent, having an identical specification, which was issued to Soled et al. (X.74), claims a Fischer-Tropsch process using this composition. The spinel was prepared using the alpha-hydroxy aliphatic carboxylic acid method that has been used for all these high surface area spinels. A Co_2MnO_4 spinel, having a surface area of 30-60 m^2/g that is isostructural with Fe_3O_4, was prepared from a solution of $Co(NO_3)_2$ and $Mn(NO_3)_2$ in the presence of citric acid and ethylene glycol, which was evaporated and calcined in air at 350^oC for 30 min. The resulting spinel was impregnated to give a 1 wt.% Cu concentration. The activity of the Cu-promoted spinel in a slurry reactor with synthesis gas was compared with the spinel without added Cu under conditions shown in Table X.49. The catalyst was first reduced in situ with synthesis gas. The Cu-promoted

Co_2MnO_4 spinel had higher activity and gave higher olefin selectivity than unpromoted Co_2MnO_4 spinel or a Co_3O_4/1% Cu catalyst.

GROUP VIII METAL SUPPORTED CATALYSTS

Several patents were issued in which inorganic metal oxides were used as supports for Group VIII metals. A patent issued McVicker and Vannice (X.75) claims catalysts prepared by depositing K or Rb Group VIII metal carbonyl cluster complexes on a high surface area support material, drying in the absence of oxygen and reducing at elevated temperatures. A companion case, issued to McVicker and Vannice (X.76), which is identical both in title and text, excluding claims, covers a process application for these catalysts. The catalysts were prepared by depositing bimetallic carbonyl compounds onto high surface area supports from solutions in organic solvents. At least some, if not all, of the materials were highly sensitive to air. A whole laundry list of potential bimetallic carbonyls were presented, of which 6 were actually used in catalyst preparations. Of the Group VIII carbonyls, only Pd and Os were not specifically included in dependent claims. Re, Ru and Ir, which were actually used in preparing catalysts, were specifically covered in dependent claims. Supports that were specifically claimed were alumina, silica, silica-alumina, titania, zirconia, hafnia, tantala, niobia, vanadia, and magnesia.

Several catalysts were tested by passing a 3/1 H_2/CO synthesis gas mixture over the catalysts at 250 to 284^oC and 1 atmosphere. Under these conditions, very low CO conversions were observed. More long chain olefins were formed over the cluster catalysts of this invention than with conventional catalysts prepared by impregnating alumina (eta) with aqueous solutions of Fe nitrate and KNO_3.

Palladium on Alumina

A patent assigned to Vannice and Garten (X.77) claims a process for producing methane by passing synthesis gas over palladium supported on an acidic metal oxide selected from alumina and HY zeolite with the palladium metal particle being maintained at <100Å. CO conversions of 3.5% were obtained when a 3/1 H_2/CO mixture at 1 atm was passed over these catalysts. Methane was essentially the only hydrocarbon product. The methane yield per Pd surface was higher for the catalysts of this invention than for Ni on a 5% Ni/Al_2O_3 catalyst, although the CO conversion over the nickel catalyst was 55% under these conditions.

Platinum on Alumina

A patent issued to Vannice and Garten (X.78) claims a process for producing dimethyl ether by passing CO and H_2 over platinum supported on alumina. Over a 1.16% Pt/Al_2O_3 catalyst at 274°C for a 1/1 H_2/CO gas mixture at 10 atm pressure, 2.5% CO was converted to hydrocarbons with a hydrocarbon selectivity of 70% methane, 8% ethane, and 23% dimethyl ether.

Nickel on Silica or Alumina

A patent issued to Yates and Murrell (X.79) claim Ni catalysts having Ni surface areas of 200-400 m^2/g prepared by slurrying a Ni metal precursor in a nonaqueous solvent with a high surface area refractory oxide, removing the solvent and reducing with H_2 to form Ni metal. A use for these catalysts is in hydrocarbon synthesis as in the FT reaction. Ethane hydrogenolysis and benzene hydrogenation are included in the examples. However, no examples are provided that cover conversion of synthesis gas. The specification states that several co-metals, of which potassium is one, should be avoided since they act as catalyst poisons.

MOLYBDENUM CATALYSTS

A patent issued to McCandlish and Kugler (X.80) claims a FT process using a catalyst comprised of molybdenum oxycarbonitride. The catalyst, in which the oxygen, carbon and nitrogen are distributed throughout the bulk structure, is prepared by thermally decomposing an ethylenediammonium molybdate at 650^{o}C in an inert atmosphere. The catalyst was pyrophoric and could be passivated with oxygen for handling in air. The active form was easily regenerated in H_2 at 450^{o}C. CO conversions up to 20% were obtained over this catalyst at 254 to 315^{o}C with a 1/1 H_2/CO synthesis gas mixture at 1 atm and 2400 GHSV. Methane was the dominant product under these conditions.

ALCOHOL SYNTHESIS

A patent issued to Apesteguia et al. (X.81) claims catalyst compositions consisting of a solid solution or coprecipitated mixture of a first oxide and a second oxide, wherein the first oxide is selected from yttria and rare earth oxides and a second oxide is a Group Ia oxide and Group Ib metal. These catalysts are useful for conversion of synthesis gas to alcohols, especially isobutanol and methanol. Several representative catalysts were prepared: Cu impregnated onto cerium oxide; coprecipitated Cu, MgO and ceria; K impregnated onto coprecipitated Cu, MgO and ceria; Cu supported on MgO and yttria. These catalysts provided very large yields of alcohols, primarily methanol along with lesser amounts of isobutanol (see Table X.50). Methane and CO_2 yields were also quite sizable.

PROCESS IMPROVEMENTS

Although the overwhelming number of FT related patents that have been assigned to Exxon are related to catalyst compositions or their use, several patents related to improvements in the design or operation of the FT process have been issued. Many of the more recently issued patents have concentrated on process improvements. The FT-type process improvements that are covered are:

- use of 2-stage process configuration to improve hydrocarbon selectivity,
- improved product selectivity through olefin addition to the feed,
- improved CO conversion and C_5+ selectivity through water addition to the feed,
- modified gas inlet system to improve axial distribution of particulate catalyst in a slurry reactor,
- use of downcomers to redistribute catalyst in a slurry reactor,
- use of pentane as heat transfer fluid,
- bundled tubular reactor with shell-side cooling,
- fixed-bed start-up protocol to prevent temperature runaway,
- method for defining operating conditions for a slurry reactor,
- method for activating ex situ reduced cobalt slurry catalyst,
- method for rejuvenating and redistributing catalyst in a slurry reactor,
- method for removing fines from particulate catalysts.

2-Stage Processes

Two different 2-stage process configurations are covered. In one, a patent issued to Kim and Fiato (X.82) claims a process in which synthesis gas contacts in a reaction zone in a first bed a first catalyst having a high olefin selectivity and contacting the resulting olefins in a second bed with a catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons. The claim specifies that the first bed catalyst is selected from a group consisting of Fe/Zn/Ce/K, Fe/Mn/K and Fe/Co/K and the second bed catalyst is selected from the group consisting of Ru/TiO_2, Ru/SiO_2, and Ru/Al_2O_3. The process operates at 150-220 psig with the temperature of the first catalyst being about 260-280^oC and the second catalyst being about 190-210^oC. The range of the preferred H_2/CO ratio, as stated in the specification, was 1.5 to 2.5. An example is provided that shows that over a Fe/Zn/Ce/K catalyst at a CO conversion of 59%, the selectivity to CO_2 was 26% with the remaining product being hydrocarbons (see Table X.51). Hydrocarbon formation is split between the 1st and 2nd catalyst beds in a ratio of 45/55. Based upon approximately equal yields from the two beds and equal yields from each of the two catalysts operating alone, a linear combination predicts a decrease in methane selectivity and an increase in C_{10}+ selectivity when operating in this fashion. Experimentally, the observed methane and C_{10}+ selectivities were even better than predicted (see Table X.52).

A second configuration involves an interstage product separation step. A patent issued to Fiato (X.83) claims a two stage hydrocarbon synthesis process comprising reacting synthesis gas at reaction conditions in a first stage in the presence of a supported cobalt or ruthenium catalyst at a pressure $\geq$10 atmospheres, separating liquid from H_2 and CO, and reacting the remaining H_2 and CO at a pressure less than 10-12 atmospheres, but no greater than the first stage, in the presence of cobalt supported on alumina at reaction conditions. This process configuration takes advantage of the apparently higher activity of Co/Al_2O_3 catalysts at lower partial pressures of CO and H_2 relative to catalysts comprising Co or Re on other oxides supports, such as titania. 2-Stage processes having interstage separation of hydrocarbon product, in which the remaining H_2 and CO are recompressed, have the additional advantage of lower energy requirement.

Product Improvement through Feed Modification

Olefin Addition to Feed. Two patents were issued for processes that reduce methane formation in the FT process through injection of olefins. The first patent issued to Kim (X.84) claims a process with a catalyst comprising Group VIII (Fe, Co, Ru) metals supported on an inorganic oxide support wherein olefins are added to the feed to reduce methane formation. The second patent issued to Iglesia (X.85) claims further methane reduction by injecting the olefins at a point below the inlet of the reactor.

Kim (X.84) showed that injection of ethylene in the feed stream increased CO conversion and decreased methane selectivity. A 2/1 H_2/CO synthesis gas mixture gave a CO conversion of 8.4% and a methane selectivity of 6.4% when passed over a Ru/TiO_2 catalyst at 200°C at 70 psig at a flow rate of 55 standard cm^3/3 g catalyst/min. When 8.2 mol % ethylene was injected into the feed stream, CO conversion increased slightly to 9.0% and methane selectivity dropped to 3.5%. When 20% ethylene was added, the methane selectivity dropped even further to 2.7%. In another case, when 4% 1-decene was substituted for ethylene, an approximate 20% decrease in methane selectivity occurred. Over a precipitated bulk Fe catalyst the introduction of 9.6% ethylene into the same synthesis gas mixture at the same temperature and pressure at a flow rate of 100 standard cm^3/10 g catalyst/min caused a 30% decrease in methane selectivity.

In the 2nd case, methane was further reduced through adding the ethylene downstream of the inlet of the reactor. A patent issued to Iglesia (X.58) claims that for a FT process using an Fe, Co or Ru catalyst, the methane yields are further reduced when the olefins are added to the reactor bed below a point equivalent to 10% of the distance from the top to the bottom of the reactor bed and above a point in the reactor bed equivalent to 10% of the distance from bottom to the top of the reactor bed. The addition level is stated as the amount sufficient to suppress methane formation. In the examples, for ruthenium and cobalt-ruthenium on titania catalysts, adding ethylene below the top 1/3rd of the catalyst bed decreased the amount of ethane produced relative to the amount of ethylene added to the feed. Likewise, the amount of C_3+ increased accompanied by a small decrease in methane yield, as shown in Table X.53.

Water Addition to Feed. A patent issued to Kim (X.86) claims enhanced CO conversion and C_5+ selectivity for a once-through, fixed or slurry bed FT process comprising contacting the synthesis gas containing 1-70 vol % water in a reaction zone with a catalyst consisting of cobalt, ruthenium and mixtures thereof on titania converting 90% of the CO to liquid hydrocarbons in the substantial absence of CO_2. This case involved numerous filings and abandonments over an eight year period from the time of the first filing on July 13, 1985. The long background discussion of numerous prior patents outlines the extensive number of related cases. Numerous examples were shown for a range of catalysts exhibiting increased CO conversion, decreased methane selectivity and increased C_{10}+ liquid yield in the presence of added water.

Reactor Design

Modified Gas Inlet System. Two patents were issued related to the design of FT reactors. One patent issued to Chang and Coulaloglou (X.87) claims a method for improving axial distribution and mixing of particulate catalyst in a slurry bubble column by introducing a secondary gas into the column at a location within the lower 20% of the vertical height of the column but above the gas distributor plate. This gas stream can be part of the synthesis gas feed, recycle gas, inert gas, condensed light hydrocarbons or light synthesis hydrocarbons which vaporize under conditions present in the column.

A figure is presented of experimental data taken in a 5 ft diameter by 30 foot high slurry bubble column that shows that the solids distribution in the reactor is more uniform when using this gas inlet configuration.

The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. The key to the method disclosed in this patent is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

<u>Downcomers.</u> A patent issued to Behrmann et al. (X.88) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. The bottom is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (X.89) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure X.15.

A patent issued to Chang (X.90) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure X.16 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. A patent issued to Stark (X.91) claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity.

Tube-in-Shell Reactor. A patent issued to Koros (X.92) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in ID x 50 ft long pipe mounted in a 12 inch pipe cooling jacket was provided. Liquid heights varied between 12 and 32 feet with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H_2/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig, and steam jacket pressure of 140 psig, CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Reactor Start-up. A patent issued to Arcuri (X.35) claims a procedure for the start-up of a fixed-bed FT reactor that allows a flexible and more effective response to a potential temperature runaway. While elevating the temperature, pressure and feed flow rate to line-out levels, the composition of the H_2 and CO in the feed is maintained at a H_2/CO mole ratio not exceeding 90% of the mole ratio at lineout. After the temperature, pressure and feed flow rate reach normal operating levels, the H_2/CO ratio is gradually increased to the operating lineout mole ratio.

The patent illustrates the advantage of using this operating protocol relative to using temperature as the main control parameter. Comparative exotherms are provided for two different startup procedures used on a 1/2 inch ID, 6 foot long tubular pilot scale FT reactor that was submerged in a sand bath, as shown in Figure X.17. Following a conventional start-up procedure in which temperature is slowly increased to bring the reactor online, a very significant temperature runaway occurred. In this example, the final target operating conditions were 359°F with a 2.08/1 H_2/CO synthesis gas mixture at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step were as follows:

1. Synthesis gas mixture and flow rate were established at lineout conditions at a pressure of 60 psig and a sand bath temperature of 337°F. The maximum exotherm in the bed during this period was 5°F.
2. Pressure was then increased to lineout pressure of 280 psig and held 3 days. A maximum exotherm of 12°F resulted.
3. Then temperature was increased slowly from 337 to 353°F and held 24 hours. During this period the maximum exotherm was 21°F.
4. Afterwards, the temperature was increased 2°F over a 40 min period to 355°F. The magnitude of the maximum exotherm remained the same at 22°F.
5. However, when the temperature was increased over a 2 hour period to 359°F, which was a 4°F change in temperature, the maximum exotherm increased to 242 F°, indicating a severe temperature runaway.

By contrast, the exotherms were much less when the procedure taught in the patent was followed, namely using a decreased H_2 content in the feed gas. In this example, the target lineout reactor conditions were 380°F with a 2.1/1 H_2/CO synthesis gas mixture flowing at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step, as shown in Figure X.18, were as follows:

1. The H_2 feed gas (1.8/1 H_2/CO) rate was brought to 910 GHSV at 60 psig and 337°F. The maximum exotherm was 7°F.
2. The pressure was increased to the lineout pressure of 280 psig over 0.5 hours. The maximum exotherm was 9°F.
3. The temperature was increased almost to the lineout temperature of 374°F in 1 hour during which the maximum exotherm was 17°F.
4. H_2 in feed gas was increased to a 2.0/1 H_2/CO ratio in 1 minute as flow rate increased to 970 GHSV. Maximum exotherm was 23°F.
5. The H_2 in feed gas was increased to a 2.1/1 H_2/CO ratio as flow rate increased to the final 1000 GHSV. The maximum exotherm was 25°F.

During this sequence the exotherm remained under control and space time yield data was higher with a higher CO conversion. Another example was also given that illustrates how rapidly an exotherm can occur in a FT synthesis reactor.

<u>Setting Operating Conditions.</u> A patent issued to Herbolzheimer and Iglesia (X.93) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

(a) injecting gas at an average gas velocity >2 cm/sec;

(b) fluidizing the particulate catalyst having an average diameter >5 μm in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D, such that

$$0.5\ (U_s - U_L) \leq \frac{D}{H},\ where\ H > 3m$$

where

$$U_s = \frac{1}{18}\ d_p^2 \frac{\rho_s - \rho_l}{\mu}\ gf\ (C_p),\ where\ d_p > 5\ \mu m$$

(c) operating at plug flow at a gas velocity U_g, expanded liquid height H, and dispersion coefficient D such that

$$U_g \geq 0.2\ \frac{D}{H}\ where\ H > 3\ m,\ U_g > 2\ cm/\mathrm{sec}.$$

In one example using a Co-Re/TiO_2 catalyst having a density of 2.7 g/cm^3, a liquid density of 0.7 g/cm^3, and a wax viscosity of 0.01 g◦cm/sec, the particle settling velocity is:

$$U_s\,(cm/\mathrm{sec}) = 1.1 x 10^{-4} [d_p(\mu m)^2]$$

For a 60 μm average particle, U_s = 0.39 cm/sec. For a liquid velocity of 0.5 U_s, and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

Catalyst Pretreatment

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (X.94) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H_2 in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (X.95) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than 40^oC below hydrocarbon synthesis temperature. Another patent issued to Mitchell (X.96) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO_2-5% Al_2O_3 catalyst by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a CO/H_2 stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2. Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non-H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure X.19.

A patent issued to Pedrick et al. (X.89) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft diameter by 35 ft high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2, which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H_2/26% CO/13% CO_2/5% CH_4, by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO_2-5% Al_2O_3 slurry catalyst at 210-230^oC and 20 atm. When operating the reactor with two-2 inch diameter and two-4 inch diameter flue-gas fed draft tubes and one-3 inch diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;
draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure X.20) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure X.21, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch rejuvenation tube was brought on line. Immediately upon addition of H_2 an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After lineout, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 10^oF, CO conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table X.54.

A patent issued to Hsia (X.97) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure X.22). Likewise, rejuvenated catalyst is fed to the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (X.98) claims a method for removing <1 μm particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The method comprises dispersing the particles to which the <1 μm particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the <1 μm particles in the supernatant liquid and separating the <1 μm particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims only apply to the latter (see Table X.55). Catalysts stirred with FT wax at 130°C gave initially a filtration rate of 5.8 gal/ft^2/min which decreased to 0.05 gal/ft^2/min after stirring for 44 hours. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to 14.5 gal/ft^2/min.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (X.92) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure X.23, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure X.24.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure X.25. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. THe bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec.). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C_{16}-C_{18} hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferrably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferrably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m^2/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferrably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76 i.d.) about 50 ft. tall mounted inside a 12" pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron dismeter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig) and higher reactor pressure (285 psig at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr^{-1}) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water, this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

This summarizes the patents abstracted through October 19, 1994; Appendix will cover later period.

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Table X.1. Activity of laser generated iron carbide catalysts
Reaction Conditions: 270°C, 2/1 H_2/CO, 200 sccm, 75 psig, in octacosane

	Carbide from Fe_3O_4	Laser derived carbide	Laser derived carbide + K	Laser derived carbide + Si
Preparation Method	Fe_3O_4 reduced in H_2@450°C/5-7 hrs and treated with H_2/CO/350°C	$Fe(CO)_5/C_2H_4$ laser feed	$Fe(CO)_5/C_2H_4$ laser feed/ impregnated with 2% K as K_2CO_3	$Fe(CO)_5/C_2H_4$/ $SiH_2(CH_3)_2$ laser feed
V/V cat/hr	2000	4000	4000	500
% CO conversion	71.9	82.5	66.5	5.0
Selectivity, wt% CO_2 free basis				
CH_4	16.1	9.5	5.6	15.9
C_2-C_4 Paraffins	17.3	7.8	0.8	27.0
C_2-C_4 Olefins	18.9	27.0	11.5	19.0
% olefins in C_2-C_4	50.7	77.6	93.5	41.0

Table X.2. Activity of high and low surface-area Fe-Co spinels for synthesis gas conversion.
In situ catalyst reduced in slurry with H_2 at 200°C and 1 atm for 1 hr.
Ex situ catalyst reduced with H_2 at 300°C+ and then H_2/CO at 350°C+.
Run in slurry reactor at 250°C, 1200 v/v/hr, 2/1 H_2/CO, 70 psig, 600 rpm in octacosane;
time on stream not specified.

	Starting Spinel					
	$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K high surface area		Fe_3O_4/1%K high surface area		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K low surface area	
	in situ	ex situ	in situ[a]	ex situ	in situ	ex situ
Spinel surface area, m_2/g	>100	>100	>100	>100	0.29	<0.3
CO Conv, mol %	60	64	8.0	65	<4.0	42
CO_2	36	36	5.2	39	na	24
Hydrocarbons	24	28	2.8	26	na	18
HC Selectivity wt%						
CH_4	4.5	8.2	11.4	12.8	na	9.3
C_2-C_4 paraffins	2.5	3.6	8.6	8.0	na	5.5
C_2-C_4 olefins	17.5	27.4	34.3	32.2	na	27.0
C_5+	75.5	60.8	31.4	47.0	na	58.2

Taken from Example 3, Table III and Example 5, Table IV U.S. Patent 4518707 (X.4).
a. Taken from Table V of U.S. Patent 4518707 (X.4).

Table X.3. Activity of *ex situ* reduced and carbided high and low surface-area Fe-Co spinels. High and low-surface-area spinels were reduced *ex situ* with H_2 at 300°C+ followed by carbiding with H_2/CO at 350°C+. Reactions run in slurry reactor at 250°C, 1200 v/v/hr, 1/1 H2/CO, 70 psig, in octacosane.

	Starting Spinel x = 2.85	
	high >100 m^2/g	low < 5 m^2/g
CO conv, mol %	45	44
CO_2, mol %	26	29
HC yield, mol %	19	15
HC Selectivity wt%		
C_1	4.4	5.9
C_2-C_4	19.3	25
C_2-C_4 olefins	90	90
C_5+	76.3	69.1

Data taken from Example 2, Table II in U.S. Patent 4544672 and Ex 4, Table III in U.S. Patent 4518707 (X.4).

Table X.4. Activity of alloys in a slurry reactor prepared *ex situ* from high surface-area Fe-Co spinels Spinels reduced *ex situ* with H_2 at 350°C /12 hrs followed by 400°C/24 hrs, but not carburized. Run in slurry reactor at 270°C, 70 psig, 1200 v/v/hr, 600 rpm in octacosane.

	Fe_3O_4/1%K high surface area		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K high surface area	
H_2/CO	1.0	2.0	1.0	2.0
CO Conv, mol %	44	28	55	54
CO to CO_2, mol %	26	15	34	34
CO to HC, mol %	18	13	21	20
HC Selectivity Wt.%				
CH_4	4.4	2.1	5.8	6.5
C_2-C_4 paraffins	1.9	0.6	3.4	2.7
C_2-C_4 olefins	25.2	10	25.2	27.3
C_5+	68.7	87.2	65.0	63.4

Data taken from Example 7, Table VI, U.S. Patent 4518707 (X.4).

Table X.5. Activity of low-surface area spinel derived catalysts in a fixed-bed reactor. Catalysts treated with flowing 90% H2/N2 at 500°C at 100 psig for 5-7 hrs. Run in fixed bed reactor with 1/1 H2/CO at 300 psig.

	Fe_3O_4/1%K		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K	
Time on stream, hrs	1	12	1	12
V/V/hr	570	1000	570	1000
Furnace Temp°C[c]	305	305	270	270
CO Conv, mol %	79	67	98	98
CO to CO_2, mol %	36	31	42	40
CO to HC, mol %	43	36	56	58
Wt% selectivity				
C_1	8.5	5.8	9.1	7.4
C_2-C_4 paraffins	5.2	4.7	6.2	6.2
C_2-C_4 Olefins	26.6	30.6[b]	39.4	50.3[b]
C_5+	59.7	-	45.2	
C_6+	-	58.9	-	36.1

Data taken from Example 1 of U. S. Patent 4537867 (X.8). Catalysts prepared by sintering mixtures of metal oxides.

b. Applies to C_2-C_5 olefins.

c. Actual bed temperatures were not reported.

Table X.6. Effect of Co concentration on Fe-Co spinel catalyst performance after 12 hrs on stream. Catalysts treated with flowing 90% H_2/N_2 at 500°C at 100 psig for 5-7 hrs. Catalysts run in fixed bed reactor at furnace temperature of 295°C, 300 psig, 1000 v/v/hr, 1:1 H_2:CO.

x in $Fe_xCo_{3-x}O_4$	2.97	2.85	2.625	2.20
Time on stream, hrs	12	12	12	12
CO Conv, mol %	97	98	97	98
CO_2, mol %	27	40	41	42
HC, mol %	70	58	56	56
Selectivity				
CH_4	8.3	7.4	18.0	13.2
C_2-C_6 olefins	46.5	53.1	41.4	53.0
C_2-C_6 paraffins	6.9	7.2	13.3	10.6
C_7+	38.3	32.3	27.3	23.2

Data taken from Example 7, Table 7 of U. S. Patent 4537867 (X.8).

Table X.7. Effect of temperature on performance of Fe-Co spinels in fixed bed reactor
Samples for 1-12 hrs on stream at 300 psig, 1000 v/v/hr, 1/1 H_2/CO.

	Starting Spinel						
	$Fe_{2.625}Co_{0.375}O_4$/1 wt.% K					$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K	
Furnace Temperature, °C	225	240	260	270	290	235	270
Bed Temperature, °C	230	248	304	325	340	na	na
CO Conv, mol %	30	31	97	98	98	29.4	98.0
CO_2, mol %	4	7	40	33	41	8.0	42.0
HC, mol %	26	24	57	55	57	21.4	56.0
Selectivity							
CH_4	8.1	8.2	19.1	16.7	19.1	2.6	5.2
C_2-C_5 olefins	42.3	55.3	37.1	31.9	24.8	18.1	33.6
C_2-C_5 paraffins	14.4	22.0	17.7	10.6	14.8	2.7	4.4
C_6+	35.2	34.5	26.1	40.8	41.3	76.8	55.9

Taken from Examples 8 and 12 of U.S. Patent 4537867 (X.8).
na = not available

Table X.8. Cu promoted high-surface area Fe-Co spinels as slurry catalysts.
Slurry reactor runs at 270°C, 2000 v/v/hr, 2/1 H2/CO, 75 psig, 600 rpm in octacosane.

	Fe_3O_4/2%K		$Fe_{2.85}Co_{0.15}O_4$/2 wt.% K	$Fe_{2.85}Co_{0.15}O_4$/2 wt.% K/1 wt% Cu	
	In-situ	Ex-situ	In-situ	In-situ	Ex-situ
CO Conv, mol %	67	49	77	86	54
Wt% Selectivity					
CH_4	2.0	3.8	4.4	4.2	4.5
C_2-C_4 Olefin %	47.5	77	91	87	85
C_{10} Distribution					
α-olefins		50	49	59	46
n-paraffins		8	14.9	15	18
n-alcohols		2	1.0	3	1
β-olefins		17	4.1	2	6.0
all else		23	31	21	29

Taken from Tables I and II, U.S. Patent 4607020 (X.6).

Table X.9. Effect of promoters on both high and low surface area $Fe_{2.25}Mn_{0.75}O_4$ spinels. Runs made at 270°C, 75 psi, 120 H2/60 CO/20 N2 cc/min flows, 70-80 g octacosane solvent, 20+ hrs on feed, 2 gm cat.

atomic % K	-	2.0	2.0	2.0	2.0	2.0
atomic % Cu	1.0	-	1.0	1.0	-	1.0
Surface area, m^2/g	>50	>50	>50	>50	<5	<5
gm catalyst	2	2	1	2	2	2
% CO conv	34	36	69	83[a]	nil	nil
wt Selectivity						
CH_4	8.8	3.5	1.7	2.3		
olefins in C_2-C_4	78	91	94	92		
olefins in C_{10}+	?	?	63	65		

Taken from Example 2, Table 2 of U.S. Patent 4618597 (X.11).

a. 30+ hours on feed

Table X.10. Effect of Fe-Mn ratio in $Fe_xMn_{3-x}O_4$ /2% K/ 1% Cu (>50 m^2/g) on synthesis gas conversion. Runs made at 270°C, 75 psi, 120 H2/60 CO/20 N2 cc/min flows, 72 g octacosane solvent, 30+ hrs on feed, 2 gm cat.

gm catalyst	2	2	2	8	8
x	0.25	1.5	2.25	2.25	2.85
CO Conv	nil	30	83	87	79
Selectivity					
CH_4	na	2.6	2.3	4.1	4.2
olefins in C_2-C_4	na	86	93	92	94

Taken from Tables 3-4 of U.S. Patent 4618597 (X.11).

Table X.11. Activity of $Fe_{2.25}Mn_{0.75}O_4$/2 at % K/1 at % Cu as catalysts for FT fixed bed and slurry reactors with 2/1 H_2/CO synthesis gas.

	Fixed-Bed		Slurry
Temperature, C	263	275	270
Pressure, psig	65	65	75
Cat mesh	40-100	40-100	>140
Fe-SV	2.0	9.0	11.2
CO Conv	50	43	69
Selectivity			
CH_4	8.6	9.5	1.1
C_2-C_4	26.4	25.0	1.8
C_5+	65	65.5	97
CO_2	35	44.0	38
Olefin % Content			
C_2-C_4 olefin fraction	82	84	93
C_{10}+ olefin fraction	65	67	63

Taken from Tables 2 and 4 of U.S. Patent 5118715 (X.13).

Table X.12. Activity of Fe-Zn Spinel. Catalysts pretreated to 500°C in a 9/1 H_2/N_2 mixture at 100 psi and 100 v/v/hr space velocity for 5-8 h. Runs made in 1.7/1 H_2/CO at 300 psi at 550 vol/vol/h, 270°C furnace temperature, 10.5 hrs on stream.

	1.0 Fe/0.065 Zn/0.030 Ce/0.030 K	Fe/1% K
CO conversion	98	96
wt% selectivity		
CH_4	3.0	9.4
C_2-C_6	36.0	50.1
C_7+	21.4	14.5
CO_2	39.6	26
Specific olefin/paraffin prodn. ratios were:		
C_2	3.1	2.5
C_3	7.5	8.0
C_4	15.0	8.3
C_5	7.5	3.7
C_6	4.6	2.0

Taken from Example 3, Table V of U.S. Patent 4639431 (X.16).

Table X.13. Activity of Fe-Zn spinels promoted with Cu and K prepared with glycolate.
Runs made with 2 g catalysts in at 270°C in 2/1 H_2/CO, 75 psig at 180 cc/min in octacosane for 40-100+ hr periods.

	CO Conv	CH_4 selectivity	% olefins in C_4	% Olefins in C_2-C_4	% α-Olefin in C_{10}+
$Fe_{2.8}Zn_{0.2}O_4$·2 at% K	33	2	89		
$Fe_{2.8}Zn_{0.2}O_4$·1 at%Cu	34	10.1	81		
$Fe_{2.8}Zn_{0.2}O_4$·2 at%K+1 at%Cu	73	1.9	89		
$Fe_{2.8}Zn_{0.2}O_4$·2 at% K, 1 at% Cu	80	1.7		93	63
$Fe_{2.45}Zn_{0.55}O_4$·2 at% K, 1 at% Cu	84	1.7		92	61
$Fe_{2.3}Zn_{0.7}O_4$·2 at% K, 1 at% Cu	32	2.3		85	nd

Taken from Example 2, 6 and 7 of U.S. Patent 5100856 (X.17). Spinels having Fe concentrations greater than $Fe_{2.5}Zn_{0.5}O_4$ fall within claimed compositions.

Table X.14

Conversion of Synthesis Gas with $Fe_{3-x}Zn_xO_4$ in 0.3 L CSTR at 270°C, C_{28} Solvent,
H_2/CO = 2, 75 psig (from U.S. Patent 5118715, (X.13)

Catalyst	$Fe_{2.8}Zn_{0.2}O_4$ A	$Fe_{2.55}Zn_{0.45}O_4$ B	$Fe_{2.3}Zn_{0.7}O_4$ C	$Fe_{2.79}Zn_{0.21}O_4$	$Fe_{2.79}Zn_{0.21}O_4$	$Fe_{2.79}Zn_{0.21}O_4$
% Fe	66.87	60.28	53.70	71.50	71.50	71.50
% g-atom K	---	---	---	2	2	0
% g-atom Cu	---	---	0	1	0	1
CO Conv., %	80	84	32	73	33	34
CH_4/% Carbon	1.7	1.7	2.3	1.9	2.0	10.1
Olefin, %						
C_2-C_4	93	92	85			
% α- in C_{10}	63	61	*			
% α- in C_4	---	---	---	89	89	81
NL/gFe-hr**	8.97 (7.18)	9.95 (7.96)	11.17 (8.94)	8.89 (7.11)	8.89 (7.11)	8.89 (7.11)
NL/g cat-hr	6.00	6.00	6.00	6.36	6.36	6.36

* Insufficient yield of liquids.
** NL total flow; parentheses, flow based on CO + H_2.

Table X.15. Comparison of Ce,K and K/Ce promoters for 1.0 Fe/0.30 Ti/0.065 Zn/0.03 Ce and/or 0.03 K in fixed-bed reactor. Pretreated at 500°C with 9/1 H_2/N_2 at 800 v/v/hr for 5-6 hrs. Runs made at 270°C, 1/1 H_2/CO at 2.6 MPa at 870 v/v/hr space velocity for time on stream of 30-50 hrs

	K	Ce	K/Ce
CO Conv	2	17	24
wt HC selectivity			
CH_4	42	24.5	14.8
C_2-C_3 paraffins	6	14.6	12.2
C_2-C_3 olefins	42	14.1	32.5
C_4+	10	46.8	40.5

Taken from Example 5, Table VII in U.S. Patent 4657885 (X.18).

Table X.16. Manganese Catalysts with Ce,K and K/Ce in fixed-bed reactor. Pretreated at 500°C with 9/1 H_2/N_2 at 800 v/v/hr for 5-6 hrs. Runs made with 1/1 H_2/CO, 870 v/v/hr, 305°C, 2.0 MPa

	K	Ce	K/Ce
CO Conv	18	62.5	54.9
HC selectivity, wt.%			
CH_4	10.2	17.5	7.5
C_2-C_3 paraffin	4.1	10.0	2.6
C_2-C_3 olefin	29.2	20.6	24.4
C_4+	56.5	51.9	65.5

Taken from Example 6, Table VIII in U.S. Patent 4657885 (X.18).

Table 17. Activity of a 10/1 Fe/Tl catalyst in a fixed bed reactor for synthesis gas conversion. Pretreated with 49 H_2/50 CO/1 N_2 at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made at 270 to 350°C, 1/1 H_2/CO at 120 psia and 150-1200 v/v/hr.

Temp, °C	270	300	325	350
CO Conv, %	90-20	65-40	96-80	97-90
Selectivity				
CH_4	6-4	6-3	6-10	9-15
C_5-C_{11}	50-54	51-57	50-51	42-51
C_4- (Gas)	35-30	34-26	35-39	39-50
Olefins in C_6+	21-26	23-26	21-16	14-8
Aromatics	2-3	2-3	4-8	7-14

Taken from Example 5, Tables 1 to 6 in U.S. Patent 4513104 (X.24).

Table X.18. Performance of Fe/Tl Catalysts in a fixed-bed reactor.
Pretreated with 49 H_2/50 CO/1 N_2 at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made with 1/1 H_2/CO at 300 GHSV and 0.9 MPa (130 psi).

	Fe/0.1 Tl			Fe/0.2 Tl	Fe/.04 K		NH_3 synthesis catalyst
Temp	350	350	270	350	350	270	350
GHSV	300	300	300	300	300	300	300
CO Conv	96.7	63.6	46.8	45.0	55.5	68.9	97.1
Selectivity to HC %	60.9	62.5	69.9	59.6	66.0	wax	69.5
C_1	10.1	13.0	3.4	16.6	11.1	3.0	3.3
C_1-C_5	38.4	44.7	30.4	46.6	31.8	-	42.2
C_6-C_{11}	45.3	45.4	44.8	39.0	32.5	-	42.3
C_{12}-C_{23}	16.0	9.7	23.8	13.6	24.9	-	14.8
C_{23}+	0.3	0.2	1.0	0.8	10.8	-	0.7
Aromatics	12.7	14.02	2.92	10.3	6.57	-	8.65
α-olefins	14.9	9.66	22.31	10.0	16.69	-	11.43

Taken from Example 9, Tables 10 and 11 in U.S. Patent 4513104 (X.24).

Table X.19. Activity of *in situ* prepared catalyst in a slurry reactor.
Runs made at 270°C, 1:1 H2/CO at 70 psig at 1200 V/V/hr in C16 paraffin solvent, 600 rpm.

Support	wt% support[a]		CO Conv	CO_2	CH_4	C_2-C_4 olefins	C_2-C_4 paraffins	C_5+
	Fe	Co						
None (Complexes only)	-	-	25	35.4	15.4	17.8	5.3	26.1
Fe_2O_3/1% K	9.5	3.2	54	50	3.0	7.2	1.1	38.5
Al_2O_3	4.8	1.6	21	25	20.0	18.3	9.0	27.7
Al_2O_3[b]	"	"	27	9.2	19.8	12.9	6.8	60.5
MgO	4.8	1.6	30	35	18.6	16.1	6.8	23.5
MgO/1% Cu	9.5	3.2	26	50	9.6	14.7	3.8	21.9

Taken from Example 1, Tables I and II, and Example 4, Table V, of U.S. Patent 4532229 (X.25).
a. Same weight of Fe and Co in reactor in all runs, except for Fe_2O_3/1% K run.
b. Product yield after 96 hours on stream.

Table X.20. Effect of air calcination on the crystalline form of titania

	Rutile content, wt%	Surface Area, m^2/g
Degussa P-25	28^a-35^b	60 m^2/g
500°C in air/16 hrs	55	33-36
500°C in air/16 hrs and H_2 at 450°C	67	22-26
560°C in air/ 4 hrs[d]	70	30
600°C in air/16 hrs	~100 (>30/1)	10-16
650°C in air/16 hrs[c]	97	14

a. From U.S. Patent 4711871 (X.32).
b. From U.S. Patent 4595703 (X.49).
c. From U.S. Patent 4663305 (X.57).
d. From U.S. Patent 4738948 (X.61).

Table X.21. Effect of calcination on rutile content of titanias

Source	Description	Binder/%	Hg PV[a], cc/g	Hg PD[b], Å	BET SA, m^2/g	% Rutile in titania	Calcination, °C/hr
Company A	-	none	0.253	140	45	27	-
Company A	-	none	0.162	270	15	92	700/1
Company A	-	none	0.134	250	14	95	700/1
Company A	-	none	0.120	481	5	100	840/1
Company A	Extrudate	none	0.154	389	8	98	650/16
$Ti(OC_3H_7)_4$ hydrolysis	-	none	0.160	n.a.	10	94	650/50
$Ti(OC_3H_7)_4$ hydrolysis	Extrudate	none	0.299	n.a.	41	n.a.	500/16
$Ti(OC_3H_7)_4$ hydrolysis	Extrudate	none	0.180	n.a.	15	n.a.	600/16
Company A	Extrudate	M/3.5	0.387	454	27	82	750/3
Company A	Extrudate	M/3.5	0.326	590	22	96	800/1
Company A	Extrudate	M/3.5	0.354	678	15	98	800/3
Company A	Extrudate	M/3.5	0.301	697	15	100	800/16
Company A	Extrudate	M/3.5	0.276	590	12	100	850/3
Company A	Extrudate	M/3.5	0.254	1151	13	100	850/10
Company A	Extrudate	M/3.5	0.237	1706	10	100	850/72

Taken from Example 1, Table 1 of U.S. Patent 4992406 (X.30).
M binder = 30 TiO_2/70 Al_2O_3
a. PV = pore volume.
b. PD = pore diameter.

Table X.22. Effect of rhenium on stability of Re/TiO_2 for synthesis gas conversion.
Conditions of run: 230°C, 280 psig, 2/1 H_2/CO, 1000 GHSV

	1% Ru and 0.5% Re/TiO_2	1% Ru/TiO_2
Half-life, days	231	26
CO Conv	97	97
HC Yield	90	94
Selectivities		
CH_4	3.7	3.5
CO_2	7.0	1.5

Taken from Example 1, Table I of U. S. Patent 4558030 (X.29).

Table X.23. Effect of Re/Ru ratios on Re promoted Ru/TiO_2 catalyst.
Conditions: 280 psig, 2/1 H_2/CO, 1000 GHSV

Wt.% Ru	Wt% Re	CO Conv	C_1 select	CO_2 select
0.1	1.0	11	4	20
0.5	0.5	33	7.5	5
0.75	0.5	43	9	6
1.0	0.5	82	5.6	6

Taken from Example 2, Table II of U. S. Patent 4558030 (X.29).

Table X.24. Effect of rutile content on activity of 1% Ru-0.5% Re on TiO_2.
Conditions: 230°C, 280 psig, 2/1 H_2/CO, 1000 GHSV at 90% CO conversion

Rutile/Anatase ratio wt	1.2/1	2/1	>30/1
Rutile, wt% in TiO_2	55	67	~100
C_1 selectivity	7	4.5	2
Half-life days	4	231	87
Deactivation, Δ *ln* k/day	−0.18	−0.003	−0.008
Pore Vol ml/g	0.4	0.2	0.15
SA m^2/g	35	24	12

Taken from Example 3, Table III of U. S. Patent 4558030 (X.29).

Table X.25. Selectivity of Ru Catalysts for synthesis gas conversion.
Conditions: Catalysts reduced in H_2 at 450°C for 1 hr before introducing 1/1 H2/Co at 980 kPa (9.5 psig),

	Temp	%CO Conv	Prod	Total wt%	Olefin, wt%	Paraffin wt%
2% Ru/TiO2	267	7	C1	14	-	-
			C_2-C_4	47	32	15
			C_5-C_7	39	23	16
			C8+	-	-	-
5% Ru/ηAl2O3	274	10	C1	24	-	-
			C_2-C_4	43	19	14
			C_5-C_7	32	6	6
			C8+	12		

Taken from Example 1, Table II of U. S. Patent 4042614 (X.31).

Table X.26. Methanol conversion over Ru/TiO_2.
Conditions: 230°C, 500 v/v/hr, fixed bed reactor

Methanol, psi	236	236	236[a]
H_2, psi	0	59	59
CO, psi	0	0	31
Methanol conv at 35 hrs, %	13	76	<3
Reactor effluent composition			
CO	38	1	84
CO_2	4	12	n.a.
CH_4	1	24	n.a.
C_2+	55	63	n.a.

Taken Example 4, Table IV and Example 6, Table VI of U.S. Patent 4513161 (X.36).
a. GHSV=560.

Table X.27. Activity of Ru on V, Nb and Ta oxides versus prior art.
Conditions: 3/1 H_2/CO, 1 atm, no other data provided.

	Temp C	CO Conv %	Hydrocarbon selectivities		
			CH_4	C_2-C_5 Olefins	C_2+
1% Ru/Nb_2O_5	234	7.8	48	22	52
1% Ru/Ta_2O_5	228	17.7	46	17	54
1% Ru/V_2O_5	243	4.1	45	28	55
1% Ru/SiO_2	232	4.1	87	2	13
1% Ru/Al_2O_3	244	14.1	71	10	29

Data taken from U. S. Patent 4171320 (X.37).

Table X.28. Reaction of a 0.76% Ru on TiO_2 in a fixed bed reactor.
Conditions: reduced at 400-450°C for 2-4 hrs in H_2. Run in 1.39/1 H_2/CO

Run No	3	5	7	14
Pressure,atm	3.0	3.0	5.0	4.3
°C	206	224	218	213
GHSV	198	301	494	1240
H_2 Conv	84	84	89	26
CO Conv	84	84	89	30
Selectivity on CO_2 free basis				
CH_4	4.8	6.1	5.4	6.9
C_2/C_4	9.15	11.6	7.9	17.8
C_5-C_{20}	76.5	74.4	72.7	64.1
C_{20}-C_{40}	8.3	6.2	11.3	8.3
C_{41}+	0.15	0.13	1.5	0.2
Oxygenates	1.13	1.4	1.2	2.7
C_2= in C_2				40
C_3= in C_3				84
C_4= in C_4				82
Total olefin in C_7-C_{12}				39
Total olefin in C_4-C_{20}				31

Taken from U. S. Patent 4477595 (X.38).

Table X.29. Effect of support on activity of Ru catalysts
Fixed bed reactor with supported Ru, reduced at 400-450°C for 2-4 hrs in H_2

	0.76 Ru/ TiO_2	0.56 Ru/ Nb_2O_3	0.67 Ru/ Ta_2O_3	1.57Ru/ SiO_2	0.56Ru/ Nb_2O_3	1.1 Ru/ TiO_2	1.57Ru/ SiO_2	1.1Ru/ TiO_2	1.1Ru/ Al_2O_3
H_2/CO	1.39	1.39	1.39	1.39	2	2	2	2	2
Pressure, atm	5.0	5.0	5.2	21	7	4.6	4.6	2.1	2.1
°C	203	196	200	251	229	209	209	214	214
GHSV	298	300	303	200	1225	300	300	303	303
H_2 & CO Conv	86	88.3	79	88.7	81	82	5	87	32
Selectivity									
CH_4	2.9	2.0	5.5	7.5		4.3	10.6	6.7	16.6
C_2/C_4	6.2	2.5	18.5	17.4		12.5	34.0	12.8	19.5
C_5-C_{20}	65.5	62.1	66.5	71.3		81.6	51.1	68.8	59.2
C_{21}+	25.4	33.4	9.5	3.8		-	-	9.2	2.1

Taken from U. S. Patent 4477595 (X.38).

Table X.30. Activity of Ru on oxide modified titania surfaces.
Conditions: 230-250°C, 300 v/v/hr, H_2/CO=2, 60 psig, fixed bed reactor

	1% Ru/TiO_2	1% Ru/TiO_2 +10%Nb	1% Ru/TiO_2 +10%Ta	1% Ru/TiO_2 +1%Ta	1% Ru/TiO_2 +2%V	Physical Mixture 1% Ru/TiO_2 +10%Ta
Temp	238	230	235	232	252	240
H_2+CO conv	37	43	19.5	31.5	71.3	47.4
CO_2	3.8	1.9	3.7	3.2	3.5	5
CH_4	14.5	10.9	10.9	15.3	12.5	8.4
C_2	8.3	6.6	14.8	4.2	3.3	4.2
C_3+C_4	23.0	17.3	13.8	24.0	10.0	16.9
C_5+	50.4	63.3	56.8	53.3	70.7	65.5
HC products						
Alcohols	5.1	0	0	1.4	3.8	3.0
olefins	39.1	67.7	6.3	44.2	15.6	46.4
paraffins	34.	32.3	93.7	54.4	80.6	50.3

Taken from U. S. Patent 4711871 (X.32).

Table X.31. Activity of Ru/TiO_2 slurry catalyst.
Conditions: 1 g catalyst, 50 g octacosane, 6/3/1 H_2/CO/N_2, 1200 v/v/hr, 6 atm, 1 std L/g catalyst/hr

Catalyst 1% Ru	^oC	% CO Conv	Selectivity			
			CO_2	CH_4	C_2-C_4	C_5+
Ru/TiO_2 Particulate, reduced 450^{o}C	250	49	3.2	14.4	8.9	73.5
Ru/TiO_2 Particulate, not prereduced	260	10	2.0	20.0	30.0	48.0
Carbonyl based						
Ru	260	15	tr	4.7	19.5	75.8
Ru/CeO_2	240	<5	nil	na	na	na
Ru/Al_2O_3	240	25	3.0	19.3	9.4	68.3
Ru/TiO_2	240	55	6.7	12.3	17.5	63.5

Taken from U.S. Patent 4752600 (X.41).

Table X.32. Effect of steam treatment of Ru/TiO_2

Treatment of Ru/TiO_2	O/Ru ratio from O_2 chemisorption	Ru crystallite size Å
None	1.46	12
Air at 1 atm, 500^{o}C/3 hrs	not reported	30
9/1 H_2O/H_2 at 280 psig, 300^{o}C/4 hrs	1.08	15
9/1 H_2O/H_2 at 280 psig, 230^{o}C/16 hrs	0.88	18
3% H_2O in N_2 at 1 atm, 500^{o}C/3 hrs	0.98	16

Taken from Table 1, U.S. Patent 4647592 (X.43).

Table X.33. Effect of air treat on activity of Ru/TiO_2
Run in 2/1 H_2/CO, 210°C, 280 psig, and 1000 v/v/hr

Hrs	CO Conv	Selectivity to HC, %	wt.% selectivity		
			CH_4	CO_2	C_2+
No air treat					
0.7	84.8	80.3	7.3	5.3	87.4
1.4	94.8	90.8	4.9	4.2	90.9
2.4	94.7	88.2	3.6	6.9	89.5
3.0	98.3	89.6	3.6	8.8	87.6
3.7	97.7	89.5	3.8	8.4	87.8
Air treated sample					
0.7	78.6	72.1	3.0	8.3	88.7
1.3	91.9	85.0	2.3	7.5	90.2
2.2	94.5	88.5	2.3	6.4	91.3
3.0	93.7	88.6	2.5	5.4	92.1
3.7	93.1	88.9	2.5	4.5	93.0

Taken from Table II, U.S. Patent 4647592 (X.43).

Table X.34. Activity of Rh Catalysts for synthesis gas conversion.
Conditions: 1.6/1 H_2/CO, 100 kPa (1 atm), Catalyst reduced 450°C 1 hr,

	Temp	%CO Conv	CH_4 mol %	C_2-C_5 yield, mol %
2% Rh/TiO_2	248	1.3	74	26
2% Rh/Al_2O_3	265	3.5	15	85

Taken from U. S. Patent 4116994 (X.45).

Table X.35. Activity of rim-impregnated Co/TiO_2 catalysts
Conditions: 200°C, 2/1 H_2/CO, 2.1 MPa

Particle size, mm	2.2	2.2	0.1-0.2	2.2
Co Conc, wt%	13.0	13	13	20.9
Co Distribution	even	rim	rim	rim
Rim thickness, µm	-	80±30	80±30	120±30
Surface area, m^2/g	80	80	80	350
Hrs on stream	193	318	175	315
GHSV	420	650	940	1750
CO Conv, %	64.5	66.0	48.0	64.0
CO Conv, vol/vol/hr	90	150	210	342
Selectivity				
CH_4	12.0	8.3	4.7	12.7
C_2-C_4	5.1	4.4	4.7	5.3
C_5+	82.0	87.0	90.5	81.3
CO_2	0.9	0.4	0.1	0.7

Taken from Tables 1, 2, and 3 or U.S. Patent 5036032 (X.48).

Table X.36. Activity of Co/TiO_2 catalyst in a fixed-bed reactor.
Runs at 230°C, 150 psig, 400 GHSV, 2/1 H_2/CO

Cat		CO Conv	Selectivities			Schulz-Flory
			CO_2	CH_4	C_2+	
A	12 Co/TiO_2[b] (this invention)	88	1.1	8.6	90.3	0.91
B	100 Co/5 ThO_2/8 MgO/200 Kieselguhr[a] (known)	43	4.3	10.3	86.4	-
C	12 Co/SiO_2 (known)	72	1.6	8.7	89.7	0.85
D	25 Co/1.8 Ti/100 SiO_2 (known)	21	1.9	13.8	84.3	0.74

Taken from Example 7 in U. S. Patent 4542122 (X.46).
a. Conventional FT catalyst
b. Rutile/anatase ratio of 3.2. Reduced in H_2 at 450°C for 1 hr

Table X.37. Activities of Co and Co-Re on TiO_2 in a fixed-bed reactor. (Data shown in Figure 1 in Patent 4542122) Catalyst impregnated with nitrate/perrhenic acid and calcined in air at 500^{o}C/3 hrs. Catalysts reduced in H_2 at 450^{o}C for 1 hr. Runs made at 200^{o}C, 2.15/1 H2/CO, 280 psig, GHSV=1000.

Metals, wt% on TiO_2	Rutile in TiO_2, wt%	Air treat^{o}C for 3 hrs	O_2 chemisorp. μ mol O_2/ g cat	%CO Conversion	Surface area m^2/g	CH_4	CO_2	C_2+
12 Co	53	250	213	67	36	9.7	0.2	90.1
12 Co	100	250	265	79	10	11.5	0.7	87.8
12 Co	56	500	178	54	33	9.9	-	90.1
12 Co	100	500	202	67	10	11.7	0.3	88.0
12 Co-0.1 Re	100	500	145	67				
12 Co-0.5 Re	56	500	343	85				
12 Co-0.5 Re	100	500	285	82				
12 Co-3 Re	56	500	399	81				

Table I in U.S Patent 4568663 (X.51).

Table X.38. Effect of Anatase-Rutile Ratio on Co/TiO_2 catalyst.
Catalysts impregnated with cobalt carbonyl from pentane solution. Run conditions: 200^{o}C, 280 psig, 1000 GHSV, H_2/CO=2.15/1

Co, wt%	10.1	9.2
Rutile in Titania, wt%	28	~100
Pretreatment Conditions:		
1st Stage	250^{o}C/ air/3 hrs	250^{o}C/ air/3 hrs
2nd Stage	450^{o}C/ H_2/1 hr	450^{o}C/ H_2/1 hr
CO Conv, mol %	5	97
CH_4 Yield, mol %	15.1	5.4
O_2 Chemisorption, umol/g cat	53	205

Example 9 in U.S. Patent 4542122 (X.46) and Example 3 in U.S. Patent 4595703 (X.49).

Table X.39. Effect of rutile content on Co/TiO_2.
Run at 230^{o}C, 40 MeOH:2 H_2:1 CO_2:7 Ar, 400 psig, GHSV=500.

Rutile content, %	55	100
MeOH Conv	66	100
Carbon Product Distribution		
CO	2.6	0.8
CO_2	15.6	27.8
CH_4	9.0	17.1
C_2+	72.8	54.3

Taken from Example 6 in U.S. Patent 4542122 (X.46).

Table X.40. Activity and selectivity of Co on titania based catalysts for methanol conversion (rutile not specified).
Run conditions: 230°C, 400 psig, GHSV=500, 40 $_2$MeOH:2 H_2:1 CO_2:7 Ar

	12% Co/TiO_2	12% Co/2% ThO_2/TiO_2		100 Co/5 ThO_2/8 MgO/200 Kieselguhr[a]	12% Co/ SiO_2	12% Co/ Al_2O_3
MeOH Conv, 35 hr	52	70[b]		97	38	64
Carbon Product Distribution						
CO	5.5	3.1	2.9	1.0	4.3	2.8
CO_2	12.9	17.0	12.6	38.4	22.3	21.8
CH_3OCH_3	0.2	0.3	0.5	-	0.1	2.4
CH_4	11.2	8.6	7.4	19.5	7.0	9.9
C_2+	70.2	71.0	76.6	41.1	66.3	63.1
Schulz-Flory Alpha	0.86	0.88	n.p.	n.p.	n.p.	n.p.

Example 5 of U.S. Patent 4542122 (X.46).
a. Conventional FT catalyst
b. Two sets of data provided for the same conditions having the same MeOH conversion that was not otherwise specified.
n.p. = not provided

Table X.41. Effect of Re on MeOH conversion over Co/TiO_2 with or without ThO_2. Run conditions: 230°C, 400 psig, GHSV=500, MeOH/Argon=4. Catalysts calcined 500°C			
	12 Co/ 2 ThO_2/TiO_2	12 Co/2 ThO_2/ 0.5 Re/TiO_2	12 Co/ 0.5 Re/TiO_2
Rutile Conc, %	56	56	56
MeOH Conv	49	100	87
Product Distribution			
CO	6	2	2
CO_2	14	28	22
CH_4	6	14	9
C_2+	74	56	67
Table III in U.S. Patent 4568663 (X.51).			

Table X.42. Effect of H_2 partial pressure on MeOH conversion. Co/ThO2/TiO2 (rutile and catalyst composition not specified) at 230°C, 500 GHSV, 400 psig			
Partial Pressures, psig			
MeOH	332	332	332
Ar	83	66	0
H_2	0	17	83
MeOH Conv, wt%	38	52	83
Carbon Product Distribution			
CO	8.5	3.9	0.9
CO_2	11.3	8.9	12.2
CH_3OCH_3	1.0	0.4	0.1
CH_4	4.6	5.7	15.9
C_2+	74.6	81.1	70.9
CH_4 in hydrocarbon, wt%	5.8	6.6	18.3
Table IV in U. S. Patent 4542122 (X.46).			

Table X.43. Effect of promoter on MeOH Conversion on Co/TiO_2.
Conditions: 230°C, 400 psig, LHSV=0.67, 20 MeOH/1 H_2/4 Argon

Catalyst composition					
Wt% Co	5.0	4.34	4.65	4.55	4.73
Promoter @ 1 wt%	none	Zr[a]	Hf	Ce	U
MeOH Conv	31	37	34	49	46
Rate MeOH Conv, g/hr/g Co	1.6	2.3	1.9	2.8	2.6
Carbon Prod Distribution					
CO	16	13	16	10	9
CO_2	8	9	7	9	13
CH_4	8	8	8	7	9
C_2+	68	70	69	74	69

Table IV, Example 2 in U.S. Patent 4663305 (X.57).
a. The Zr salt was $ZrO(O_2CCH_3)_2$.

Table X.44. Effect of silica promotion on CoRe/TiO_2 in a fixed-bed reactor.
Conditions: 200°C, 2.1 MPa, H_2/CO=2, run at space velocity to give ~60% CO conversion.

	(A) CoRe/TiO_2		(D) CoRe/TiO_2		(B) CoRe/TiO_2 +SiO_2		(C) CoRe/TiO_2 +SiO_2	
% SiO_2	0		0		4		5.2	
Steam treat H_2O (40 Torr)/He at 400°C/13 hrs	No		Yes		Yes		Yes	
reduction in H_2	250°C for 13 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs	
Hrs on stream	50	139	49	190	47	120	49	119
CO Conv	61.5	64	67	58	69	61	60	55
mol CO conv/g atom Co-hr	5.7	5.5	5.1	4.4	7.5	6.8	8.3	7.5
CH_4	5.3	5.1	4.6	5.0	5.2	5.6	5.4	5.8
C_2 (O/P)	0.6 (0.12)	0.6 (0.14)	0.6 (0.17)	0.6 (0.19)	0.7 (0.11)	0.7 (0.13)	0.6 (0.13)	0.6 (0.14)
C_3 (O/P)	2.1 (1.9)	1.9 (2.1)	2.2 (2.6)	2.1 (2.8)	2.4 (2.0)	2.5 (2.1)	2.3 (2.0)	2.3 (2.1)
C_4 (O/P)	2.3 (0.70)	2.16 (0.63)	2.0 (1.6)	1.9 (1.6)	2.4 (1.1)	2.6 (1.3)	2.6 (1.2)	2.5 (1.3)
C_5+	89.5	89.9	90.3	90.1	89.3	88.5	89.1	89.1
CO_2	0.2	0.2	0.3	0.3	0.07	0.06	0.05	0.04

Combined Table 1 and Table 2 of U.S. Patent 4794099 (X.58).
(O/P) = olefin/paraffin ratio

Table X.45. Effect of Precalcination on FT activity of Co-Ru/TiO_2 catalyst in fixed-bed reactor. Runs made at 200°C, $60H_2/30CO/7N_2$, 75 psia, space velocity adjusted; catalysts 70% rutile titania,

	D	A	B	C
	20% Co/ SiO_2	11.6% Co/ TiO_2	Reduced 11.6% Co/ 0.14% Ru/TiO_2	Calcined-reduced 11.6% Co/ 0.14% Ru/TiO_2
1st Calcination	none	400°C/16 hrs	400°C/16 hrs[a]	400°C/16 hrs[b]
Reduction/oxidation /reduction step[c]	No	No	No	Yes
CO Conv	65	50	64	68
CH_4 select	7.4	9.3	6.8	6.5
C_5+ select	82	80.2	87.3	87.8
Co time yield[d]	1	0.6	2.0	2.9

Taken from Table III in U. S. Patent 4738948 (X.61).
a. Ru impregnated to catalyst A after 1st calcination.
b. Started with catalyst B.
c. Calcined in air at 300°C/4 hrs and then reduced in H_2
d. moles CO converted per hr g-atom Co in catalyst.

Table X.46. H_2 Regeneration of Air-calcined-reduced Co-Ru/TiO_2Catalysts Aged 10-30 days

	CO Conv, %	Co time yield, hr^{-1}	CH_4	C_5+
Cat A. Co/TiO_2	At 560 kPa, 200°C, H_2/CO=1			
Initial	20	0.6	8.9	80.1
Aged	20	0.5	9.5	81
H_2 Treated	20	0.5	9.5	80.5
Cat. B CoRu/TiO_2	At 2060 kPa, 200°C, H_2/CO=1			
Initial	50-60	2.6	7.0	86
Aged	50-60	2.0	8.2	84
H_2 Treated	50-60	2.6	6.5	87
Cat. C. CoRu/TiO_2 Calc	At 2060 kPa, 200°C, H_2/CO=1			
Initial	50-60	4.5	5.5	91.0
Aged	50-60	3.9	6.4	88.8
H_2 Treated	50-60	4.8	4.9	91.5

Taken from Example 5, Table IV in U. S. Patent 4738948 (X.61).

Table X.47. Synthesis gas conversion activity of Fe-coated, vanadia and niobia modified titanias in a fixed-bed reactor. Runs made with 1:1 H_2/CO, 500 v/v/hr, 300 psig

	4% Fe/TiO_2			4% Fe/TiO_2+V			4%Fe/TiO_2+Nb
Temp	305	315	270	290	305	270	270
CO Conv	47	60	27.0	49	70	34.3	20.1
Selectivity (CO_2 free)							
CH_4	21.0	24.4	21.0	16.1	17.8	13.0	14.6
C_2-C_4 olefins	14.6	13.3		42.7	23.4		
C_2-C_4 paraffins	35.9	36.3	55.0	21.2	44.2	41.5	32.9
C_5+	27.5	26.0	24.0	20.0	14.6	45.5	52.5

Taken from Tables 1 and 2 in U. S. Patent 4559365 (X.68).

Table X.48. Selectivity of TiO_2 Promoted Nickel Catalysts for Synthesis gas conversion in a fixed-bed reactor.
Run conditions: 250°C, 3/1 H_2/CO, 1 atm., catalyst reduced in H_2 at 250°C/1 hr.

	CO Conv %	HC Selectivity, wt%			umol/min/g of Ni[a]		H_2 chemisorption umol/g	BET SA m^2/g	H/M
		CH_4	C_2-C_3	C_4-C_6	CH_4 formation rate	CO Conv rate			
Ni Powder	4.9	88	12	-	9.7(.0115)	11.0 (.0131)	7.0	0.41	0.0131
0.007% TiO_2 on Ni	11.6	74	16	9	19.1(.0295)	26.3 (.0406)	5.4	0.48	0.00063
0.07% TiO_2 on Ni	27.2	38	42	19	21.9(.0468)	60.2 (.129)	3.9	0.60	0.00046
0.20% TiO_2 on Ni	25.4	39	44	17	21.2 (.0281)	56.6 (.0748)	6.4	1.15	0.00075
1.66% TiO_2 on Ni	15.9	36	44	21	11.7 (.0244)	34.7 (.0723)	4.0	7.69	0.00047
8.40% TiO_2 on Ni	18.8	33	42	24	14.3	46.0			
10% Ni on TiO_2	49.0	37	34	28	14.6 (0.0194)	41.6 (0.0550)			
1/1 Ni powder + TiO_2	2.1	92	8	-	7.6 (0.0101)	8.3 (0.0110)			

Taken from U.S. Patent 4273724 (X.70).

a. ( ) numbers in parenthesis are reactions/site/sec or turnover number.

Table X.49. Activity of Cu-promoted Co-Mo spinel catalysts in a slurry reactor.
Conditions: CSTR: 2/1 H_2-CO feed, 270^oC, 75 psig, and 2000 h^{-1} gas space velocity in octacosane.
Catalyst first reduced *in situ* at 100-270^oC with H_2/CO at 1000-2000 v/v/hr flow rate at 75 psig.

	Co_2MnO_4/1% Cu	Co_3O_4/1% Cu	Co_2MnO_4
CO Conv	45	23	nil
wt% Prod Select			
CO_2	16	54	-
CH_4	7	40	-
C_2-C_4	26	6	-
C_5+	51	nil	-
%olefins in C_2-C_4	83	52	-

Taken from U. S. Patent 5162284 (X.73).

Table X.50. Synthesis gas conversion for making alcohols
Conditions: 1/1 H_2/CO, 50 atm.. GHSV 1832

	$Cu_{0.5}Mg_5CeO_x$	0.9%K on $Cu_{0.5}Mg_5CeO_x$	$Cu_{0.45}NdCeMgO_x$
Temp, ^oC	290	320	290
CO conv, %	25.5	15.5	20.6
CO_2	22.5	31.0	17.1
Selectivity, % C exclusive of CO_2			
Methanol	70.7	57.2	82.6
Isobutanol	8.2	10.4	8.2
Other alcohols	4.9	6.9	2.4
Methane	8.4	11.5	3.7
Higher Hydrocarbons	4.1	12.8	2.7
DME	3.3	1.2	1.6

Taken from U. S. Patent 5387570 (X.81).

Table X.51. Synthesis gas reaction in dual fixed-bed reactors with different catalysts . First stage bed: 20g Fe/Zn/Ce/K Second stage bed: 1.5 g Ru/TiO_2 + quartz	
Temp, ^oC	220
Pressure, atm	6.47
H_2/CO mole ratio	1.64
Flow rate, sccm/min	36.5
CO Conv	59.0
CO_2 Selectivity in upper bed	26
CH_4 Selectivity	2.5
HC Selectivity in upper bed	33
HC Selectivity in lower bed	41

Taken from U. S. Patent 4624968 (X.82).

Table X.52. Hydrocarbon selectivity from one and two-stage beds

	First stage Fe/Zn/Ce/K	Second stage Ru/TiO_2	2-Stage Beds	
			Predicted	Observed
CH_4	3.5	6.1	4.9	3.9
C_2-C_4	18.5	11.0	15.4	13.8
C_5-C_9	22.9	24.7	23.9	22.6
C_{10}+	55.1	58.2	56.8	60.3

Taken from U. S. Patent 4624968 (X.82).

Table X.53. Effect of adding ethylene to the feed

	Catalyst					
	Ru-Co/TiO_2			Ru/TiO_2		
C_2H_4 in feed, %	0	2.5	2.5	0	6.2	6.2
Location of C_2H_4 Addition[a]	-	inlet	below top one-third	-	inlet	below top one-third
CO Conv %	25-27	25-27	25-27	35-45	35-45	35-45
C_2H_4 Conv		99.5	89.5		97	45.3
C_2H_4 Selectivity	-			-		
to C_2H_6	-	86.5	69.5	-	82	44
to C_3+	-	13.5	30.5	-	18	56
Added C_2H_4 that appears as C_3+ %		13.5	27.3	-	17	26
% Selectivity[b]						
CH_4	9.4	8.3	7.2	5.5	4.3	3.9
C_2	1.3	-	-	0.7	-	-
C_3	2.7	3.3	3.7	2.1	2.6	3.4
C_4	2.4	2.9	3.7	3.5	4.0	5.1
CO_2	0.4	0.5	0.4	0.7	0.7	0.7
C_5+	83.8	92.9	99.3	87.5	105.6	117.0

Example 3 in U.S. Patent 4754092 (X.85).

a. Downflow reactor.

b. Selectivity defined as percent CO converted. When ethylene is added, the sum of selectivities is >100%.

Table X.54. Effect of heating rejuvenation tubes on catalyst activation.

Heat addition	no	Yes
Gas rate in tube, scfh	5100	4800
Avg reactor temp, °F	427	427
Avg rejuvenation temp, °F	430	440
CO conv, start to end of run, %	32 to 26 (over 12 hrs)	26 to 36 (over 24 hrs)
Conv, change/day	-12.4	+10.4

Example 4 in U.S. Patent 4754092 (X.85).

Table X.55. Improvement in catalyst/wax separation in slurry FT processes by removal of catalyst fines.

Classification Solvent	Catalyst/solvent wt/wt	Other	Cycles	Acetone cycles	Filter time	Filter rate	
						(gm/min)	gal/ft^2/min
0.45 µm Millipore filter paper							
Blank	-	-	-	-	95.0	0.5	
Water	15/85	-	6	2	0.9	55.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% Oleic acid added	7	2	1.0	50.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% Aerosol OT-100 added	7	2	1.0	50.0	
0.3 µm glass fiber filter							
FT wax @ 130°C	2/98	Stirred 5 min	none	none	-	-	5.8 @ 14 psig
		Stirred 44 hrs	none	none	-	-	0.05 @ 14 psig
FT wax @ 120°C	2/98	Stirring per cycle19/48/24	3	none	-	-	14.5 @ 14 psig

Taken from U.S. Patent 5070064 (X.98).

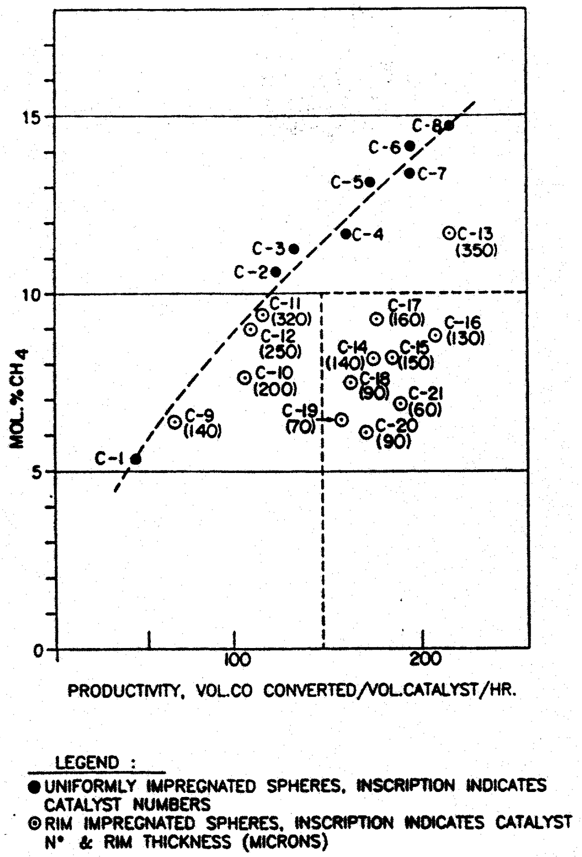

Figure X.1. Plot of methane production for various catalysts (from ref. X.50).

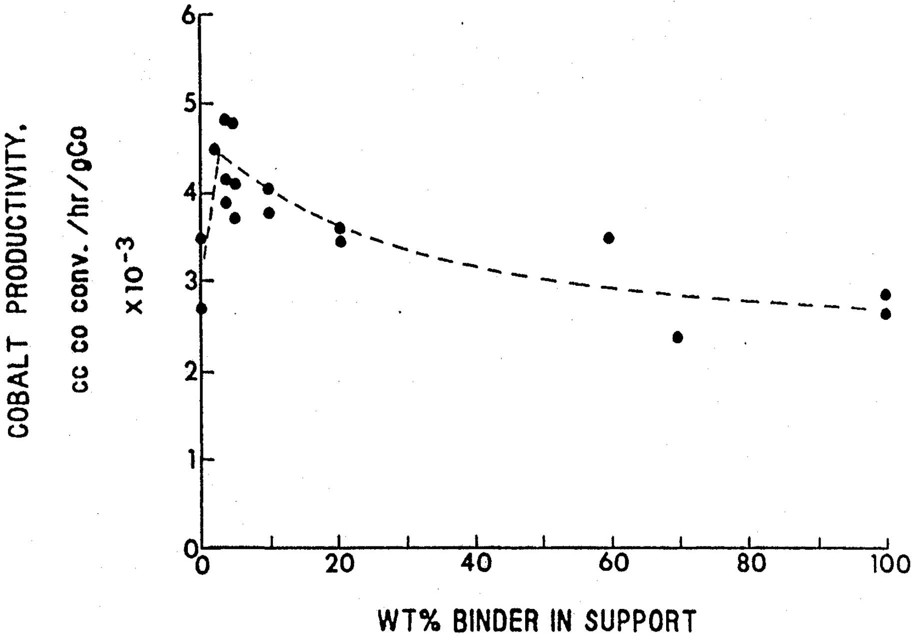

Figure X.2. Plot of cobalt productivity versus binder content in the titania support (from ref. X.30).

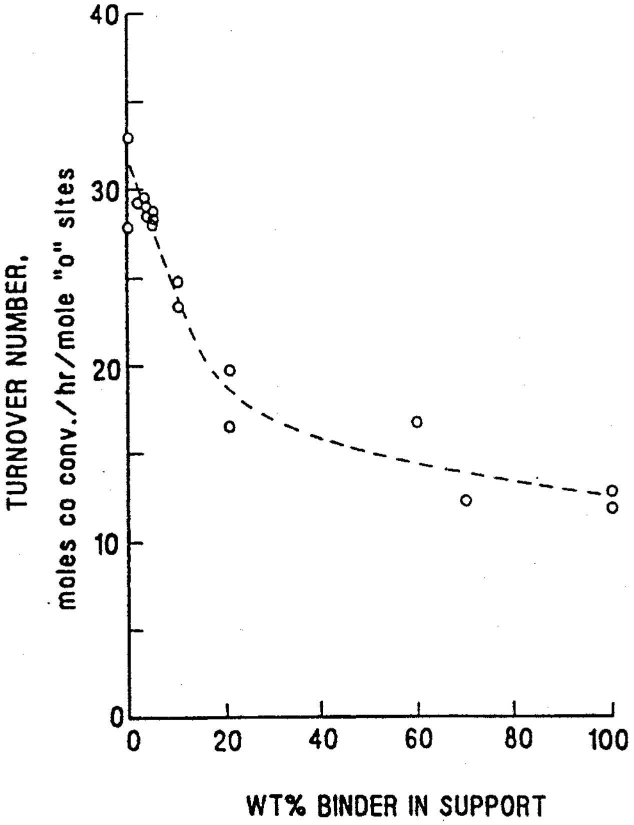

Figure X.3. Plot of wt.% of binder versus turnover number (TON) (from ref. X.30).

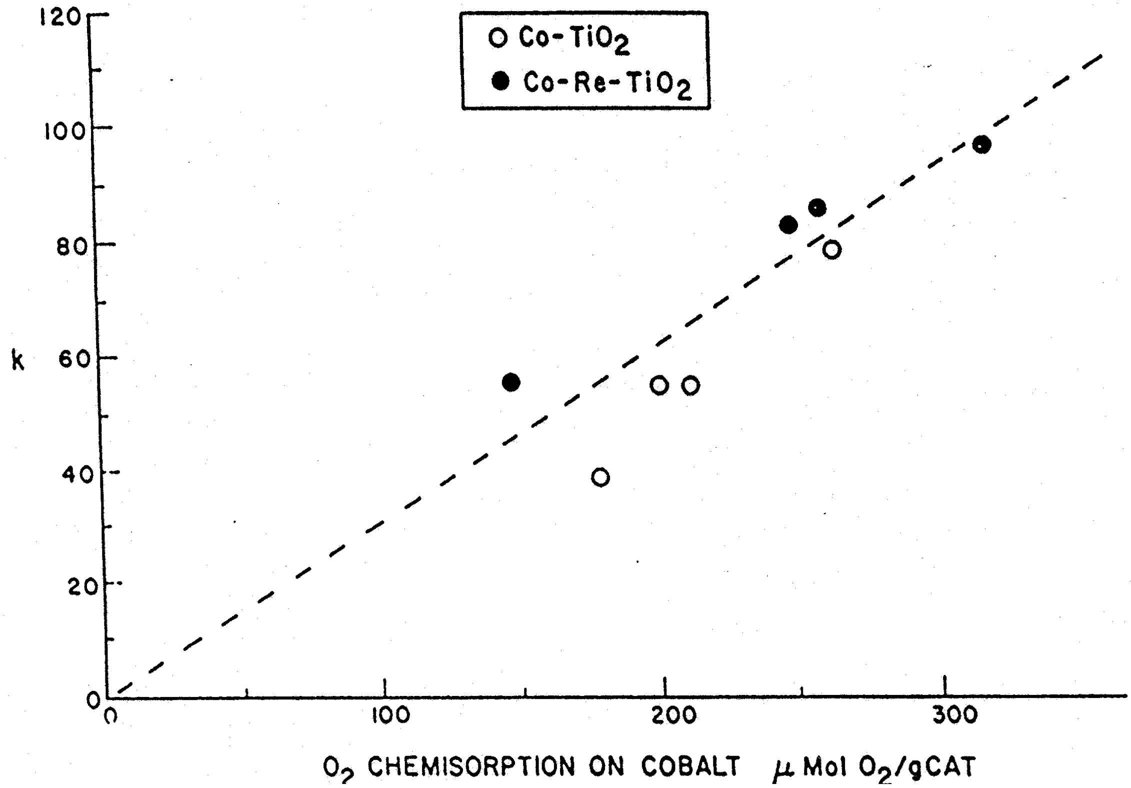

Figure X.4. Effect of dispersion on cobalt catalyst activity (from ref. X.51).

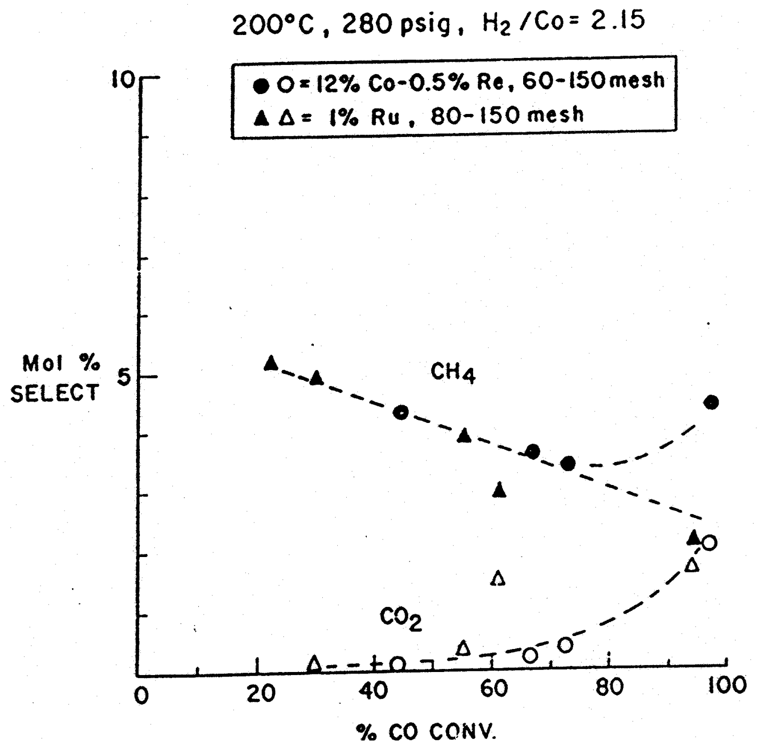

Figure X.5. Dependence of CH_4 and CO_2 production on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

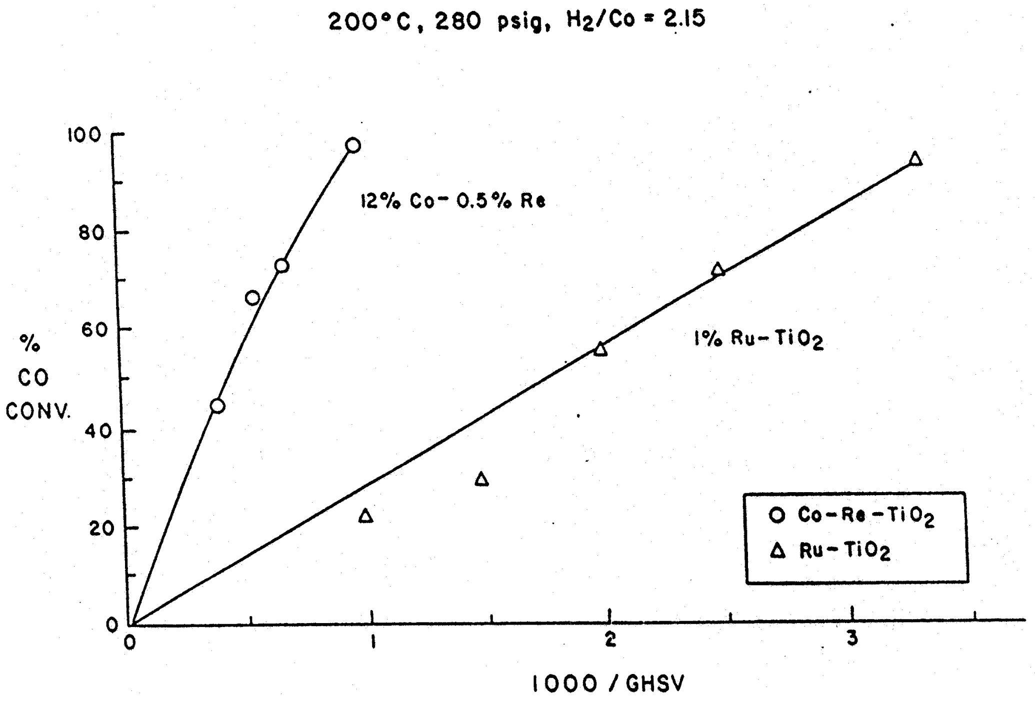

Figure X.6. Dependence of CO conversion on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

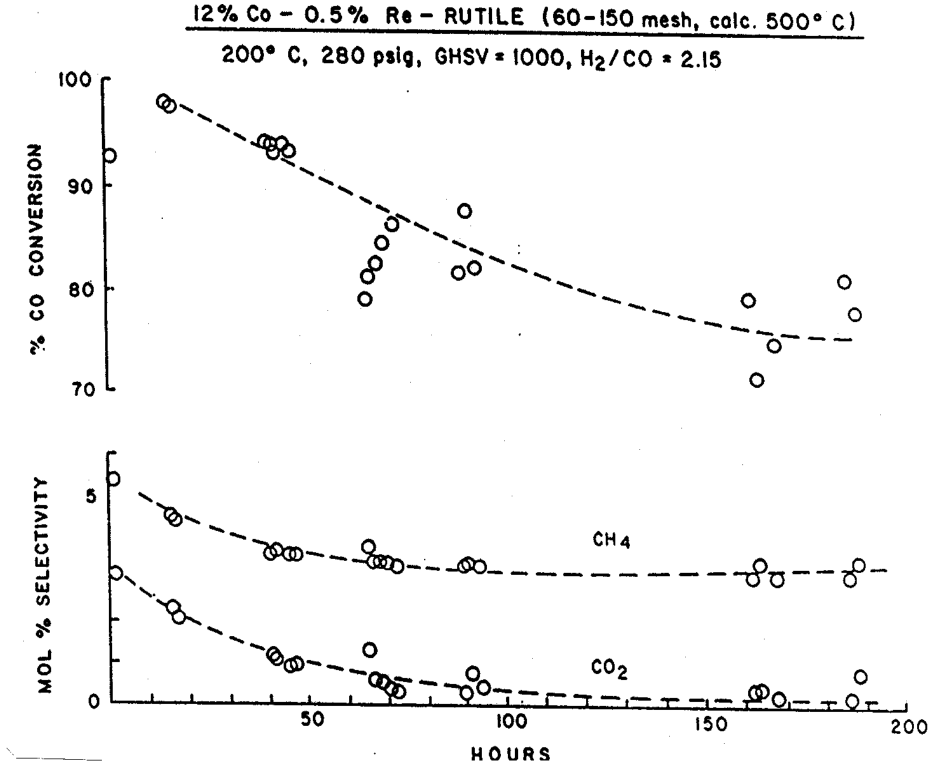

Figure X.7. The CO conversion and the methane and CO_2 production at increasing conversion time using a Co-Ru-TiO_2 catalyst (from ref. X.51).

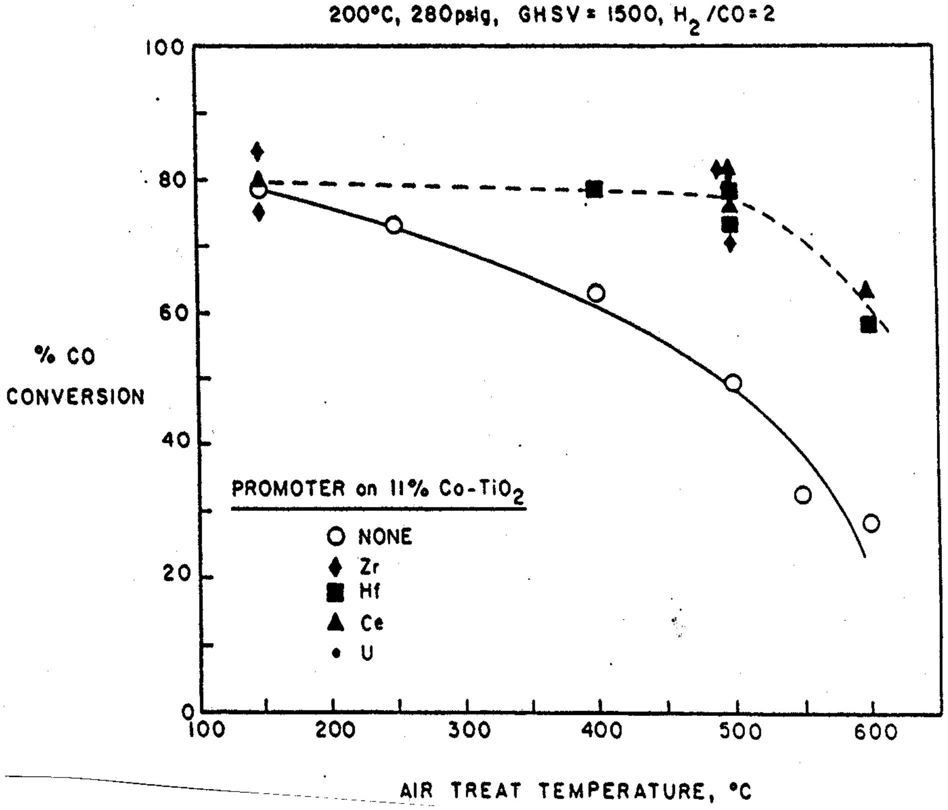

Figure X.8. Comparison of activity for Zr, Hf, Ce and U promoted Co-TiO_2 catalysts and unpromoted catalysts after simulated catalyst regeneration (from ref. X.57).

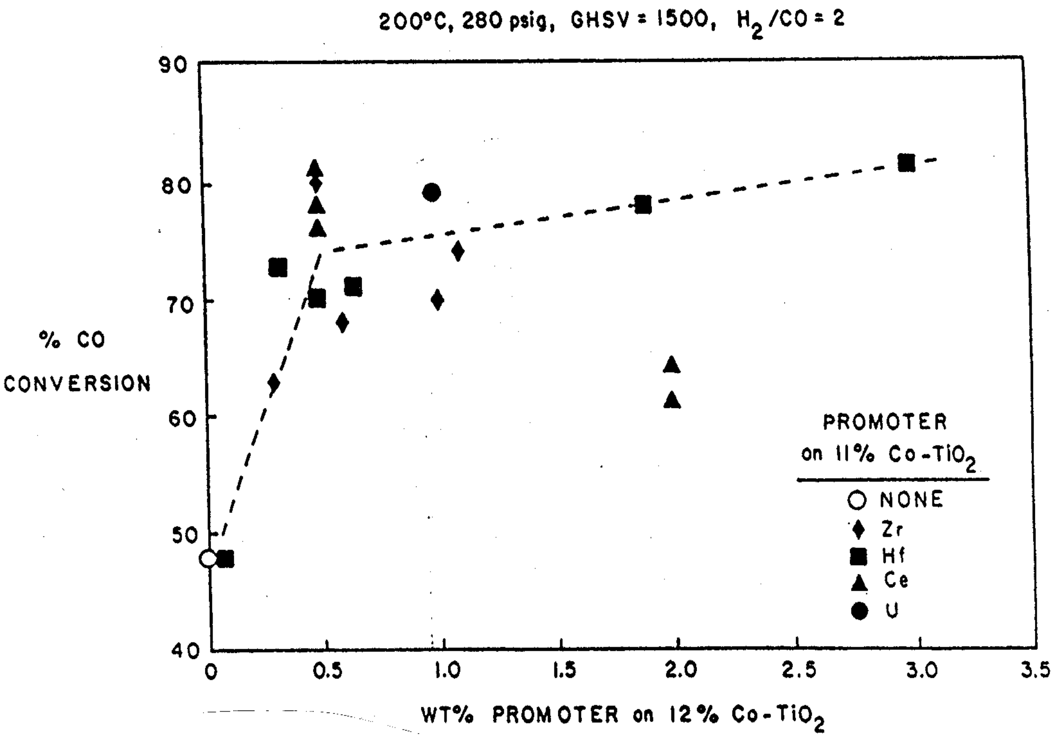

Figure X.9. Effect of promoter loading on Co-TiO_2 catalyst after simulated regeneration at 500°C (from ref. X.57).

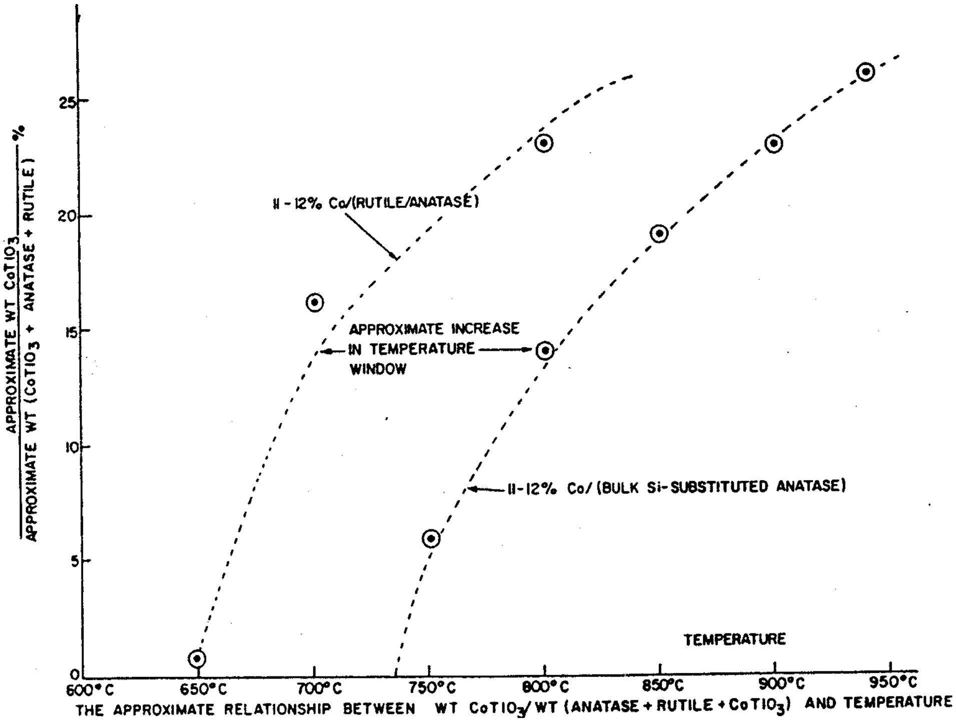

Figure X.10. Relationship between wt.% Co-TiO_3 and total TiO_2 versus temperature (from ref. X.60).

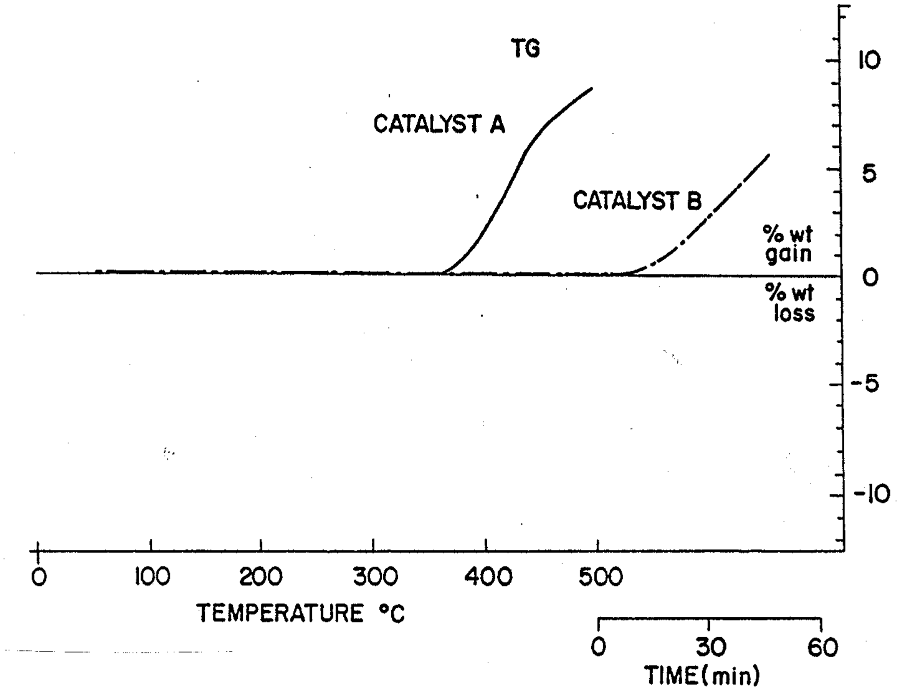

Figure X.11. Effect on catalysts A and B (see text) of carburization showing that silica suppresses carbon growth (from ref. X.58).

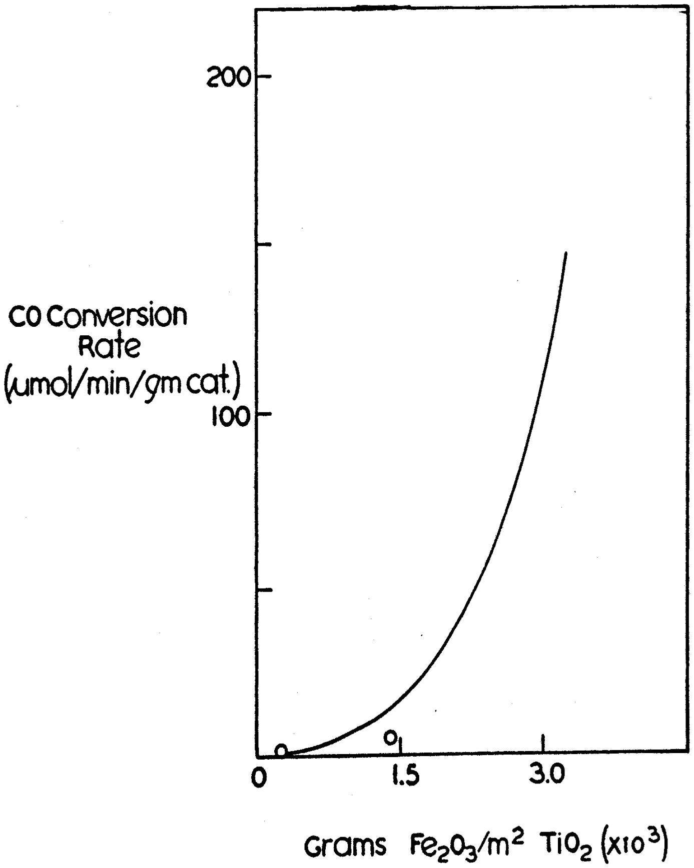

Figure X.12. Plot of CO conversion rate as a function of the iron loading on titania (from ref. X.64).

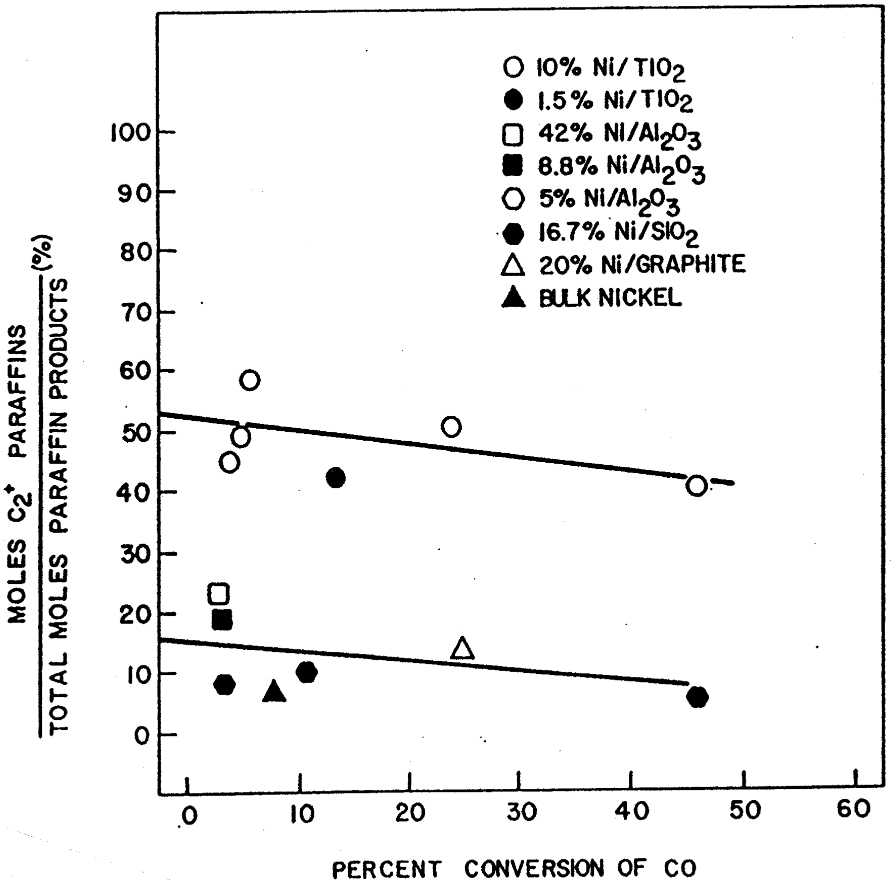

Figure X.13. C_{2+} selectivity for increasing conversion with nickel catalysts (from ref. X.69).

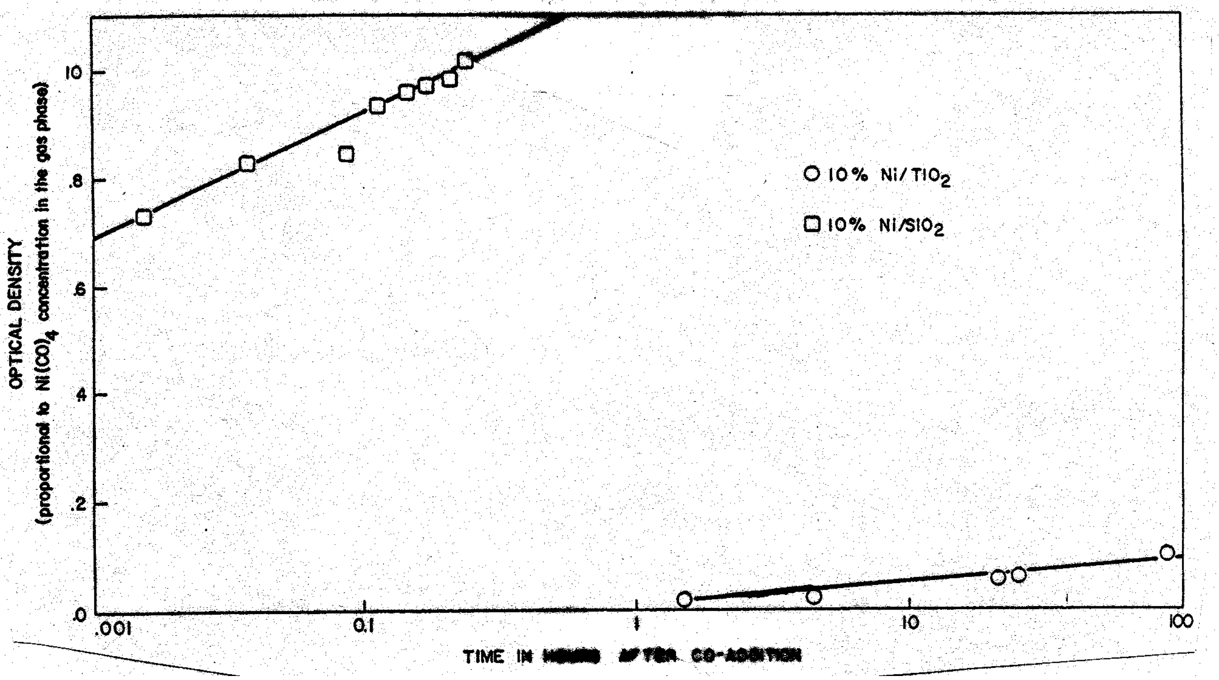

Figure X.14. Impact of support on the rate of nickel carbonyl fraction (from ref. X.69).

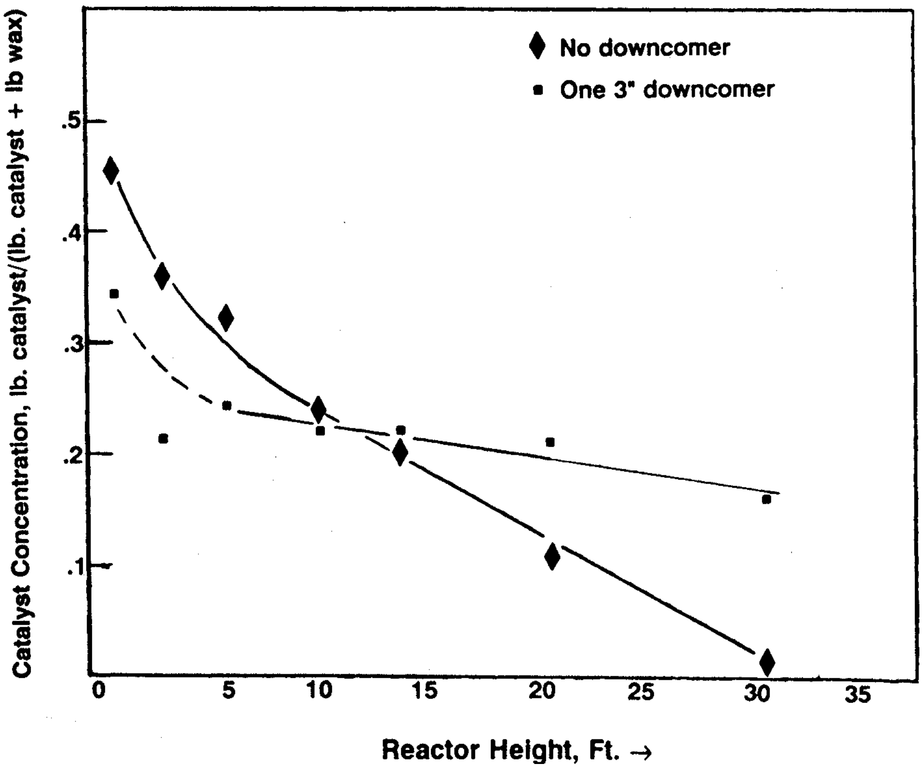

Figure X.15. Catalyst concentration versus reactor height for (!) no downcomer and for one 3" downcomer (Q).

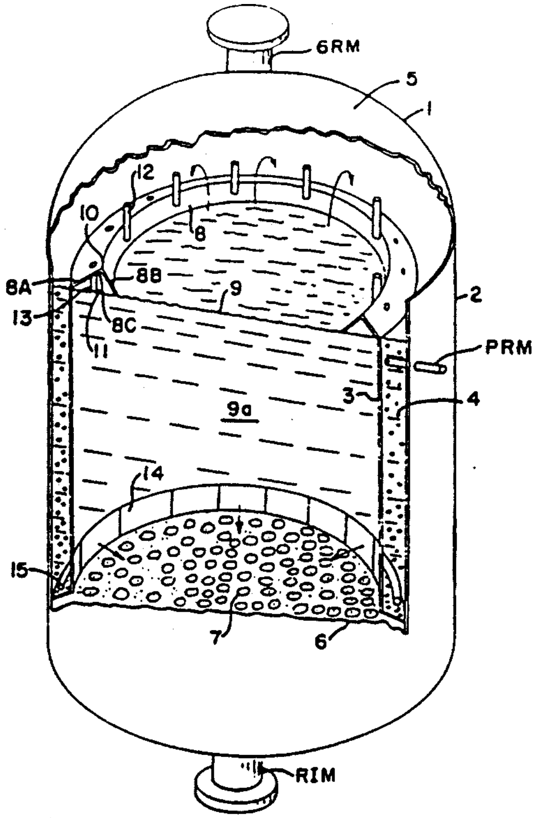

Figure X.16. Schematic of reactor for enhanced gas separation for bubble column draft tubes (from ref. X.90).

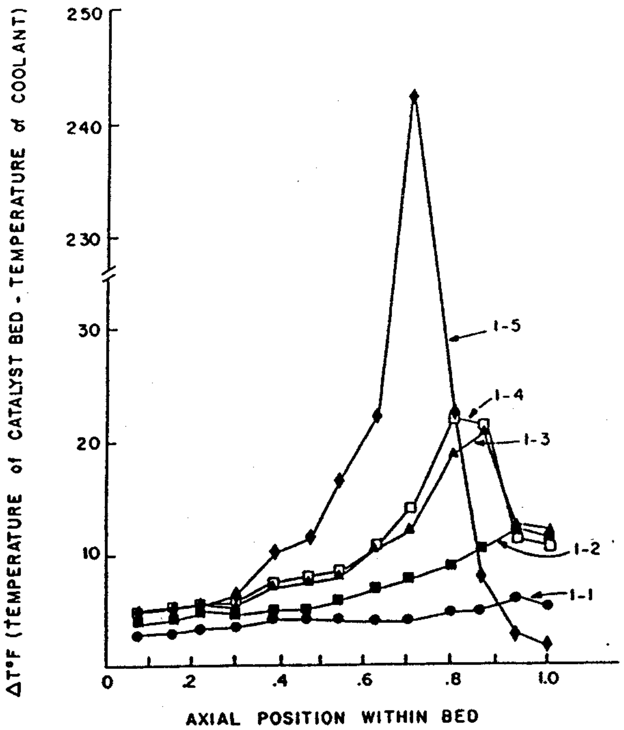

Figure X.17. Temperature exotherm within bed position for different start-up procedure (see text) (from ref. X.35).

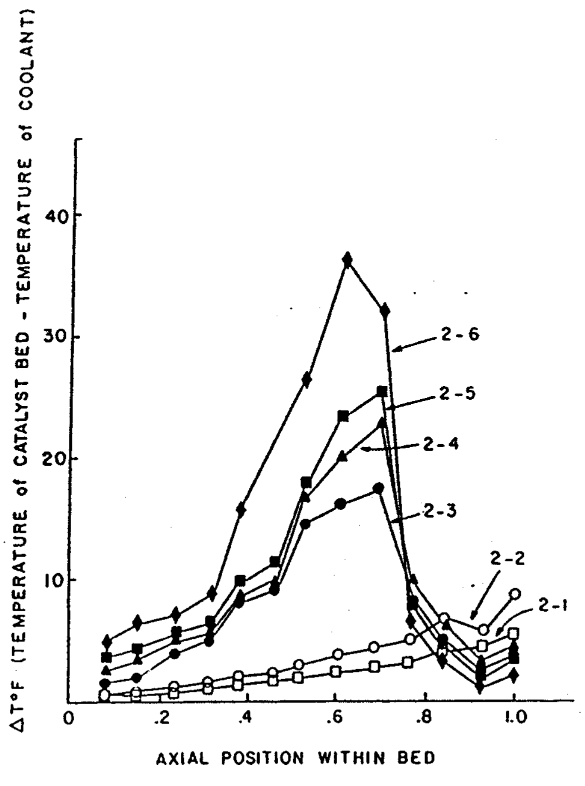

Figure X.18. Temperature exotherm within bed position for low H_2:CO ratio start-up (from ref. X.35).

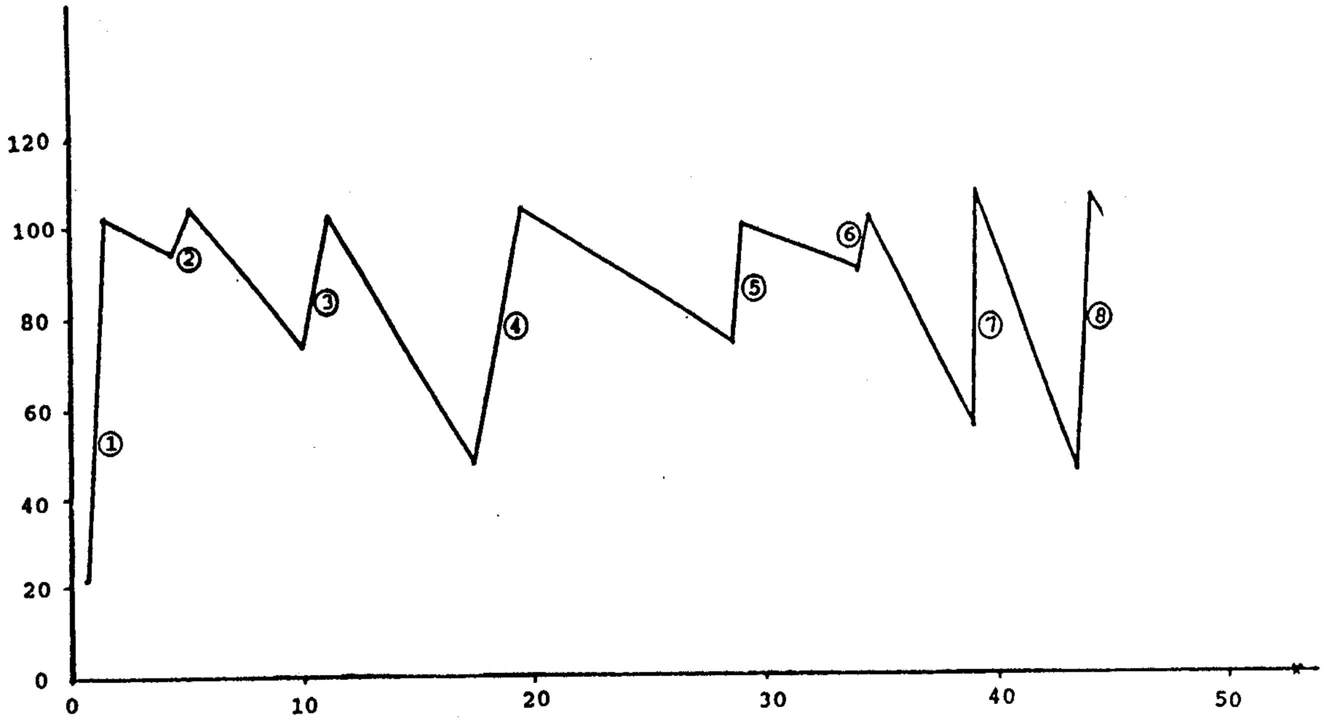

Figure X.19. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

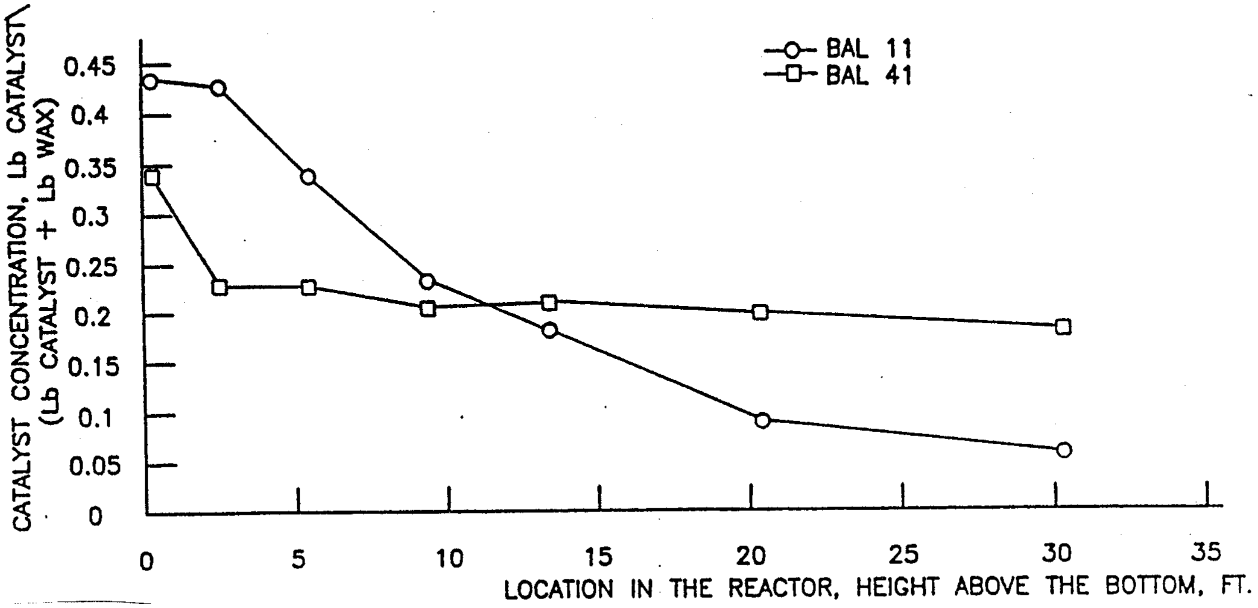

Figure X.20. Catalyst concentration versus elevation in the reactor with (Q) and without (F) use of draft tubes (from ref. X.89).

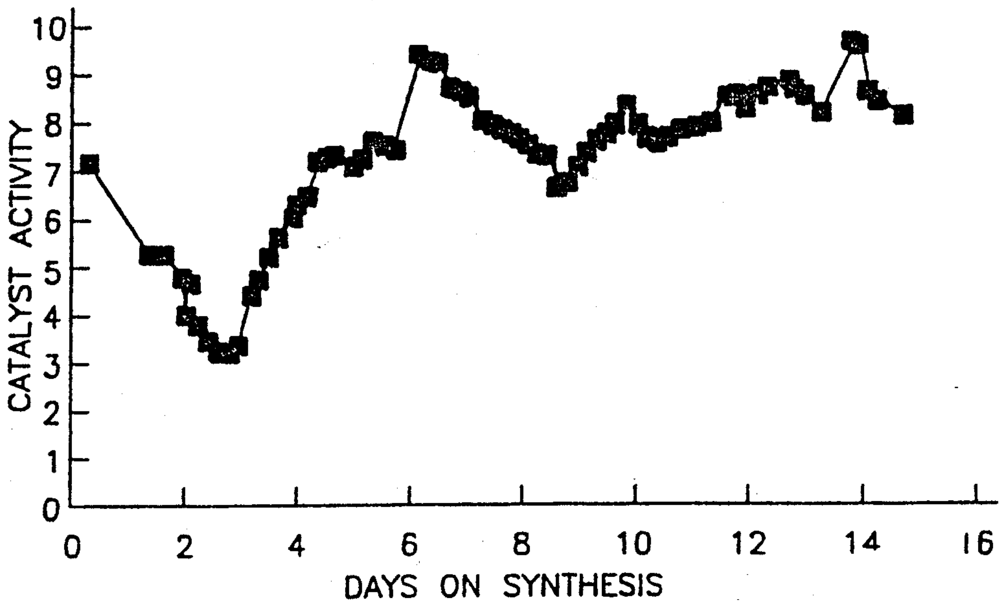

Figure X.21. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) (from ref. X.89).

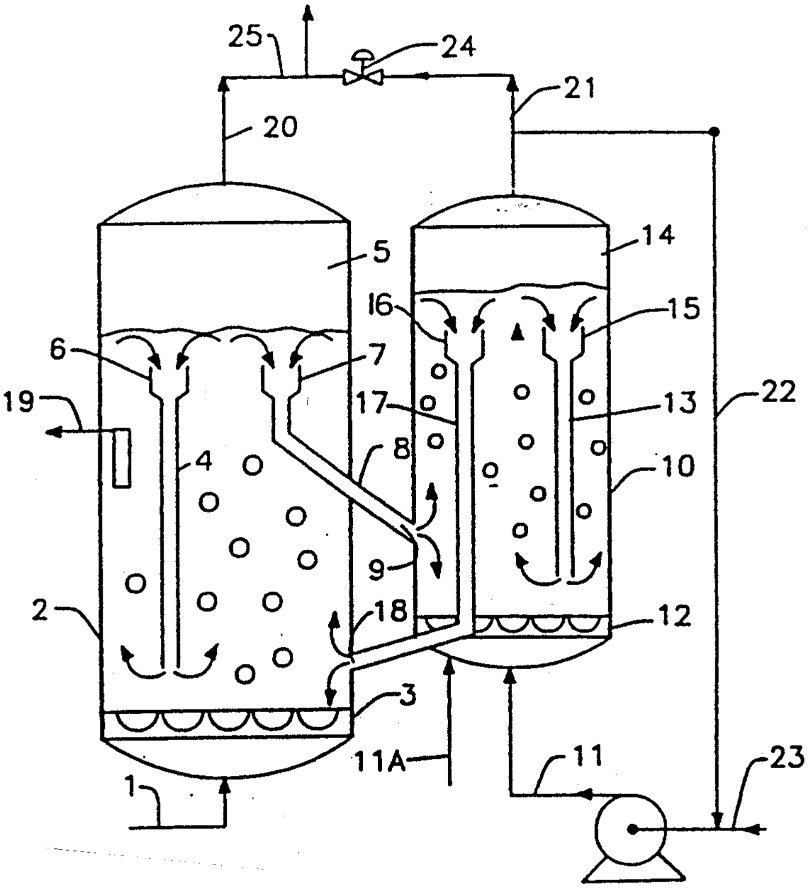

Figure X.22. Schematic of multiple vessels for catalyst rejuvenation (from ref. X.97).

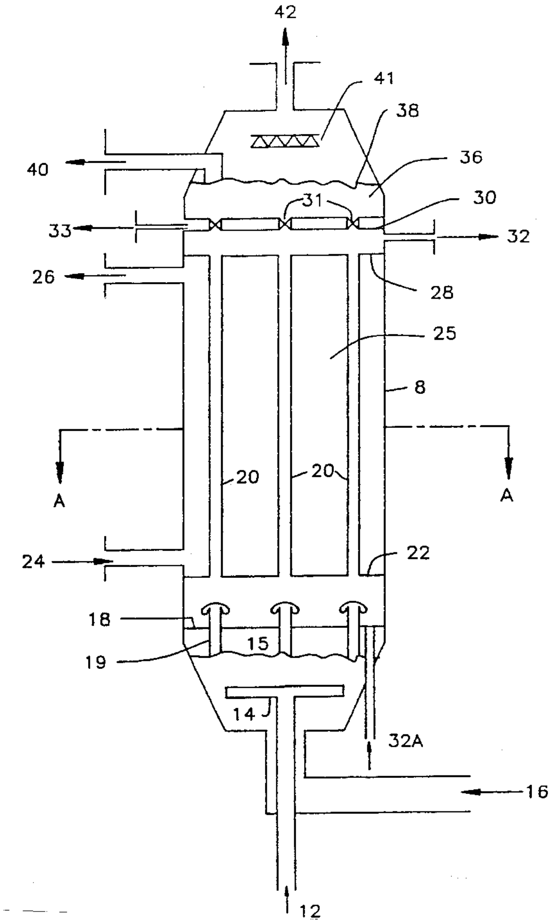

Figure X.23. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets.

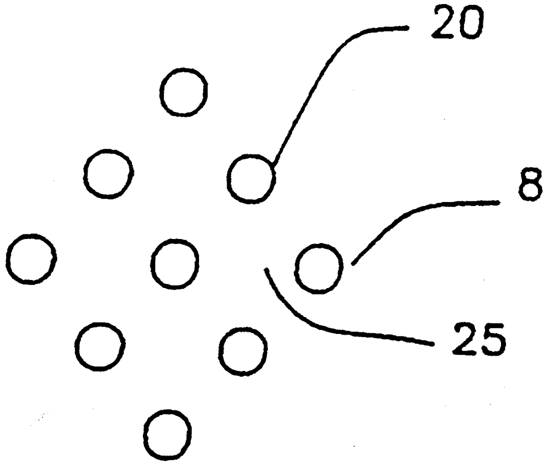

Figure X.24. Horizontal Section A - A through the elevation of Figure 23 showing a possible arrangment of tubes, that is, reaction zones.

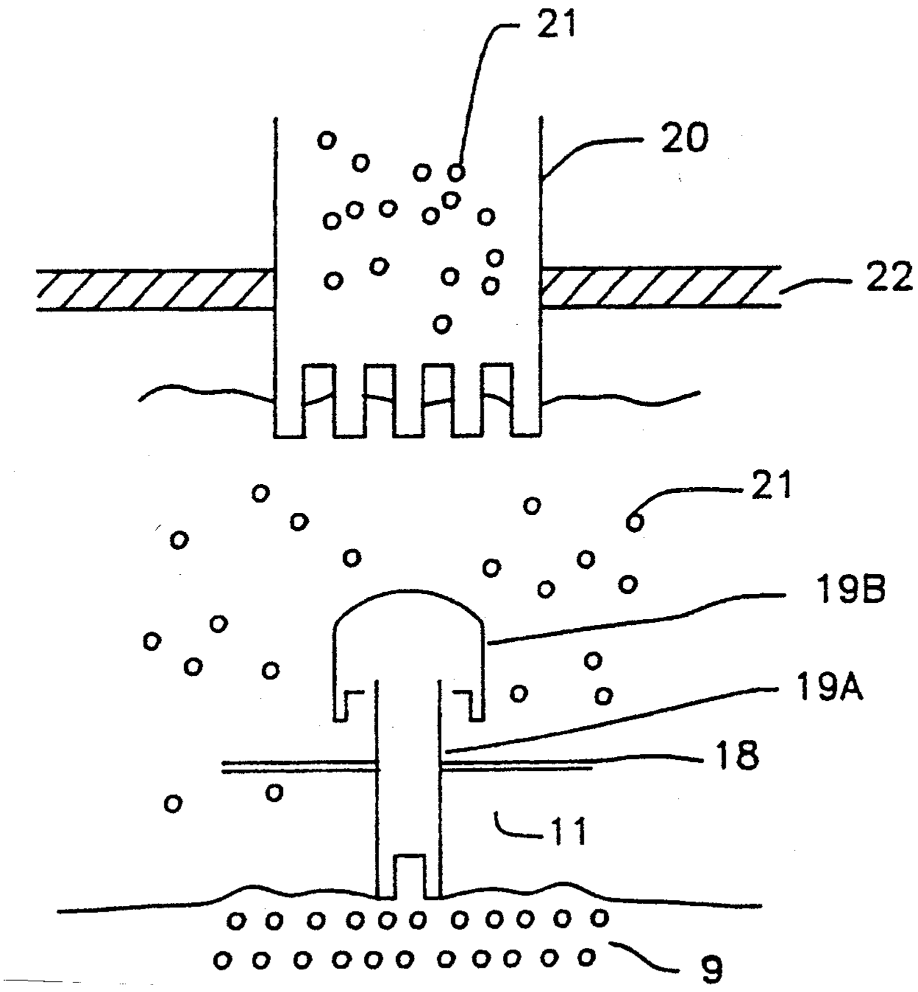

Figure X.25. Detail of a possible distribution zone for one reaction tube/zone.

APPENDIX - EXXON PATENTS

The following provides a listing of the primary claim from the patents reviewed during the preparation of this document. It is intended to provide a scope of the coverage of the initial report and the first addendum.

1. Gates, William, R. Fiato; Catalysts in FT process for producing olefins; Patent 4,639,431 (1987). **Claim 1:** A hydrocarbon synthesis catalyst comprising a sintered combination of metal oxides having the following components: (a) an oxide of a Group VIII metal; (b) an oxide of a Group IIB metal; (c) an oxide of a Group IA alkali metal; and (d) an oxide of a lanthanide metal, such that said sintered combination comprises a series of the Group VIII metal and the Group IIB metal spinels and the alkali metal oxide dispersed in a lanthanide metal oxide matrix.

2. Kim, Chang; R. Fiato; Multi-state FT process, patent 4,624,968, (1986). **Claim 1:** A process for producing paraffinic hydrocarbons from carbon monoxide and hydrogen comprising: (a) introducing carbon monoxide and hydrogen into a reaction zone wherein the carbon monoxide and hydrogen contact in a first bed a first catalyst having a high olefin selectivity selected from the group consisting of Fe/Ce/Zn/K, Fe/Mn/K and Fe/Co/K; and (b) contacting the resulting olefin in a second bed with a second catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons selected from the group consisting of Ru/TiO_2, Ru/SiO_2 and Ru/Al_2O_3.

3. Fiato, Rocco; S. Soled; FT hydrocarbon synthesis with high surface area Cu and K-promoted reduced-carbided iron/manganese spinels; Patent 4,621,102, (1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising contacting a catalyst composition, comprising at least one unsupported, single phase, iron-manganese spinal dual promoted with both copper and a Group IA and IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/G and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_2-C_{20} olefins.

4. Soled, Stuart, R. Fiato; Copper promoted iron/cobalt spinels and their preparation; patent 4,607,020 (1986). **Claim 1:** A composition of matter comprising a reduced and carbided, copper promoted iron-cobalt alloy, said composition being substantially isostructural with chi-Fe_5C_2, as determined by X-ray diffractometry and possessing a BET surface area of greater than 5 m^2/g, said composition produced by contacting, with a carbiding atmosphere for a time sufficient to produce said composition, said copper-promoted iron cobalt alloy, being isostructural with metallic alpha iron as determined by powder X-ray diffractometry, possessing a BET surface area of greater than 5 m^2/g, wherein said alloy was produced by contacting, with a reducing atmosphere, an

unsupported Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4, and possessing a BET surface area greater than 5 m^2/g and an iron-cobalt atomic ratio of 4 to 1 or above.

5. Iglesia, Enrique, S. Soled, R. Fiato, J. Baumgartner; Selective fixed-bed FT synthesis with high surface area Cu and K promoted, iron/manganese spinels; Patent 5,118,715 (June 1992). **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-400^{o}C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

6. Soled, Stuart, S. Miseo, E. Iglesia, R. Fiato; Iron-zinc based catalysts for the conversions of synthesis gas to alpha-olefins; patent 5,100,856 (Mar. 1992). **Claim 1:** A composition comprising of iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, or mixtures thereof, wherein the iron:zinc atomic ratio is at least about 5:1, and the alkali metal:copper atomic ratio is at least about 2:1.

7. Fiato, Rocco; G.McVicker, A. Montagna; Process for preparing a Fe-CO catalyst slurry system for alpha olefin production; Patent 4,532,229 (Jul 1985). **Claim 1:** A process for preparing a slurry Fischer-Tropsch catalyst system comprising the steps of: (a) heating a slurry mixture comprised of a Fischer-Tropsch slurry liquid, an iron carbonyl compound, a cobalt carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in an atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound; and (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating and slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products.

8. Cody, Ian; D. Brown; Wax isomerization using small particle low fluoride content catalysts; patent 4,923,588 (May 1990). **Claim 1:** A method for the isomerization of waxes into liquid hydrocarbons comprising passing the wax to be isomerized in the presence of hydrogen and under isomerization conditions over an isomerization catalyst comprising a noble Group VIII metal on small particle size, fluorided, refractory metal oxide wherein the catalyst possesses a fluoride content in the range of 0.1 to up to but less than 2.0 wt.% and the small particle size refractory metal oxide has a particle diameter of less than 1/16 inch.

9. Pedrick, Larry; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; Patent 5,268,344 (Dec. 1993); **Claim 1**: A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst int the top of the slurry phase in the slurry phase reactor through the open to of the draft tube means.

l0. Kugler, Edwin, S.Tauster, S. Fung; Ruthenium supported on manganese oxide as hydrocarbon synthesis catalysts in Co/H2 reactions; patent 4,206,134 (June 1980). **Claim 1:** A process for the enhanced synthesis of C_2-C_4 olefins with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO ratio of from about 10 to about 0.1 over a catalyst reduced at a temperature greater than about 300°C comprising ruthenium on a manganese-containing oxide support, wherein said manganese-containing oxide support is selected from the group consisting of MnO, Al_2O_3-MnO, SiO_2-MnO, MnO-carbon, Group IVB-manganese oxide, Group VB-manganese oxides, Group IA-manganese oxides, Group IIA-manganese oxides, rare earth-manganese oxides and mixtures thereof, at a space velocity of from about 100 hr^{-1} to about 50,000 hr^{-1}, at a temperature of from about 100°C to about 500°C at a pressure of from about 103 to about 1.03×10^5 kPa for a time sufficient to effect the generation of the desired olefinic product, wherein the concentration of said ruthenium in said catalyst is from about 0.01 to about 15% by weight.

ll. Madon, Rostam; Liquid hydrocarbon synthesis using supported ruthenium catalysts; patent 4,477,595 (Oct. 1984). **Claim 1:** A process for selectively producing paraffins comprising (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon,TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates,V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-NbO_5, SiO_2-Ta_2O_5, V_2O_3-carbon,

Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth Group VB oxides, alkali-group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at Fischer-Tropsch conditions such that the temperature ranges from about 100 to 400^{o}C, the pressure ranges from about 0.2 to 10 MpaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr, and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/MPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5-C_{40} hydrocarbons, containing C_5-C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least about 1.5.

12. Wachs, Israel, C. Chersich; Catalysts comprising tantala supported on titania; patent 4,544,649 (Oct. 1985). **Claim 1:** A catalyst composition comprising an oxide of tantalum supported on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

13. Kim, Chang; Reducing methane productions in FT reactions; patent 4,547,525 (Oct. 1985). **Claim 1:** A process for reducing methane formation in a Fischer-Tropsch process for synthesizing hydrocarbons which comprises contacting, at an elevated temperature of 100-500^{o}C and a pressure of from about 100-10,000 kPa, a H_2/CO feed mixture with a heterogeneous catalyst comprising one or more Group VIII metals supported on an inorganic refractory oxide support for a time sufficient ro produce hydrocarbons, including methane, wherein one or more olefins is added to the H_2/CO feed mixture in an amount sufficient to reduce said methane formation to a level lower than it would be without adding said olefin to said feed.

14. Mauldin, Charles; Cobalt catalysts for the conversion of methanol to hydrocarbons and for FT synthesis; patent 4,568,663 (Feb. 1986). **Claim 1:** A catalyst useful for the conversion at reaction conditions of methanol or synthesis gas to hydrocarbons by contact with a catalyst which comprises cobalt and thoria in catalytically active amounts and ruthenium, composited with an inorganic oxide support in weight ratio of ruthenium:cobalt ranging from about 0.025:1 to about 0.10:1.

15. Arcuri, Kym; C. Mauldin, D. Shaw; Ruthenium rhenium catalyst on titania support for FT synthesis; patent 4,558,030 (Dec. 1985). **Claim 1:** A catalyst composition useful for the synthesis of hydrocarbons from admixtures of carbon monoxide and hydrogen at reaction conditions which comprises: ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

16. Payne, Virgil; C. Mauldin; Preparation of hydrocarbons from synthesis gas; patent 4,959,703 (June 1986). **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

17. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalyst in CO/H2 FT synthesis reactions; Patent 4,154,751 (May 1979). **Claim 1:** In a Fischer-Tropsch process reaction for the production of hydrocarbons from CO and H_2 wherein CO and H_2 are passed over a catalyst the improvement comprising using as the catalyst a supported potassium or rubidium-Group VIII metal cluster catalyst which catalyst is prepared by depositing a known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complex on a high surface area support, drying the carbonyl cluster complex impregnated support in the absence of oxygen and reducing the supported complex at elevated temperatures, wherein using this catalyst in Fischer-Tropsch processes results in the selective formation of higher molecular weight paraffinic and olefinic hydrocarbons.

18. Fiato, Rocco; S. Soled; Cobalt promoted catalyst for use in FT slurry process; patent 4,544,672 (Oct. 1985). **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2-C_4 olefins comprising the step of contacting a liquid slurry catalyst system, comprised of a slurry liquid and a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst containing a Group IA or IIA metal salt promoter agent, and said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of up to 5 m^2/g, said process being conducted with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said product C_2-C_4 olefins.

19. Fiato, Rocco, S. Soled, A. Montagna; Cobalt promoted FT catalysts patent 4,544,674 (Oct. 1985). **Claim 1:** A fixed bed process for synthesizing a hydrocarbon mixture containing C_2-C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported Group IA or IIA metal salt promoted iron-cobalt spinel: said spinel exhibiting a single spinel phase, being isostructural with Fe_3O_4 as determined by X-ray diffractometry and possessing a BET nitrogen surface area of up to 5 m^2/g, and an iron-cobalt atomic ratio of 7:1 or above; with a mixture of CO/hydrogen under process

conditions of pressure, space velocity (SHSV) and elevated temperature for a time sufficient to produce said C_2-C_6 olefins.

20. Vaughan, David; K. Strobmaier; Synthesis of ECR-26(C-2646); patent 5,283,047 (Feb. 1994). **Claim 1:** A synthetic transition metal aluminosilicate crystalline zeolite having the gmelinite structure and a chemical composition in the dehydrated form: 0.8 to 1.3 $M_{2/n}O:(Al,Fe,Cr)_2O_3$:4 to 8 SiO_2, where n is the valence of metal M; the atoms of Al$\geqq$ atoms of

$$(Cr + Fe), \frac{Cr}{Cr + Al + Fe} \geq 0.05$$

and characterized by an X-ray diffraction pattern having the following essential lines:

dD	I/Io
11.9	VS
6.8	S
5.0	VS
5.59	M
4.11	MS
3.44	MS
2.97	MS
2.85	M
2.59	M

21. Iglesia, Enrique, S. Soled, R. Fiato; SiO2 promoted cobalt catalyst on a support of TiO2 for converting synthesis gas to heavy hydrocarbons; patent 4,794,099 (Dec. 1988). **Claim 1:** A hydrocarbon synthesis catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprised of a major portion of titania to which a lesser portion up to about 15 wt.% of silica in the form of silica or a silica precursor has been added.

22. Iglesia, Enrique, R. Madon; Reducing methane production and increasing liquid yields in FT reactions; patent 4,754,092 June (1988); **Claim 1**: A process for reducing methane formation and increasing liquid (C_5+) yields in a Fischer-Tropsch hydrocarbon synthesis process comprising adding an olefin to a gas feed and contacting said gas feed comprising a mixture of H_2 and CO with a catalyst at an elevated temperature of at least about 100^{o}C, said addition of said olefin and said contacting with said gas feed occurring within the reactor bed in the area of the reactor bed below 10% of the distance from the top to the bottom

of the reactor bed and above 10% of the distance from the bottom to the top of the reactor bed in an amount sufficient to reduce said methane formation, wherein said catalyst comprises a catalytic metal selected from the group consisting of iron, cobalt and ruthenium supported on an inorganic refractory oxide support.

23. Fiato, Rocco, S. Miseo; Process for the preparation of slurried CO hydrogenation catalysts; patent 4,749,677 (June 1988) **Claim 1**: A process for forming a slurry catalyst composition produced by the steps of: (a) adding to a stirred slurry reactor TiO_2, ruthenium carbonyl complex and an inert alkane hydrocarbon; (b) sealing said stirred slurry reactor and adding a gas mixture of N_2:CO at room temperature and one atmospheric pressure to said stirred slurry reactor to purge said stirred slurry reactor; (c) heating said stirred slurry reactor t o about 100^oC and raising the pressure of said stirred slurry reactor to about 4 to about 10 atmospheres and adding a gas mixture of $N_2:H_2$ to said stirred slurry reactor; and (d) increasing the temperature of said stirred slurry reactor to about 230^oF to about 270^o and the pressure of said stirred slurry reactor from about 4 to about 20 atmospheres for about 2 to about 6 hours to cause the decomposition of said ruthenium carbonyl complex to form said slurry catalyst composition.

24. Iglesia, Enrique, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patnet 4,738,948 (Apr. 1988). **Claim 1**: A hydrocarbon synthesis catalyst prepared by a process comprising impregnating a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

25. Wachs, Israel, D. Yang; Catalysts comprising ruthenium on titania surface modified with group VA oxide of vanadium, niobium or tantalum; patent 4,711,871 (Dec.1987). **Claim 1:** A process for preparing a catalyst comprising ruthenium supported on a surface-modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania wherein said process comprises the sequential steps of: (a) forming said support comprising titania whose surface has been modified with and supports an oxide of a metal selected from the group consisting of niobium, tantalum, vanadium or mixture thereof wherein said supported, modifying oxide is a non-crystalline form; (b) impregnating said so-formed surface modified titania support with a solution of a ruthenium precursor compound; and (c) converting said ruthenium precursor compound to ruthenium to form said catalyst.

26. Mauldin, Charles, S. Davis, K. Arcuri; Cobalt catalysts for the conversion of methanol and for FT synthesis to produce hydrocarbons; patent 4,663,305 (May 1987). **Claim 1:** A regeneration stable catalyst for the conversion at reaction conditions of methanol or synthesis gas to liquid hydrocarbons which consists

essentially of from about 2% to about 25% cobalt, based on the weight of the catalyst composition, composited with titania, or a titania-containing support, to which is added sufficient of a zirconium, hafnium, cerium, or uranium promoter to provide a weight ratio of the zirconium, hafnium, cerium, or uranium metal:cobalt greater than about 0.101:1.

27. Fiato, Rocco, R. Bar-Gadda, S. Miseo; Cerium promoted FT catalysts; patent 4,657,885 (Apr. 1987). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising sintered combination metal oxides having the following components in the stated weight percentage of the catalyst composition: (a) about 5 to about 80 wt.% of a Group VIII metal oxide; (b) about 4 to about 40 wt.% of a Group IIB metal oxide; (c) about 10 to about 40 wt.% of a Group IVB and/or VIIB metal oxide; (d) about 1 to about 5 wt.% of a Group IA metal oxide; and (e) about 1 to about 10 wt.% of a Lanthanum Group metal oxide, such that where the catalyst contains a Group VIII metal, said sintered combination comprises a series of spinels of a Group VIII metal, a Group IIB metal, and/or a Group IVB metal, and/or a Group VIIB metal, and a Group IA metal oxide in a lanthanum Group metal oxide matrix.

28. Mauldin, Charles; Start-up with ruthenium catalysts; patent 4,647,592 (MAR. 1987). **Claim 1:** In a process for the conversion of synthesis gas to hydrocarbons by contacting at reaction conditions a feed characterized as an admixture of carbon monoxide and hydrogen with a bed of particulate ruthenium catalyst constituted of a catalytically active amount of ruthenium composited with titania, or a titania-containing support, the improvement comprising contacting and pretreating the catalyst, prior to initiating the conversion reaction, with an admixture of steam and hydrogen at temperatures ranging from about 200°C to about 550°C sufficient to mildly agglomerate and ruthenium and form on the particles of catalyst larger agglomerates of ruthenium of average crystallize size from about 15 D to about 25 D approximating that obtained on completion of the startup portion of a synthesis gas operating run.

29. Arcuri, Kym; Process for the start-up of a FT reactor; patent 4,626,552 (Dec. 1986). **Claim 1**: In a process for the startup of a reactor wherein a feed comprised of hydrogen and carbon monoxide is contacted with a bed of hydrocarbon synthesis catalyst in which perturbations of the temperature profile across the bed can develop, and which, at line-out conditions defined by feed flow rate, pressure, temperature, and the molar ratio of hydrogen:carbon monoxide of the feed is sufficient to synthesize hydrocarbons from the hydrogen and carbon monoxide, the improvement which comprises: elevating, while maintaining the molar feed ratio of hydrogen:carbon monoxide at below about 90% of its line-out value, the feed flow rate, pressure and temperature to values approaching line-out feed flow rate, line-out pressure and line-out temperature and then gradually increasing the molar feed ratio of hydrogen:carbon monoxide to essentially that employed at line-out.

30. Davis, Stephen M.; Silica modified hydroisomerization catalyst; U.S. patent 5,187,138 (Feb. 1993). **Claim 1:** A catalyst composition comprising: a Group VIII metal; a support therefore of alumina or silica-alumina wherein the silica content is less than about 35 wt.%; at least about 0.5 wt.% silica other than the support silica; and a surface area of about 180-400 m^2/gm.

31. Hamner, Glen P.; Process for the isomerization and hydrocracking of FT waxes to protect a syncrude and upgraded hydrocarbon products; patent 4,832,819 (May 1989). **Claim 1:** A process for producing a pumpable syncrude from a Fischer-Tropsch wax containing oxygenate compounds, which comprises: (1) separating the FT wax into (a) a low-boiling fraction which contains most of the oxygenate compounds and (b) a high-boiling fraction which is substantially free of water and oxygenate compounds, (2) reacting the high-boiling fraction from step (1) with hydrogen at hydroisomerization and mild hydrocracking conditions in the presence of a fluorided Group VIII metal-on-alumina catalyst to produce a C_5+ hydrocarbon product, and (3) combining the C_5+ hydrocarbon product from step (2) with the low-boiling fraction from step (1) to produce a pumpable, refinery processable syncrude that can be transported at atmospheric conditions.

32. Hsia, Stephen J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; patent 5,260,239 (Nov. 1993). **Claim 1**: A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down this first downcomer C conduit means from the top of the first vessel means to the bottom of a reactivation C rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated C rejuvenated in said second vessel means, collecting reactivated C rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated C rejuvenated catalyst down the second downcomer C conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.

33. Mitchell, Willard N.; Activation of hydrocarbon synthesis catalyst; patent 5,292,705 (Mar. 1994). **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with

hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

Examples. In a hydrocarbon synthesis process demonstration unit, lhydrogen treatment of the catalyst to enhance initial activity for slurry phase operations was demonstrated. In the unit, fresh catalyst 12 st% Co, 1 wt% Re on a titania support with 6 wt% Al_2O_3 as a binder material, was activated by first reducting the catalyst in hydrogen to reduce the cobalt oxide to the cobalt metal. This was accomplished in a **fluid bed reactor** at temperatures up to about 375°C. The H_2 treat gas rate was 8-18 SCFH H_2/lb catalyst with a H_2 concentration of 18-25% in N_2. Following the reduction the catalyst was passivated with 0.25-1.3 SCFH of CO in N_2+H_2 for 1-2 hours.

> The dry reduced catalyst [presumably they mean the dry reduced and passivated catalyst] with was combined with a wax to form a slurry in a slurry mix vessel. The slurry was transferred to the hydrocarbon synthesis reactor and synthesis was initiated. Followingg a shor test to measure initial catalyst productivity, a hydrogen treat was conducted in the slurry reactor ("super" activation). The following table shows two samples of this "super" activation:

	Relative Productivity	
	Before	After
Example 1	60	100
Example 2	25	100

In the first example the relative productivitry increased from 40% to 100% and the second case from 25% to 100%. The conditions for the H_2 treat of the slurry were typical of conditions described earlier.

> In order to determine the real increase in initial activity, the catalyst had to be run at synthesis conditions for a period sufficient to obtain an initial activity or productivity. However, this minimal operation at synthesis conditions is not believed to change or effect the catalyst in any substantive way and the catalyst may be considered as essentially fresh catalyst.

34. Chang, Min; C. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); patent 5,252,613 (Oct. 1993). **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas

distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

35. Kim, Chang J.; Water addition for increased Co/N2 hydro-carbon synthesis activity over catalysts comprising cobalt, ruthenium and mixtures thereof which may include a promoter metal; patent 5,227,407 (Jul 1993). **Claim 1:** A once-through, fixed or slurry bed FT process with CO conversion activity and C_5+ liquid hydrocarbon selectivity comprising contacting a feed mixture of carbon monoxide and hydrogen in a reaction zone with about 1 vol.% to about 70 vol.% water based on the total volume of feed mixture, at a pressure above one atmosphere and a temperature ranging from about 150^oC to about 300^oC, wit a catalyst selected from the group consisting of cobalt, ruthenium, and mixtures thereof on a titania support, wherein said titania support is less than 40 m^2/g, converting at least 90 vol.% of the carbon monoxide to liquid hydrocarbons, and in the substantial absence of CO_2 formation.

36. Soled, Stuart, E. Iglesia, R. Fiato, G. Ansell; Method for stabilizing titania supported cobalt catalyst and the catalyst for use in FT process; patent 5,169,821 (Dec. 1992). **Claim 1:** A method of preparing a 400-750^oC regeneration stable catalyst composition comprising: (a) coprecipitating a titanium metal complex from a solution of a titanium alkoxide and a metal alkoxide or a solution of titanium chloride and a metal chloride wherein said metal is selected from the group consisting of silicon, zirconium and tantalum; (b) recovering the coprecipitate and calcining at temperatures of 400-750^oC, to form a ternary metal oxide support; (c) depositing a cobalt compound onto said calcined ternary metal oxide support; (d) activating said cobalt calcined support to form a catalyst comprised of cobalt on a substituted ternary metal oxide support of titania having the general formula $Co/Ti_xM_{1-x}O_2$ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum, wherein the titania is an anatase polymorph.

37. Soled, Stuart, E. Iglesia, R. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for FT synthesis; patent 5,162,284 (Nov. 1992). **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2.

38. Mauldin, Charles, K. Riley; Process for the preparation of surface impregnated dispersed cobalt metal catalysts; patent 4,977,126 (Dec. 1990). **Claim 1**: In a process for the production of catalysts wherein a catalytically effective amount of cobalt is impregnated and dispersed on the outer surface of a particulate porous inorganic oxide support to form a catalyst useful for the conversion of synthesis gas to hydrocarbons, and the support particles are contacted with a spray containing a decomposable compound of cobalt, the improvement comprising: maintaining a bed of the support particles in a fluidized state at temperature ranging from about 50^oC to about 100^oC by contact with a gas at temperature ranging from about 50^oC to about 100^oC; spraying the bed of the heated support

particles with a liquid in which a cobalt compound is dispersed at flow rate sufficient to provide a ratio between the flow rate of the liquid: flow rate of the fluidizing gas below about 0.6 grams liquid/ft^3 of fluidizing gas to form on the particles a surface layer of cobalt compound in average thickness ranging from about 20 microns to about 250 microns, with the loading of cobalt compound ranging from about 0.01 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst.

39. Iglesia, Enrique; S. Soled, R. Fiato; Synthesis gas to heavy hydrocarbons on SiO2 promoted Co/TiO2; patent 4,960,801 (Oct. 1992). **Claim 1:** A process for preparing C5+ hydrocarbons which comprises reacting hydrogen and carbon monoxide at hydrocarbon synthesis reaction conditions in the presence of a catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprising a major portion of titania to which a lesser portion up to about 15 qt.% silica in the form of silica or a silica precursor has been added.

40. Pedrick, Larry E.; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; patent 5,268,344, (Dec. 1993). **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

45. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalysts in CO/H2 FT synthesis reactions; patent 4,192,777 (Mar. 1980). **Claim 1:** Supported, highly dispersed, high activity potassium or rubidium-Group VIII metal cluster catalysts demonstrating improved selectivity olefinic and paraffinic hydrocarbons in CO/H_2 reactions prepared by the process which comprises depositing known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complexes and mixtures thereof on a high surface area support material, drying the carbonyl cluster complex impregnated support in the absence of oxygen, and reducing the supported complex at elevated temperatures to effect the essentially complete reduction of the supported potassium or rubidium-Group VIII metal carbonyl cluster complexes to discrete potassium or rubidium-Group VIII clusters of metals on the support surface.

46. Wright, Franklin; M. Richard, J. Pirkle; Process using iron-thallium catalysts in CO hydrogenation; patent 4,513,104 (Apr. 1985). **Claim 1:** A process for producing liquid hydrocarbons, including those in the C_6-C_{11} hydrocarbon range,

comprising the steps of: (a) first depositing thallium on the surface of a supported or unsupported iron catalyst wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compounds contain iron value substantially in the trivalent state; (b) contacting said iron-thallium catalyst with a mixture of CO and H_2 in a volume ratio of about 1:4 to 4:1, respectively, at a temperature ranging from 270 to 550°C, a pressure ranging from 0.1 to 10 MPa and a space velocity ranging from 10 to 10,000 v/v/hr, or equivalent conditions, for a sufficient time to substantially convert said thallium compounds to metallic thallium and said iron compounds to reduced and carbided iron; and (c) continuing said contacting as described in step (b) at a pressure above 0.1 MPa, a temperature ranging from 230 to 550°C, to produce liquid hydrocarbons comprising about 40 wt.% and greater C_6-C_{11} liquid hydrocarbons and below about 5 wt.% C_{23}+ hydrocarbons.

47. Wright, Franklin; Iron-thallium catalysts for use in CO hydrogenation and process of preparing the catalysts, Patent 4,436,834 (Mar. 1984). **Claim 1:** A catalyst composition consisting essentially of a mixture of an iron compound and a thallium compound, being supported or unsupported, said compound of iron and thallium being selected from the group consisting of an oxide, hydroxide, carbonate, sulfate, carbide, halide, nitrate, or mixtures thereof, wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compound contains iron value substantially in the trivalent state, and wherein said thallium compound is substantially deposited on the surface of said iron compound.

48. Soled, Stuart, R. Fiato; Process for preparing high surface area iron/cobalt FT slurry catalysts; patent 4,518,707 (May 1985). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4, and possessing a BET surface area greater than 5 m^2/g and an iron-cobalt atomic ratio of 4 to 1 or above.

49. Soled, S. L. and R. A. Fiato; Process for preparing high surface area iron/cobalt Fischer-Tropsch slurry catalysts; U.S. Patent 4,544,671, Oct. 1, 1985. **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial BET surface area greater than 5 m^2/g and an Fe:Co atomic ratio of 7:1 and above, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

50. Fiato, Rocco; S. Soled, A. Montagna; Promoted iron-cobalt spinel catalyst for FT process; patent 4,537,867 (Aug. 1985). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising an unsupported, Group IA or IIA metal salt

promoted iron-cobalt single phase spinel, said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the proviso that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and said spinel having an initial BET surface area of up to about 5 m^2/g.

51. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ni supported on a titanium oxide; U. S. Patent 4,042,615, Aug. 16, 1977. **Claim 1:** A process for the synthesis of higher molecular weight paraffins comprising the steps of passing CO and H_2 in a CO/H_2 ratio of 10 to 0.1 over a catalyst comprising nickel on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 tp 50,000 v/v/hr and a temperature of from 100 to 500 and ^oC at pressure of from 103 to 1.03×10^5 kPa for a time sufficient to effect the generation of the desired paraffinic products in the desired ratio, wherein the concentration of said nickel in said catalyst is from 0.01 to 75% by weight.

52. Tauster, S. J. and S. C. Fung; Group VIII metals on manganese-containing oxide supports which exhibit strong supports which exhibit strong metal support interactions; U.S. Patent 4,402,869, Sept. 6., 1983. **Claim 1:** Improved catalytic compositions comprising catalytic metal selected from the group consisting of iron, nickel, cobalt and mixtures thereof supported on a manganese-containing oxide support, the improvement comprising as a final step before use, contacting said catalyst composition with a reducing atmosphere at a temperature of at least about 300^oC to produce at catalyst composition which exhibits suppressed hydrogen chemisorption.

53. Wachs, Israel; R. Fiato, C. Chersich; Iron carbide on titania surface modified with group VA oxides as FT catalysts; patent 4,559,365 (Dec. 1985). **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous feed mixtures of CO and H_2 comprising contacting said feed, at a temperature ranging from about 200 to 350^oC and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum and mixture thereof supported on titania wherein at least a portion of said supported oxide is in a non-crystalline form.

54. Soled, Stuart, R. Fiato; FT hydrocarbon synthesis with copper promoted iron/cobalt spinel catalyst; patent 4,584,323 (Apr. 1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising contacting a catalyst composition, comprising an unsupported, copper promoted iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial

BET surface area greater than 5 m^2/g and an Fe:Co atomic ratio of 4:1 and above, with a mixture of CO and hydrogen in a slurry liquid under conditions of pressure, space velocity and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

56. Kugler, E. L. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using titanium promoted bulk nickel catalysts; U.S. Patent 4,273,724, June 16, 1981. **Claim 1:** A process for the synthesis of higher molecular weight paraffinic hydrocarbons of from C_2 to C_7 carbon number comprising the steps of passing CO and H_2 at a CO/H_2 ratio of from 10 to 0.1 at a space velocity of from 100 hr^{-1} to 50,000 hr^{-1}, at a temperature of from 100 to 500°C and at pressures of from 103 to 1.03×10^5 kPa over a catalyst comprising bulk nickel promoted with from 0.07 to 10 wt.% titanium containing oxide (calculated as TiO_2) for a time sufficient to effect the generation of the desired paraffinic products.

57. Vannice, M. A. and S. J. Tauster; Hydrocarbon synthesis from CO and H_2 using Ru supported on group VB metal oxides; U.S. Patent 4,171,320, Oct. 16, 1979. **Claim 1:** A process for the synthesis of olefins of from C_2 to C_5 chain length inclusive, said process comprising the steps of passing H_2 and CO at a H_2/CO ratio of 0.1 to about 10 over a catalyst comprising ruthenium on a support selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth group VB oxides, alkali Group VB oxides, rare earth Group VB oxides, Group IVB-Group VB oxides and mixtures thereof, at a space velocity of from 100 to 50,000 hr^{-1}, at a temperature of from 100 to 500°C, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic products wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15 wt.% based on total catalyst weight.

58. Fiato, Rocco; S. Soled; High surface area dual promoted iron/manganese spinel compositions; patent 4,618,597 (Oct. 1986). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal and copper promoted, single phase, iron-manganese spinel, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and possessing a BET surface area greater than 30 m^2/g and an iron-manganese atomic ratio greater than about 2:1.

59. DeLuca, J. P., L. L. Murrell, R. P. Rhodes and S. J. Tauster; Stabilized ruthenium catalysts for selective reduction of oxides of nitrogen; U.S. Patent 3,922,235, Nov. 25, 1975. **Claim 1:** A stabilized supported ruthenium catalyst, said catalyst comprising ruthenium metal in combination with an oxide support, said support being one selected from the group consisting of zirconium titanate, and zirconium titanate mixed with titania, the ruthenium being present in an amount which does not exceed 0.003 grams of ruthenium per gram of oxide support.

71. Kugler, E. L. and S. J. Tauster; Catalyst comparison nickel supported on tantalum oxide or niobium oxide and their use as hydrocarbon synthesis catalysts in CO/H_2 reactions; U.S. Patent 4,206,135, June 3, 1980. **Claim 1:** A process

for the enhanced synthesis of paraffinic hydrocarbons of from 2 to 6 carbon atoms inclusive with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO mole ratio of from about 0.1 to about 10 over a catalyst reduced at a temperature of at least 375°C comprising nickel on a tantalum or niobium-containing oxide support wherein said tantalum or niobium-containing oxide support is selected from the group consisting of tantalum oxides, niobium oxides, Al_2O_3-Ta_2O_5, Al_2O_3-Nb_2O_5, SiO_2-Ta_2O_5, SiO_2-Nb_2O_5, Ta_2O_5-carbon, Nb_2O_5-carbon, alkaline earth-tantalum oxides, alkaline earth-niobium oxides, alkali-tantalum oxides, alkali-niobium oxides, rare earth-tantalum oxides, rare earth-niobium oxides, Group IVb-tantalum oxides, Group IVb-niobium oxides, and mixtures thereof, at a space velocity of from 100 hr^{-1} to about 50,000 hr^{-1}, at a temperature of from about 100°C to about 500°C, at a pressure of from about 100 to about 1×10^5 kPa, for a time sufficient to effect the generation of the desired paraffinic product, wherein the concentration of said nickel in said catalyst is from about 0.01 to about 75 wt.%.

72. Murrell, L. I. and S. J. Tauster; Catalytic process for NO_x reduction under lean conditions; U.S. Patent 4,039,622, Aug. 2, 1977. **Claim 1:** A process for effecting the selective reduction of NO_x in lean effluent waste streams containing NO_x, CO, O_2, H_2, CO_2 and water, wherein the concentration of CO is at least equivalent to the concentration of NO_x present in the waste stream, a lean effluent waste stream being defined as one in which the concentration of oxygen is in excess over the concentration of reductants to a level as high as 8%, i.e,. about 800% excess oxygen, over the total of reductants present, said reductants being selected from the group comprising CO and H_2 so that when such a waste stream is reacted to completion, the residuum is oxidizing in character, said process comprising the steps of contacting said lean exhaust stream in a reaction zone with an iridium catalyst, said contacting occurring at a temperature between 300OC to 750°C thereby effecting the selective reduction by CO of the oxides of nitrogen to molecular nitrogen.

73. ;Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and $_2$ using Rh supported on titanium oxides; U.S. Patent 4,116,994, Sept. 26, 1978. **Claim 1:** A process for the enhanced synthesis of olefins and paraffins, wherein said paraffins are other than methane, comprising the steps of passing H_2 and CO in a H_2/CO ratio of 0.1 to 10 over a catalyst comprising rhodium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr and at a temperature of from 100 to 500°C, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic and paraffinic products in the desired ratio, wherein the concentration of said rhodium in said catalyst is from 0.01 to 10% by weight.

74. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO, H_2 mixtures and process for maintaining catalytic activity; U.S. Patent 4,093,643,

June 6, 1978. **Claim 1:** A process to produce low molecular weight organic compounds comprising substantially methane, said process consisting of the steps of passing a mixture of CO and H_2 over palladium supported on an acidic metal oxide selected from the group consisting of alumina and hydrogen-y-zeolite wherein the palladium metal particle size is maintained at less than 100 A by running at a reactor bed temperature of less than 350^{o}C, at a pressure ranging from 1 to 500 atm. and a GHSV of from 1200-4600 hr^{-1}.

75. Voorhies, Alexis, Jr., Hydrocarbon synthesis process, U.S. Patent 2,479,439, Aug. 16, 1949. **Claim 1:** An improved hydrocarbon synthesis process which comprises reacting together, under synthesis conditions, hydrogen and carbon monoxide initially in the presence of an unpromoted powdered iron catalyst in the form of a fluidized bed contained in a reaction zone, adding an alkali metal compound to the reaction zone at a slow rate during such a period of time as to cause a slow and homogeneous impregnation of said alkali metal compound within said catalyst, and to the extent that the desired yields or normally liquid hydrocarbons are obtained from the reaction zone, whereupon the feeding of the alkali metal compound is discontinued, the amount of said promoter with respect to the catalyst and contained thereon lying within the limits of from about 0.1 to 5 wt.% after the initial period, and adding water to the reaction zone to repress carbon formation in an amount such that the feed to the reaction zone contains 5 to 25 mols of hydrogen per mol of water.

76. Aldridge, C. L. and T. Kalina; Shift process for new catalysts; U.S. Patent 3,850,841, Nov. 26, 1974. **Claim 1:** A process for the preparation of hydrogen and carbon dioxide which comprises introducing a gas mixture containing monoxide and steam at a temperature varying from about 300 to 700^{o}F, and introducing at least a portion of said cooled reaction mixture to at least one additional shift reaction stage and contacting the same therein with a catalyst, the temperature within each said reaction stage being maintained above the dew point temperature of the reaction mixture and the pressure within each said reaction stage being maintained below the dew point pressure of said reaction mixture and ranging from about atmospheric to about 3000 psig, the catalyst in each reaction stage comprising (i) an alkali metal compound derived from an acid having an ionization constant of less than about 1x10^{-3} and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of (a) a metal composition comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof or (b) mixtures of materials comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof with a nickel, iron or chromium material or mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component to said alkali metal compound, each calculated on the basis of the oxides thereof, being less than 5:1.

77. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO hydrogen mixtures; U.S. Patent 3,941,819, March 2, 1976. **Claim 1:** A process for producing substantial amounts of dimethyl ether, said process comprising the

step of passing CO and H_2 over platinum supported on alumina, wherein the amount of platinum ranges from 0.3 to 2 wt.% based on total weight of the support including platinum at a temperature ranging from 200 to 300°C and a pressure ranging from 10.10 to 40 atm. and wherein the mol ratio of hydrogen to CO ranges from 0.1 to 2.

78. Kwang, K. K., R. E. Pennington, L. W. Vernon and N. C. Hahas; Methane production, U. S. Patent 3,958,957, May 25, 1976. **Claim 1:** A method for the production of a methane-rich gas which comprises introducing a gaseous mixture of hydrogen and at least one carbon oxide into a reaction zone containing a carbon-alkali metal catalyst at a temperature between about 800°F and about 1500°F and at a pressure between about atmospheric and about 2000 psig, said catalyst being prepared by heating an intimate mixture consisting essentially of a carbonaceous solid and an alkali metal constituent to an elevated temperature sufficient to produce a reaction between the carbon and alkali metal in said mixture and form a carbon-alkali metal reaction product, and recovering a methane-rich gas from said reaction zone.

79. Vannice, M. A.; Method for the direct preparation of halogenated hydrocarbons by the reaction of CO, H_2 and halogen in the presence of a catalyst; U.S. Patent 4,041,087, Aug. 9., 1977. **Claim 1:** method for the preparation of halogenated hydrocarbons of the formula $C_AH_{2A+2-B}X_B$ wherein x is a halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, A is an integer ranging from 1 to 4 inclusive and B is an integer ranging from 1 to 10 inclusive, except that 2A+2-B may not be less than zero, which method comprises the steps of: (1) preparing a system comprising CO, H_2 and a source of halogen wherein the source of halogen is selected from the group consisting of molecular halogen and hydrogen halides; (2) passing said system over a catalyst metal selected from the group consisting of Group VIII metals, rhenium, and platinum-iridium and platinum-rhenium alloys, which catalyst metal is in combination with an acidic inorganic oxide material; (3) heating the system containing the CO, H_2 and halogen source over the catalyst to a temperature in the range of 200-1000°C; and (4) pressurizing the system to a level in the range of 0.1 atm to 500 atm.

80. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ru supported on a titanium oxide; U.S. Patent 4,042,614, Aug. 16, 1977. **Claim 1:** A process for the selective synthesis of olefins from C_2 to C_{10} chain length inclusive, said process comprising the steps of passing H_2 and CO at a H_2/CO ratio of 0.1 to 10 over a catalyst comprising ruthenium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr at a temperature of from 100 to 500°C at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic products in the desired ratio wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15% by weight.

81. Yates, D. J. C. and L. L. Murrell; Method for preparing a highly dispersed supported nickel catalyst; U.S. Patent 4,073,750, Feb. 14, 1978. **Claim 1:** A highly dispersed nickel catalyst having a nickel surface area of from 200 to 400 m^2/g nickel prepared by the method which comprises slurrying a nickel metal precursor dissolved in a nonaqueous organic liquid solvent with a high surface area refractory oxide support, removing the solvent to obtain a composite of said nickel metal precursor and said support, and activating said composite by reducing in hydrogen or hydrogen dilutes with an inert gas at conditions sufficient to convert substantially all of the nickel metal precursor to nickel metal.

82. Tauster, S. J., L. L. Murrell and S. C. Fung; Supported metal interaction catalysts; U. S. Patent 4,149,998, April 17, 1979. **Claim 1:** Improved catalytic composition consisting of a metal selected from the group consisting of iridium, osmium, rhodium, and mixtures thereof and an oxide of titanium support prepared by depositing said iridium, osmium, rhodium and mixtures thereof on the oxide of titanium and pretreating the composition prior to use, the improvement comprising, as a final step before use, reducing the composition in a hydrogen atmosphere at a temperature of at least 200^oC, thereby producing a composition which exhibits suppressed hydrogen chemisorption.

83. Wheelock, K. S., Catalyst and a process for its preparation; U.S. Patent 4,219,447, Aug. 26, 1980. **Claim 1**: A catalyst useful for the conversion of a hydrocarbon feed by contact thereof at hydrocarbon conversion conditions which comprises a cluster of titanium metal oxide and a Group VIII noble metal deposited on the surface of an inorganic oxide support.

84. Murrell, L. L., C. J. Kim, and D. C. Grenoble; Acid catalyzed hydrocarbon conversion process utilizing a catalyst comprising a group IVB, VB or VIB metal oxide on an inorganic refractory oxide support; U.S. Patent 4,233,139, Nov. 11, 1980. **Claim 1:** In a hydrocarbon conversion process wherein hydrocarbon fractions are cracked over acid catalysts at elevated temperatures, the improvement comprising using as the catalyst a material comprising a catalytic metal oxide selected from the group consisting of the oxides of tungsten, niobium and mixtures thereof and tungsten or niobium oxides in combination with one or more additional metal oxides selected from the group consisting of tantalum oxide, hafnium oxide, chromium oxide, titanium oxide and zirconium oxide supported on an inorganic refractory metal oxide base selected from the group consisting of alumina, zirconia, boria, thoria, magnesia, zirconium-titanate, titania, chromia, kieselguhr and mixtures thereof, said catalyst being steamed prior to use.

85. McCandlish, L. E. and E. L. Kugler; CO hydrogenation process using molybdenum oxycarbonitride catalyst; U.S. Patent 4,418,154, Nov. 29, 1983. **Claim 1:** A process for preparing paraffinic hydrocarbons including linear and branchedC_1-C_{10} carbon chain numbers comprising contacting a gaseous mixture of CO and H_2 in a CO/H_2 volume ratio of 10:1 to 1:10, respectively, with a catalyst comprised of face-centered cubic molybdenum oxycarbonitride, in which the

interstitial oxygen, carbon and nitrogen atoms are distributed throughout the bulk structure, at a temperature of about 100 to 600^{o}C, a pressure of about 0.1 to 50,000 v/v/hr and recovering product paraffinic hydrocarbons.

86. Hallulin, A. P. and A. E. Burnett; Coprecipitated Si-Al-metal-particle catalyst; U. S. Patent 4,497,907, Feb. 5, 1985. **Claim 1:** A calcined support catalyst comprised of: (a) one or more metals which are catalytically active for the hydrogenation of organic compounds, (b) alumina and silica at a weight ratio of 0.45:1 to 1:0.45, respectively, and (c) solid porous particles, the catalyst being characterized as having a BET total surface area ranging from about 150 to about 350 m^2/g wherein the total amount of catalytically active metal in the catalyst ranges from about 10 wt.% to about 70 wt.% and wherein the catalyst has been prepared by: (aa) coprecipitating ions of one or more catalytically active metals, aluminum ions and silicate ions, with the solid porous particles, (bb) drying the coprecipitated catalyst and (cc) calcining the dried coprecipitated catalyst at a temperature from about 300 to 450^{o}C.

87. Mauldin, C. H.; Conversion of methanol to hydrocarbons; U.S. Patent 4,513,161, Apr. 23, 1985. **Claim 1:** A process useful for the conversion of methanol to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of methanol and hydrogen, in methanol:hydrogen molar ratio equal to or greater than about 2:1 at total pressure equal to or greater than about 160 psig, over a catalyst which comprises ruthenium in catalytically active amount composited with titania or titania-containing support.

88. Soled, S. L., A. Wold and R. Kershaw; Reduction process for forming powdered alloys from mixed metal iron oxides; U.S. Patent 4,525,206. **Claim 1:** A process for producing a powdered metal-based iron alloy comprising the steps of: (a) heating a mixture comprised of a powdered mixed metal iron oxide, being difficulty reducible in hydrogen gas, with at least a stoichiometric amount of calcium metal, in a non-oxidizing atmosphere, at a temperature below the melting point of the mixed metal iron oxide for a time sufficient to substantially reduce all the metal oxide present, and form said product metal-based iron alloy, as determined by X-ray diffractometry, (b) contacting said reduced mixed metal iron oxide with aqueous acid to remove calcium impurities and by-products; and (c) recovering said product metal-based iron alloy.

89. Payne, V. L. and C. H. Mauldin; Cobalt catalysts for the preparation of hydrocarbons from synthesis gas and from methanol; U.S. Patent 4,542,122, Sept. 17, 1985. **Claim 1:** A catalyst composition useful for the conversion of methanol or synthesis gas to hydrocarbons which consists essentially of cobalt, or cobalt and thoria in catalytically active amount composited with titania or a titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

90. Wachs, I and C. C. Chersich; Catalysts comprising tantala supported on titania; U.S. Patent 4,544,649, Oct. 1, 1985. **Claim 1:** A catalyst composition comprising

an oxide of tantalum support on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

91. Madon, R. J.; Liquid hydrocarbon synthesis using supported ruthenium catalysts; U.S. 4,477,595, Oct. 16, 1984. **Claim 1:** A process for selectively producing paraffins comprising: (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates, V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth Group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at FT conditions such that the temperature ranges from about 100 to 400^{o}C, the pressure ranges from about 0.2 to 10 mPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/he and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/mPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5-C_{40} hydrocarbons, containing C_5-C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least 1.5

92. Fiato, R. A. and E. L. Kugler; Production of alkanes from mixtures of CO and H_2; U.S. Patent 4,548,953, Oct. 22, 1985. **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous mixtures of CO and H_2 comprising contacting said mixture, at a temperature ranging from about 200 to 350^{o}C and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising a mixture of iron carbide and ilmenite supported on titania wherein the amount of said supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3, is at least about 2×10^{-3} grams per square meter of titania support surface.

93. Arcuri, K. B., C. H. Mauldin and D. H. Shaw; Ruthenium catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,567,205, Jan. 28, 1986. **Claim 1:** A process useful for the synthesis of hydrocarbons at reaction conditions from a feed constituting an admixture of carbon monoxide and hydrogen, which comprises contacting said feed with a catalyst which comprises ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

94. Halluin, A. P. and A. E. Barnett; Catalyst support compositions; U.S. Patent 4,593,014, June 3, 1986. **Claim 1:** A catalyst support composition consisting essentially of alumina and titania at a weight ratio of about 0.3:1 to 1:0.3

respectively, and solid porous particles selected from the group of kieselguhr, infusorial earth, diatomaceous earth and siliceous earth.

95. Fiato, R. A. and E. L. Kugler; Improving activity of iron carbide and ilmenite on titania Fischer-Tropsch catalyst; U.S. Patent 4,594,331, June 10, 1986. **Claim 1:** A process for improving the activity of a FT catalyst present in a FT reaction zone wherein said catalyst comprises a mixture of iron carbide and ilmenite supported on a titania support wherein the amount of iron present in said supported iron carbide and ilmenite mixture, calculated as Fe_2O_3, is at least about 2×10^{-3} grams per square meter of titania support surface and wherein said reaction zone contains a FT feedstream comprising a mixture of H_2 and CO, said process comprising reducing or eliminating the hydrogen content of the FT feedstream, raising the temperature in said reactor between about 50 to about 150°C above the FT reaction temperature for from about 1 to 6 hrs. and then lowering the temperature back to the reaction temperature and reestablishing the hydrogen content of the feedstream.

96. Payne, V. L. and C. H. Mauldin; Preparation of hydrocarbons from synthesis gas; U.S. Patent 4,595,703, June 17, 1986. **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

97. Wachs, I. E., R. A. Fiato and C. C. Chersich; Iron carbide on titania surface modified with Group VA oxides as Fischer-Tropsch catalysts; U.S. Patent 4,608,359, Aug. 26, 1986. **Claim 1:** A catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof supported on said titania wherein at least a portion of said supported oxide of niobium, vanadium, tantalum or mixture thereof is in a non-crystalline form, wherein the amount of said supported oxide ranges from about 0.5 to 25 wt.% metal oxide on the titania support based on the total support composition and wherein the catalyst contains at least about 2 milligrams of iron, calculated as Fe_2O_3 per square meter of support surface.

98. Fiato, R. A., G. B. McVicker and A. A. Montagna; Fe-Co catalyst slurry system for use in alpha olefin production; U.S. Patent 4,624,967, Nov. 25, 1986. **Claim 1:** A process for synthesizing hydrocarbons containing alpha olefins comprising contacting a gaseous feed mixture of H_2 and CO, in a reaction zone, with a slurry catalyst system at elevated temperature for a time sufficient to convert at least a portion of said gaseous feed to said alpha olefins, wherein said catalysts slurry system is prepared by a process comprising the steps of: (a) heating a slurry mixture comprised of: a FT slurry liquid, an iron carbonyl compound, a cobalt

carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in a atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound, (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition temperature of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating said slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products to form said catalyst.

99. Rice, G. W., R. A. Fiato and S. L. Soled; Promoted iron-carbon-based catalysts produced in the presence laser radiation; U.S. Patent 4,659,681, April 21, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm, and which particles are subsequently impregnated with at least 2% of a promoter selected from the group of the salts and oxides of alkali and alkaline earth metals.

100. Rice, G. W., R. A. Fiato and S. L. Soled; Iron carbide-based catalyst produced in the presence of laser radiation; U.S. Patent 4,668,647, May 26, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene, and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm.

101. Mauldin, C. H.; Improved cobalt catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,670,475, June 2, 1987. **Claim 1:** A process useful for the conversion or synthesis gas feed comprised of hydrogen and carbon monoxide to hydrocarbons which comprises contacting said feed at reaction conditions with a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with a titania or titania-containing support, to which is added sufficient rhenium to obtain, with a similar feed at

corresponding process conditions, improved activity, as contrasted with a catalyst composition otherwise similar except that it does not contain rhenium.

102. Fiato, R. A. and E. L. Kugler; Iron on titania Fischer-Tropsch catalyst; U.S. Patent 4,689,313, Aug. 25, 1987. **Claim 1:** A catalyst composition consisting essentially of catalytic components being selected from the group consisting of a mixture of iron carbide and ilmenite and a mixture of iron carbide and ilmenite containing at least one alkali metal promoter wherein the ratio of supported iron present in said supported iron carbide and ilmenite, calculated as FE_2O_3, to the surface area of said titania support ranges between about 2 to 25 milligrams per square centimeter, and wherein said catalyst has been formed by depositing an iron precursor salt of said catalytic component on said titania support, calcining said deposited salt and support to form a calcined composite and sequentially contacting said composite with a hydrogen containing reducing gas free of CO at elevated temperatures of from about 300 to about 500^{o}C for a time sufficient to reduce the calcined composite followed by contacting said reduced composite with CO at a temperature from about 100 to about 200^{o}C lower than the temperature used for said hydrogen contacting.

103. Fiato, R. A., R. Bar-Gadda and S. Miseo; Cerium promoted Fischer-Tropsch catalysts; U.S. Patent 4,719,240, Jan. 12, 1988. **Claim 1:** A hydrocarbon synthesis process comprising contacting a feed stream of CO and H_2 in a molar ratio of about 0.5 to about 4:1 with a catalyst at a temperature in the range of about 200 to 350^{o}C, a pressure in the range of about 1 to 50 atm, a space velocity in the range of about 10 to 10,000 v/v/hr to produce a hydrocarbon product containing ethylene and ethane in which the ethylene/ethane mole ratio is greater than one, and recovering the product; the catalyst being comprised of a sintered composition containing: (a) about 5-80 wt.% Fe oxide; (b) about 4-20 wt.% Zn oxide, (c) about 10-40 wt.% Ti and/or Mn oxide, (d) about 1-5 wt.% of a Group IA metal oxide selected from the group consisting of K, Rb and Cs, and mixtures thereof, (e) about 1-10 wt.% Ce oxide such that said sintered combination comprises a series of spinels of Fe, Zn and/or Ti and/or Mn and said Group IA metal oxide in a cerium oxide matrix.

104. Fiato, R. A.; Slurried CO hydrogenation catalysts; U.S. 4,752,600, June 21, 1988. **Claim 1:** A slurry catalyst composition consisting essentially of: (a) TiO_2, (b) the decomposition product of a ruthenium carbonyl complex which is $Ru_3(CO)_{12}$, said decomposition product being formed by the decomposition of said $Ru_3(CO)_{12}$ in the presence of a gas mixture of $CO:H_2N_2$ at a temperature of about 230^{o}C to about 270^{o}C and a pressure of about 230 to about 270^{o}C and a pressure of about 4 to about 20 atm. for a sufficient period of time to form said decomposition product, said decomposition product being supported on said TiO_2, and (c) an inert alkane hydrocarbon.

105. Iglesia, E., S. L. Soled and R. A. Fiato; Cobalt-ruthenium catalysts for Fischer-Tropsch synthesis; U.S. 4,822,824, April 18, 1989. **Claim 1:** A hydrocarbon synthesis process which comprises reacting hydrogen and carbon monoxide in

the presence of a catalyst comprised of cobalt and ruthenium on titania, at reaction conditions suitable for the formation of higher hydrocarbons, the catalyst being prepared by impregnating titania with solutions of cobalt and ruthenium salts, drying the impregnating support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

106. Wachs, I. E. and D. B. Yang; Catalysts comprising ruthenium on titania surface modified with Group VA oxide of vanadium, niobium or tantalum; U.S. 4,861,747, Aug. 29, 1989. **Claim 1:** A catalyst comprising ruthenium supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania.

107. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts; U.S. Patent 4,962,078, Oct. 9, 1990. **Claim 1:** A catalyst composition useful for the conversion of synthesis gas to liquid hydrocarbons which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support, the support being at least about 80% by weight titania, the layer ranging in average thickness from about 0.2 mm to about 0.20 mm with the cobalt loading being about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalysts, and having a productivity and methane selectivity at 200°C of at least 150 hr^{-1} and no more than 10 mole %, respectively.

108. Mauldin, C. H. and K. L. Riley; Titania-supported catalysts and their preparations for use in Fischer-Tropsch synthesis; U.S. Patent 4,992,406, Feb. 12, 1991. **Claim 1:** A support composition for forming a catalyst useful for the conversion of synthesis gas to hydrocarbons which comprises titania in which there is incorporated from 0.1 to about 20 wt.% of an inorganic oxide binder selected from the group consisting of alumina and zirconia based on the weight of the titania-binder support, to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.5 cc/g, and surface area ranging from about 8 m^2/g to about 70 m^2/g.

109. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U. S. Patent 5,004,862, April 2, 1991. **Claim 1:** A process for purifying a condensate stream from a hydrocarbon synthesis or alcohol synthesis process which comprises: (a) contacting the condensate with a hot gaseous mixture comprising methane and steam to strip contaminants comprising lower molecular weight hydrocarbons and oxygenates; (b) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (c) separately recovering purified water.

110. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U.S. Patent 5,053,581, Oct. 1, 1991. **Claim 1:** A process for producing heavy hydrocarbons which comprises: (a) reacting CO and H_2 over a catalyst at reactive conditions in a hydrocarbon synthesis to form heavy hydrocarbons and a product condensate; (b) separately recovering the heavy hydrocarbons from the product condensate; (c) contacting the product condensate with a hot gaseous mixture comprising CH_4 and steam to strip the product condensate of contaminants, said contaminants comprising lower molecular-weight hydrocarbons and oxygenates; (d) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (e) converting the gaseous stream recovered in step (d) to CO and H_2 and utilizing at least a portion of said CO and H_2 in step (a).

111. Fiato, R. A.; Two stage process for hydrocarbon synthesis; U.S. Patent 5,028,634, July 2, 1991. **Claim 1:** A two stage hydrocarbon synthesis process comprising:
(a) reacting in a first stage, hydrogen and carbon monoxide in the presence of a supported cobalt or ruthenium catalyst and obtaining a CO conversion to C_2+ hydrocarbons of at least 50% at reaction conditions including a pressure of at least 10 atmospheres;
(b) recovering a reaction product comprisiong hydrogen and carbon monoxide and separating liquid therefrom;
(c) reacting in a second stage, at a pressure below 10-12 atmospheres and no greater than the outlet pressure of the first stage, the remaining reaction products in the presence of a catalyst comprising catalytically effective amounts of cobalt supported on alumina at reaction conditions and
(d) wherein the second stage catalyst is at least as active for CO conversion to C_2+ hydrocarbons as the first stage catalyst at second stage reaction presssure.

112. Iglesia, E., H. Vroman, S. Soled, J. Baumgartner and R. A. Fiato; Selective catalysts and their preparation for catalytic hydrocarbon synthesis; U.S. Patent 5,036,032, July 30, 1991. **Claim 1:** A method for preparing a supported cobalt catalyst particle which comprises: (a) contacting a support particle with a molten cobalt salt, for a period sufficient to impregnate substantially all of the molten cobalt salt on the support to a depth of less than about 200 :m; (b) drying the supported cobalt salt obtained in step (a); and (c) reducing the cobalt of the supported cobalt salt in step (b) to metallic cobalt by heating the salt in the presence of H_2, wherein the heating is conducted at a rate of less than about 1^oC/min up to a maximum temperature ranging from about 200^oC to about 500^oC to produce a supported cobalt catalyst particle.

113. Hsu, E. C. and J. L. Robbins; Catalyst pretreatment method; U.S. Patent 5,070,064, Dec. 3, 1991. **Claim 1:** A liquid phase method for removing sub-1 micron particles adhering to catalyst particles the catalyst containing a Group VIII metal supported on an inorganic refractory oxide as a result of preparation of the

catalyst which comprises: (a) dispersing the catalyst particles to which the sub-1 micron particles adhere within a liquid comprising a FT; (b) agitating the dispersion and separating the sub-1 micron particles from the catalyst particles, and concentrating the sub-1 concentrating the sub-1 micron particles in the liquid phase; and (c) separating the sub-1 micron containing liquid phase from the particulate material.

114. Mauldin, C. H. and K. L. Riley; Titania catalysts,. their preparation, and use in Fischer-Tropsch synthesis; U.S. Patent 5,140,050, Aug. 18, 1992. **Claim 1:** A process for the conversion of synthesis gas to hydrocarbons at high activity which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than 0.5:1 at pressure greater than or equal to 80 psig, over a catalyst composition comprised of a catalytically effective amount of a Group VIII non-noble metal catalytically active for the conversion of synthesis gas to hydrocarbons dispersed upon a titania support in which there is incorporated from about 0.1% to about 10% of an inorganic oxide binder selected from the group consisting of alumina, and zirconia based on the weight of the titania-binder to support to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.55 cc/g and surface area ranging from about 8 m^2/g to about 70 m^2/g.

115. Soled, S. L., G. B. McVicker and W. E. Gates; Metal on rare earth modified silica alumina as hydrocarbon conversion catalyst; U.S. 5,248,409, Sept. 28, 1993. **Claim 1:** A catalytic hydroconversion process which includes hydroisomerization of at least a feedstream comprising: contacting and feedstream with a catalyst composition comprising an amorphous silica-alumina support having at least about 50 wt..% silica, a rare earth oxide, and a metal selected from the group consisting of Group VIII noble metals, rhenium, and mixtures thereof.

116. Herbolzheimer, E. and E. Iglesia; Slurry bubble column; U.S. Patent 5,348,982, Sept. 20, 1994. **Claim 1:** A method for optimally operating a large diameter three phase (gas, liquid, solid) slurry bubble column having a diameter greater than 15 cm for FT synthesis over a supported cobalt catalyst in which solid particles are fluidized in the liquid phase by bubbles of the gas phase, comprising: (a) injecting the gas phase into said column at an average gas velocity along said column, U_g>2 cm/sec, such that the flow regime is in the substantial absence of slug flow; (b) fluidizing the solid supported cobalt catalyst particles of average diameter, d_p>5 :m, to the height, H>3m, of the expanded liquid in the column by operating with a catalyst settling velocity, U_s, and dispersion coefficient, D, such that

$$0.5\ (U_s - U_L) \le \frac{D}{H},\ \textit{where}\ H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu}\ g f(C_p),\ \textit{where}\ d_p > 5 \mu m$$

and (c) maintaining plug flow in said column by operating with a gas phase velocity, U_g, expanded liquid height, H, and dispersion coefficient, D, such that $U_g \geq 0.2$ D/H, where H >3m, $U_g > 2$ cm/sec, wherein D_s = effective density of the particles; D_l = density of the liquid; : = viscosity of the liquid; $f(C_p)$ = hindered settling function; = volume fraction of solids in the slurry (liquid plus solids); U_L = liquid velocity along the column; H = height of the expanded liquid in said reactor; g = gravitational constant; d_p = diameter of particles; m = meters.

117. Agesteguia, C. R., S. L. Soled and S. Miseo; Catalysts for iso-alcohol synthesis from CO + H_2, U.S 5,387,570, Feb. 7, 1995. **Claim 1:** A catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof, and wherein said second oxide is a Group IIA oxide and a Group IB metal.

118. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Structurally modified alumina supports, and heat transfer solids for high temperature fluidized bed reactions; U.S. 5,395,406, March 7, 1995. **Claim 1:** A composition of matter which comprises: a support components comprising particulate alpha alumina solids of fluidizable particle size of 30-150 microns modified by compositing a metal therewith to form particles represented by formulas (1) and (2), a composite particle being represented by formula (1), as follows;

$$M_xAl_2O_{3+Y} \qquad \textbf{(1)}$$

with the core of the particle being represented by formula (2), as follows:

$$M_yAl_2O_{3+Y} \qquad \textbf{(2)}$$

where in formulas (1) and (2), M is a Group IIA metal, x is a number ranging from about 0.01 to about 0.4 and is representative of the number of moles of the metal M per mole of Al_2O_3, y is a number equal to or greater than zero, and x is greater than y.

119. Pruett, R. L. and J. S. Bradley; Transition metal bimetallic clusters of ruthenium with thallium, indium and gallium, U.S. 4,360,475, Nov. 23, 1982. **Claim 1:** A composition of matter comprising a bimetallic cluster compound of the formula $[M]_n[(Ru_6C\text{-}(CO)_{16})_2L]$ where M is alkali metal cation, alkaline earth metal cation, N(RN)4+, P(RN)4+ or As(R^o)4+ where RN is C_1-C_{20} aliphatic, C_3-C_8 cycloaliphatic, C_7-C_{14} aralkyl or C_6-C_{10} aryl, n is a number which satisfies valence requirements and L is Tl, In or Ga.

120. Iglesia, E., S. L. Soled and J. E. Baumgartner; Selective fixed-bed Fischer-Tropsch synthesis with high surface area Cu and K promoted, iron/manganese spinels; U.S. 5,118,715, June 2, 1992. **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition

wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-240°C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

121. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts (C-2448); U.S. 5,128,377, July 7, 1992. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons, which comprises contacting at reaction conditions a feed comprising carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support containing at least about 80 wt% titania ranging in average thickness from about 0.02 mm to about 0.20 mm, with a cobalt loading of about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst and with a productivity and methane selectivity at 200°C of at least 150 hr^{-1} and no more than 10 mole%, respectively.

122. Say, G. R., J. H. Taylor, D. C. Long and R. A. Fiato; Synthesis gas generation of startup process (C-2556); U.S. 5,143,647, Sept. 1, 1992. **Claim 1:** A method for starting up a fluidized bed or spouted bed steam reforming partial oxidation process for converting a feed gas comprising methane to a product comprising hydrogen and carbon monoxide and unconnected methane which comprises the sequential steps of: (a) heating to reaction temperature the fluidized bed or spouted bed comprised of essentially inert particles, in the presence of oxygen, in an oxiding atmosphere, and in the substantial absence of a reforming catalyst; (b) converting to a reducing atmosphere; and (c) introducing into the fluidized or spouted bed sufficient Group VIII metal containing catalyst and converting, in the presence of oxygen, the feed gas to the product.

123. Soled, S. L., E. Iglesia and R. A. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for Fischer-Tropsch synthesis; U.S. 5,162,284, Nov. 10, 1992. **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2.

124. Soled, S. L., S. Miseo, E. Iglesia and R. A. Fiato; Iron-zinc catalysts for the conversion of synthesis gas to alpha-olefins; U.S. 5,185,378, Feb. 9, 1993. **Claim 1:** A process for preparing a liquid product containing olefins and paraffins wherein the olefin/paraffin ratio is at least about 2.5/1, and the C_5+/C_4-ratio is at least about 4.5/1 which comprises reacting in a slurry liquid, at suitable reaction

conditions, hydrogen and carbon monoxide in the presence of a catalyst comprising: iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof, wherein the iron:zinc atomic ratio is at least a 5:1, and the alkali:copper atomic ratio is at least 2:1.

125. Soled, S. L., E. Iglesia and R. A. Fiato; Substituted cobalt catalysts for Fischer-Tropsch synthesis; U.S. 5,248,701, Sept. 28, 1993. **Claim 1:** A FT process for the conversion of synthesis gas to hydrocarbons which comprises activating a copper promoted, cobalt-manganese spinel catalyst having the formula $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2 by contacting the catalyst with a reducing atmosphere and contacting the activated catalyst in a reactor with hydrogen/carbon monoxide synthesis gas.

126. Chang, M. and C. A. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); U.S. 5,252,613, Oct. 12, 1993. **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributiong catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

127. Hsia, S. J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; U.S. 5,260,239, Nov. 9, 1993. **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel menas to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by menas of a first downcommer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down the first downcomer-conduir means from the top of the first vesssel means to the bottom of a reactivation-rejuvenation second vessel menas, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catlayst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated-rejuvenated in said second vessel menas, collecting reactivated-rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer-conduit means to theop of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated-rejuvenated catalyst down the second downcommer-conduit means from the top of the second vessel means to the bottom of the first vessel means, all catlayst downward flows on both the first and second downcomer means occurring solely inder the influence of gravity.

128. Pedrick, L. E., C. H. Mauldin and W. C. Behrmann; Draft tube for catalyst rejuvenation and distribution; U.S. 5,268,344, Dec. 7, 1993. **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the oppen bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

129. Mitchell, W. N.; Rejuvenation of hydrocarbon synthesis catalyst; U.S. 5,283,216, Feb. 1, 1994. **Claim 1:** A method for rejuvenating a partially deactivated, Group VIII metal containing Fischer-Tropsch catalyst having an initial catalyst activity which comprises: suspending the catalyst in slurry liquid hydrocarbons and treating the suspended catalyst with hydrogen or a hydrogen containing gas at elevated temperatures and pressures and recovering a substantial portion of the metal catalyst activity.

130. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,292,705, March 8, 1994. **Claim 1:** Amethod for activating an essentially fresh, reduced cobalt containing Fischer-Tropsch catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

131. Chang, M.; Enhanced gas separation for bubble column draft tubes; U.S. 5,332,552, July 26, 1994. **Claim 1:** A slurry bubble column reactor comprising a double walled vessel defined by an inner vessel wall having a peripheral circumferential top rim and a bottom edge, and an outer main containment vessel wall surrounding said inner vessel wall, said outer main containment vessel having a top and a bottom, and wherein the inner vessel wall and the outer vessel wall are substantially co-axial and have a space between them forming an annulus between said respective walls, the outer main containment vessel wall having a synthesis gas inlet means at the bottom, gas outlet means and product recovery means at the top, and a floor above the gas inlet means which floor is fitted wigh gas distribution means, the inner vessel wall serving as a main reactor zone, the peripheral circumferential top rim of the inner vessel wall having attached to it an inverted channel having an apex and two edges, the point of attachment of the inverted channel to the inner wall being along a first one of said two edges of said inverted channel, a second of said two edges of said inverted channel extending over the main reaction zone thereby creating a gas space within its inverted contour and which inverted channel has a gas vent extending out of, and upwardly from, said inverted channel, and having a liquid by-pass pipe extending from a point on one side of the inverted channel below the apex

of said inverted channel and between said apex and the edge of attachment to the inner vessel wass, to under said top rim of said inner vessel wall and which by-pass pipe empties into the annulus, and liquid exit means at the bottom of the annulus defined by openings in the bottom edge of the interior vessel wall and above the gas distributor means of the main containment vessel.

132. Clavenna, L. R., S. M. Davis, G. R. Say and R. A. Fiato; Synthesis gas from particulate catalysts, and admixutres of particulate catalysts and heat transfer solids; U.S. 5,348,717, Sept. 20, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of oxygen, or both stean and oxygen, the improvement wherein the fludizing bed is comprised of an admixture of
a particulate consisting essentially of a non-leachable barium hexaaluminate solids of fluidizable particle diameter in concentration ranging from about 10 percent to about 99.9 percent, based on the weight of the admixture, and a catalyst comprised of a carrier component composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons when contacted with a fluidized bed of the catalyst, in concentration ranging from about 0.1 percent to about 90 percent, based on the weight of the admixture.

133. Clavenna, L. R., S. M. Davis and B. E. Beasley; Process for the reactivation of nickel-alumina catalysts; U.S. 5,356,845, Oct. 18, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, the steps comprising: withdrawing a portion of said catalyst and contacting said catalyst with an oxygen-containing gas at a temperature elevated sufficiently to convert the nickel component of said catalyst to nickel aluminate, and disperse said nickel aluminate within the alumina support, without sintering and alumina support; and reducing said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-a-vis that of the catalyst initially withdrawn from the reaction zone.

134. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U.S. 5,360,778, Nov. 1, 1994. **Claim 1:** In a process for the preparation of a particulate heat transfer solid characterized as particulate refractory inorganic oxide solids containing silicon, or boron, or both silicon and boron impurities, the steps comprising: contracting, and treating, said particulate refractory inorganic oxide solids containing silicon in concentration no greater than about 0.5%, based on the total weight of the solids, and boron in concentration no greater than about 500 parts, per million parts by weight total solids, with an acid sufficient to reduce the concentration of silicon and boron in the outer peripheral surface layer of the

particles to no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer.

135. Behrmann, W. C., C. H. Mauldin and L. E. Pedrick; Hydrocarbon synthesis reaction employing vertical downcomer with gas disengaging means; U.S. 5,382,748, Jan. 17, 1995. **Claim 1:** A method for uniformly redistributing particulate catalyst in a slurry phase reactor, said method comprising using a substantially vertical conduit means open at both ends, fully submerged in the slurry of the slurry phase reactor, the bottom end of the substantially vertical conduit means is near the bottom of the slurry phase reactor and the top of the conduit means is topped by gas disengaging means which are below the top surface of the slurry in the slurry phase reactor and wherein the bottom of the substantially vertical conduit means is shielded by a baffle means which diverts gases rising from the botytom of the slurry phase reactor from entering into the bottom of the substantially vertical conduit whereby catalyst in slurry which passes down the substantially vertical conduit and is ejected from the bottom of said conduit near the bottom of the slurry phase reactor.

136. Koros, R. M., Bubble column, tube side slurry process and apparatus; U.S. 5,384,336, Jan 24, 1995. **Claim 1:** A hydrocarbon synthesis process comprising reacting a gaseous mixture of hydrogen and carbon monoxide at a pressure of 1 to 100 atmospheres and a temperature of about 175^{o}C to about 400^{o}C in the presence of a hydrocarbon synthesis catalyst dispersed in a liquid thereby forming a slurry liquid, wherein the catalyst dispersion is disposed in a plurality of vertically arranged elongated reaction tubes having an L/D (length/diameter) of at least about 10, each tube being surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not being in fluid communication with the slurry liquid.

137. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,389,690, Feb. 14, 1995. **Claim 1:** A FT process which comprises activating an essentially fresh, reduced cobalt containing FT catalyst with hydrogen or a hydrogen containing gas, the catalyst being dispersed in hydrocarbon liquids and subsequently using the catalyst in a FT process at FT reaction conditions.

138. Soled, S. L., E. Iglesia, R. A. Fiato and G. B. Ansell; Method for stabilizing titania supported cobalt catalyst; U.S. 5,397,806, March 14, 1995. **Claim 1:** In a FT process, under FT reaction conditions, including contacting with a feedstream comprising a CO and H_2 reaction mixture, a 400-750^{o}C regeneration stable catalyst composition comprising cobalt on a substituted ternary metal oxide of titania having the general formula $Co/Ti_{l-x}M_xO_2$ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium and tantalum, wherein the titania is an anatase polymorph.

139. Stark, T. M.; Pentane energy transfer medium in gas conversion; U.S. 5,409,960, April 25, 1995. **Claim 1:** A method for removing heat from a slurry FT hydrocarbon synthesis process reaction zone which comprises passing a cooling

medium comprising a C_4-C_{10} normal, iso- or cyclic paraffin liquid in cooling tubes in indirect heat exchange through the slurry reaction zone, thereby vaporizing the cooling medium at its boiling point, the cooling medium being inert for FT processes, condensible, and vaporizing at a pressure greater than the pressure in the reaction zone, and recovering the vaporized cooling medium heat.

140. Wittenbrink, R. J., S. M. Davis and K. L. Riley; Supported Ni-Cu hydroconversion catalyst; Int. Pub. No. WO 97/03750, Feb. 6, 1997. **Claim 1:** A hydroconversion catalyst comprising nickel in an amount of less than about 15 wt.% catalyst and copper in a copper:nickel ratio of less than about 1:2 supported on an amorphous silica-alumina carrier having less than about 30 wt.% alumina, the carrier having a surface area of greater than about 200 m^2/gm and a pore volume of less than about 1.0 mL/gm.

141. Davis, S. M. and D. F. Ryan; Distillate fuel production from Fischer-Tropsch wax; U.S. 5,378,348, Jan. 3, 1995. **Claim 1:** A process for producing middle distillate transportation fuel components from the waxy product of a hydrocarbon synthesis process which comprises: (a) separating the waxy product into a heavier fraction and at least one lighter fraction; (b) catalytically isomerizing the heavier fraction in the presence of hydrogen and recovering products with improved cold flow properties; (c) catalytically hydrotreating the lighter fraction and removing hetero atom compounds therefrom: (d) catalytically isomerizing the product of step (c) to produce jet fuel component having a freeze point of -30^{o}F or lower.

144. Behrmann, W. C., K. B. Areuri and C. H. Mauldin; Surface supported cobalt catalysts, process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas and process for the preparation of said catalysts; U.S. Patent 5,545,674, August 13, 1996. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons less than about 10 mole% methane which comprises contacting at reaction conditions a feed comprised of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition having a productivity of at least 150 hr^{-1} at 200^{o}C and which comprises cobalt dispersed as a catalytically active layer upon the outer surface of an inorganic oxide support of a thickness of less than about 200 microns, with the loading of cobalt at least about 0.04 g/cc in said catalytically active layer, calculated as metallic cobalt per packed bulk volume of catalyst.

145. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U. S. Patent 5,496,531, March 5, 1996. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed constituted of a catalyst and particulate alpha alumina containing both silicon and boron impurities, at high temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the alpha alumina is comprised of particles of alpha alumina the outer peripheral surface

layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer, thereby improving resistance to sintering and agglomeration of the fluidized bed, said particles being produced by acid washing of the alpha alumina.

148. Beadle, S. W., W. H. Summerlin and E. T. A. Van Driessche; Airless cobalt demetalling in the cobalt flash combination catalyst cycle; U.S. Patent 5,410,090, April 25, 1995. **Claim 1:** A method for removing cobalt values from the crude product of a cobalt-catalyzed hydroformylation reaction formed from an olefinic feedstock, said crude product containing cobalt compounds in addition to an organic hydroformylation reaction product, which comprises: (a) contacting said crude product with an organic acid and water, in the absence of any oxygen-containing gases, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (b) separating said substantially cobalt-free crude product from said water soluble cobaltous salt aqueous product; (c) diverting said substantially cobalt-free organic hydroformylation reaction product for further downstream treatment such as distillation or hydrogenation; (d) concentrating said water soluble cobaltous salt aqueous product thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free water containing said organic acid, whereby said concentrated aqueous solution of cobaltous salt is separated from said substantially cobalt-free water containing said organic acid; (e) recycling said substantially cobalt-free water containing said organic acid to step (a); (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol stream and synthesis gas, and passing this mixture to a preformer reactor where said concentrated aqueous solution of cobaltous salt is converted to a cobalt carbonyl; (g) contacting said cobalt carbonyl with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas and to generate as bottoms alcohol products and dissolved cobaltous salts, whereby said entrained volatile cobalt compounds are taken out overhead and the alcohol products and dissolved cobaltous salts are taken out as bottoms; (h) separating said alcohol products of step (g) from said dissolved cobaltous salts; (i) recycling said alcohol products from step (h) to step (f); (j) recycling said dissolved cobaltous salts from step (h) to step (a); and (k) contacting said volatile cobalt compounds from step (g) with said olefinic feedstock, whereby said volatile cobalt compounds are absorbed into said olefinic feedstock.

149. Beadle, S. W. and C. A. Poulin; Use of stripper reactor reflux as an initiator for preforming reaction of cobaltous salts to cobalt carbonyls, U.S. Patent 5,457,240, October 10, 1995. **Claim 1:** A method for producing higher aldehydes and higher alcohols which comprises: (a) hydroformylating an olefinic feedstock with synthesis gas in the presence of a cobalt-containing catalyst to form a crude product containing higher aldehyde, higher alcohol, secondary products and dissolved cobalt catalysts; (b) contacting said crude product with an oxygen-containing gas, an organic acid and water, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (c) separating said substantially cobalt-free

crude product from said water soluble cobaltous salt aqueous product; (d) concentrating said water soluble cobaltous salt aqueous product, thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free aqueous solution; (e) separating said concentrated aqueous solution of cobaltous salt from said substantially cobalt-free aqueous solution; (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol and synthesis gas, and passing this mixture to a preformer reactor where said concentrated solution of cobaltous salt is converted to a cobalt carbonyl; (g) passing said cobalt carbonyl to a stripping reactor wherein said cobalt carbonyl is contacted with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas; whereby said entrained volatile cobalt compounds are taken overhead; and (h) recycling at least a portion of said entrained volatile cobalt compounds taken overhead in step (g) to said preformer reactor.

150. Vanderspurt, T. H. and J.-L. Kao; Noble metal large pore zeolite catalyst for methanol-ethanol coupling; U.S. Patent 5,493,064, February 20, 1996. **Claim 1:** An alcohol coupling process, comprising: contacting a vaporized mixture of starting alcohols of methanol in combination with a second alcohol selected from the group consisting of ethanol, n-propanol, and mixtures thereof with a carrier gas containing CO and H_2 in the presence of an alumina-bound highly dispersed metallic Pd-loaded, alkali metal cation exchanged L zeolite wherein the zeolite and alumina have an essential absence of strongly acidic catalytic sites and wherein said contacting is carried out at a temperature and partial pressure of CO and H of from about 300 to 400°C and from 3000 kPa to about 15,000 kPa at a sufficient pressure to minimize the decomposition of methanol to CO and H_2 and at a space velocity of from about 4000 hr^{-1} to about 10,000 hr^{-1} to produce isobutanol and n-propanol in the substantial absence of light gaseous alkanes and C_{6+} oxygenates.

151. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials; U. S. Patent 5,395,813, March 7, 1995. **Claim 1:** As a composition, a fluidizable contact mass for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon contacted with a fluidized bed of said contact mass at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, which comprises: an admixture of, a particulate, fluidizable precalcined zirconia heat transfer solid which contains from 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15, and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

160. Davis, S. M., L. R. Clavenna, R. A. Fiato and G. R. Say; High performance alumina heat transfer solids for high temperature fluidized bed synthesis gas reactions; U.S. 5,360,777, Nov. 1, 1994. **Claim 1:** As a composition of matter, a heat transfer solid resistant to sintering and agglomeration for admixture with a catalyst to form a fluidized bed useful in the conversion of a low molecular weight hydrocarbon to hydrogen and carbon monoxide on contact therewith at high temperature in the presence of steam, or oxygen, or both steam and oxygen which comprises: alumina solids particles: (i) the outer peripheral surface layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of aluminum cations within said outer peripheral surface layer, while the bulk concentration of silicon in the particles does not exceed about 0.5%, based on the weight of the alumina solids, and the bulk concentration of boron in the particles does not exceed about 500 ppm, based on the weight of the alumina solids; (ii) the outer peripheral surface layer of which contains no more than 20 atom percent impurities based on the sum-total concentration of sodium, iron, calcium, and titanium as impurities; (iii) the tapped bulk density of the particles ranges from about 1.2 g/cc to about 2.5 g/cc; (iv) the Davison Attrition Index of the solids particles is no greater than about 12; and the sum total effect of these relationships between surface purity particle density, and attrition resistance is such as to provide a performance index categorized by the formula:

$$\textit{Performance Index} = \frac{1}{(i)x(ii)x(iii)x(iv)} > 20.$$

161. Vanderspurt, T H. and R. J. Koveal; Isoalcohol synthesis; U.S. Patent 5,703,133, Dec. 30, 1997. **Claim 1:** A method for producing isobutanol and methyl butanols from syngas, comprising: (a) contacting a reactant stream containing syngas with a first stage catalyst having alkali promoted La-stabilized, highly dispersed microcrystalline Cu_2O having a particle size of $\leq$ 6 nm interspersed with metallic copper crystallites having a particle size of $\leq$ 25 nm, and zinc oxide crystallites having a particle size of $\leq$ 6 nm in the presence of an alumina structural promoter, wherein on a mol % alkali free metals only basis, Cu is present in from about 45% to about 55%, Zn from about 10% to about 20%, Al from about 10% to about 25%, La from about 5% to about 15% and wherein the alkali is between about 0% to about 1% K and from about 3% to about 6.5% Cs, wherein the first stage catalyst is produced by the process of: coprecipitating at a constant pH of from 0.7 to 11.0 at a temperature of from about 30°C to about 100°C in the essential absence of CO_2 from a solution of soluble metal salts of copper, zinc, lanthanum and aluminum with alkali hydroxide solution selected from the group consisting of LiOH, NaOH, KOH, CsOH and RbOH and mixtures thereof; aging the washed precipitate for from about 1 to 24 hrs at from to 50 to 90°C in the essential absence of CO_2; washing the precipitate in the essential absence of CO_2; drying the washed coprecipitate in air at up to about 120°C; calcining the dried coprecipitate in air for greater than 3 hrs at a temperature of from about 300 to 700°C; contacting the calcined coprecipitate with from 0.01% to 0.91% K and 3% to 6.5% Cs to form a promoted catalyst; drying the promoted catalyst at up to

120^{o}C; recalcining the promoted catalyst at from about 300 to 700^{o}C to produce a catalyst precursor containing highly dispersed CuO crystallites of up to about 10 nm; activating the promoted catalyst in flowing hydrogen for at least 1 hr at 175 to 185^{o}C then for at least 1 hr at 250 to 270^{o}C; wherein said contacting of reactant stream and first stage catalyst is carried out at a pressure of from about 850 psi (5,840 kPa) to about 1500 psi (10,310 kPa) a temperature of from about 240^{o}C to about 340^{o}C for a time sufficient to produce a product stream containing methanol, ethanol, propanol, and methyl butanols; (b) contacting methanol, ethanol and propanol from step (a) with a second stage catalyst having at least a first phase of mixed oxide crystallite containing from about 60 to 74 atomic % zirconium, from about 21 to 31 atomic 5 manganese and from about 5 to 9 atomic % zinc, and less than about 1 atomic % alkali, a second phase of zirconium doped hetaerolite containing from about 65 to 69 atomic % manganese, about 31 to 35 atomic % zinc, 0.5 to 5 atomic % zirconium, and optionally a trace atomic % alkali, and a third phase containing from about 20 to 55 atomic % manganese, from about 13 to 55% atomic zinc and 13 to 35 atomic % zirconium wherein the first phase mixed oxide crystallites have a zirconium oxide like structure have a particle size of at least about 40 D to about 100 D, the second phase of at least about 200 D to greater than about 2000 D and the third phase of at least about 1000 D to greater than 400 D at a pressure of from about 850 psi to about 1500 psi (10,300 kPa) a temperature of from about 340 to about 380^{o}C to produce additional isobutanol and methyl butanols from the methanol, ethanol and propanol and trace ethylene and propylene.

162. Koveal, R. J and T. H. Vanderspurt; Isoalcohol synthesis catalyst; US Patent 5,691,268, Nov. 25, 1997. **Claim 1:** A syngas-to-alcohol catalyst, comprising: highly dispersed, alkali promoted, La stabilized, microcrystalline Cu_2O having a particle size of $\leq$ 6 nm in the presence of an alumina structural promoter, wherein on a mole % alkali free metals-only basis Cu is present in from 45% to 55%, Zn from 10% to 20%, Al from 10% to 25%, La from 5% to 15%, and wherein the alkali is from 0.01% to 0.91% K and from 3% to 6.5% Cs.

163. Apesteguia, C. R., S L Soled and S. Miseo; Catalysts for iso-alcohol synthesis from $CO+H_2$; US patent 5,508,246, Apr. 16, 1996. **Claim 1:** A syngas conversion process, having increased selectivity to methanol and isobutanol and conducted under syngas conversion conditions at pressures of about 20 to about 250 atmospheres, comprising contacting a carbon monoxide and hydrogen feedstream with a catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof and wherein said second oxide is a Group IIA oxide, and a Group IB metal.

164. Vanderspurt, T H., M A Greaney, D Pl Leta, R J Koveal, M M Disko, A V Klaus, S K Behal and R. B. Harris; Isobutanol synthesis catalyst; US patent 5,707,920, Jan 13, 1998. **Claim 1:** A catalyst composition, comprising: a noble metal supported on at least a first phase having a poorly crystalline manganese and

zinc coped zirconium oxide phase containing about 71 to about 91 atomic % zirconium, about 10 to about 16 atomic % manganese and about 4 to about 8 atomic % zinc and a second phase of irregularly shaped hetaerolite crystals containing about 65 to about 69 atomic % manganese, about 31 to about 35 atomic % zinc and 0 to about 5 atomic % zirconium embedded in the first phase.

165. Herskowitz, M.,, Method for hydrocarbon synthesis reactions; US patent 5,652,193, July 29, 1997. **Claim 1:** A method for making a CO hydrogenation catalyst wherein said catalyst includes a metal selected from the group consisting of cobalt and ruthenium deposited in a porous, inorganic, refractory oxide support, said catalyst having said metal located in a rim on the outer surface of said support, said method comprising: (a) determining the rim thickness by: (i) determining intrinsic kinetic rate data including the intrinsic rate of reaction of carbon monoxide hydrogenation and the rate of CO conversion to methane for said catalyst; (ii) determining the thickness of said rim by relating the rates of diffusion of said carbon monoxide and said hydrogen to the intrinsic rate of reaction in said rim for a support geometry selected from the group consisting of a sphere, a ring, a cylinder, and a semi-circle and combinations thereof, such that said rim thickness optimizes both the rate of carbon monoxide hydrogenation and the reduction in methane selectivity; and (b) making a catalyst having a rim thickness determined in step (a).

166. Davis, S. M. and J. W. Johnson; Process for hydroisomerization of waxy hydrocarbon feeds over a slurried catalyst; EP 0 753 563 A1; 04/07/96. **Claim 1:** A hydroisomerization process for the conversion of a C_{5+} paraffinic feedstock to middle distillates which comprises contacting and reacting at hydroisomerization reaction conditions said C_{5+} paraffinic feedstock, and hydrogen, with a catalyst comprising a Group IB metal component, or a Group VIB metal component, or a Group VII metal component or a mixture of two or more of said metal components, supported on an acidic particulate solid, of average particle diameter in a range of from about 30 microns (30 :m) to about 150 microns (150 :m), dispersed in a paraffinic liquid hydrocarbon.

167. Wittenbrink, R. J., R. F. Bauman, P. J. Berlowitz, and B. R. Cook; Synthetic diesel fuel and process for its production; WO 97/14769, 24 April 1997. **Claim 1:** A material useful as a fuel heavier than gasoline or as a blending component for a distillate fuel comprising: 1 250-700^{o}F fraction derived from a non-shifting FT catalyst process and containing at least 95 wt.% paraffins with an iso to normal ratio of about 0.3 to 3.0, $\leq$ 50 ppm (wt.) of sulfur and nitrogen less than about 2 wt.% unsaturates, and about 0.001 to less than 0.3 wt.% oxygen.

168. Wittenbrink, R. J., S. E. Silverberg and D F Ryan; High purity paraffinic solvent compositions, and process for their manufacture; WO 97/21787, 19 June 1997. **Claim 1:** A high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to about C_{20}, has a molar ratio of isoparaffins:n-paraffins ranging from about 0.5:1 to about 9:1 and the

isoparaffins of the mixture contain greater than 50% of the mono-methyl species, based on the total weight of the isoparaffins of the mixture.

169. Stark, T M; Heat removal in gas conversion process, EP appl. 0 614 864 A1, 03/03/94. **Claim 1:** A method for removing heat from a hydrocarbon synthesis process reaction zone, which comprises passing a cooling medium through the reaction zone, in indirect heat exchange therewith, thereby vaporizing the cooling medium; the cooling medium being inert, condensible, and vaporizing at a pressure which is at least as great as the pressure in the reaction zone.

171. Hershkowitz, F. and G. Kiss; Unsaturates recovery and recycle process; U.S. patent 5,516,965, May 14, 1996. **Claim 1:** A process for recovering unreacted acetylene from an effluent stream of a process for synthesizing oxygenated hydrocarbons from unsaturated hydrocarbons, said stream containing unreacted unsaturated hydrocarbons, oxygenated reaction products, and low-boiling gaseous components selected from the group including CO, H_2, CO_2, H_2O, C_1-C_5 alkanes, nitrogen, helium, and argon, comprising: (a) absorbing the unreacted acetylene and the oxygenated hydrocarbons of the synthesis process effluent stream in a solvent wherein said solvent is an acetylene-depleted stream of the oxygenated product of said synthesis process; and (b) stripping the acetylene from the solvent to produce a first stream concentrated in acetylene and a second stream of oxygenated product depleted in acetylene, wherein said acetylene-depleted stream is the absorption solvent and the synthesis process product.

172, Clavenns, L. R., R A Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials, U.S. patent 5,476,877, Dec. 19, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the fluidized bed is comprised of an admixture of a particulate, fluidizable precalcined zirconia heat transfer solid which contains from abut 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15 and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

173. Herfbolzheimer, E., F J Kaiser, Jr and E. Iglesia; Catalyst fluidization improvements; U.S. patent 5,157,054, Oct. 20, 1992. **Claim 1:** A slurry phase hydrocarbon synthesis process for the conversion of hydrogen and carbon monoxide at reaction conditions to products which comprises: injecting a gas comprising hydrogen and carbon monoxide at or near the bottom of a bubble

column containing a slurry liquid, a catalytically active first solid and at less a second solid, dispersing the solids in the slurry liquid, all of the energy thereof being supplied by the gas, in the absence of liquid product recycle, the amount of the second solid being sufficient to increase the bed height of the first catalytic solid by at least 10%, and recovering liquid product.

174. Long, D. C.; Staged hydrocarbon synthesis process; U.S. patent 5,498,638, March 12, 1996. **Claim 1:** A once through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst containing cobalt or ruthenium, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.

175. Long, D. C.; Staged hydrocarbon synthesis process; EP appl. 0 679 620 A2, 26/04/95. **Claim 1:** A substantially once-through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.

176. Taylor, J. H., and G. R. Say; Production of synthesis gas via fluidized bed/fixed bed process combination; U.S. patent 5,421,840, June 6, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide, the steps comprising: contacting, in a first reaction zone, low molecular weight hydrocarbons comprising methane, oxygen, and steam, at high temperature in a net reducing atmosphere, with a fluidized bed of catalyst, or catalyst and a solids diluent, to convert from about 85% to about 92% of the hydrocarbons to hydrogen and carbon monoxide and form a reaction mixture of hydrogen, carbon monoxide and unreacted hydrocarbons, oxygen and steam, withdrawing said reaction mixture as an effluent from said first reaction zone, and contacting said effluent, in a second reaction zone, with a fixed bed of catalytic metal solids with a void fraction of at least about 0.9 to convert, sufficient of the unreacted hydrocarbons, oxygen, and steam and increase the hydrocarbon conversion to a level ranging from about 0.5% to about 5% above that obtained in said first reaction zone.

ADDENDUM - EXXON FISCHER-TROPSCH WORK

Fischer Synthesis Process

A patent (A.1), a continuation of four prior applications with the first dated October 3, 1989, claimed a method for hydrocarbon synthesis reactions. This patent relates to the use of a catalyst of the "rim" type, as the terminology is used by Exxon. These are catalysts where the active metal(s) are deposited in the outermost layer of the support particle, and in a mannor that the interior of the support particle is essentially devoid of the metal(s). This approach is widely used in the manufacturer of auto exhaust catalysts that are shaped into spheres, cylinders, etc. The specific experiments were conducted with a 6 wt.% cobalt and 0.5 wt.% ruthenium on silica or titania support; since the surface area of the catalyst used in the example was reported to be about 20 m^2/g it is assumed that the support was titania. The description of the preferred embodiment includes a derivation of the theoretical aspects of the determination of the rim loaded thickness needed to optimize CO conversion and/or minimize methane production. This theory has been included in several of the reviews of Fischer-Tropsch synthesis that have recently been published by Exxon workers. It is surprising that the authors of these reviews are not inventors of this method for hydrocarbon synthesis reactions and that the inventor (M. Herskowitz) is not an author of the review articles.

The outer layer containing the catalytic metal has a thickness determined so as to optimize CO conversion to heavy hydrocarbons so that conversion to methane is maintained at a predetermined level. The inventor maintains that it is not possible to simultaneously maximize CO conversion and minimize methane conversion. However it is possible to define a rim thickness so as to optimize one of these products. The thickness of the rim-loaded catalyst is determined by relating the rate of diffusion of CO and H_2 to a rate of reaction in the porous inorganic oxide for a predetermined support geometry, partial pressures and temperatures.

The fluxes of the two reactants at steady state must be equal since there is no accumulation; thus,

$$\beta D_{e,CO} [dC_{CO}/d\chi] = D_{e,H} [dC_H/d\chi] \qquad [A.1]$$

where the flux is expressed as a product of the effective diffusivity, D_e, and the concentration gradient. β is the stoichiometric coefficient and is equal to 2.07 in the reported work. Since hydrogen diffuses more rapidly than CO, the relative concentration of hydrogen should increase from the surface to the center of the catalyst pellet.

The differential mass balance inside the pores of the catalyst pellet of carbon monoxide, the limiting reactant, is

$$[D_{e,CO} (1/\chi^s)] d/d\chi[\chi^s (dC_{CO}/d\chi)] = \rho_p r_{CO} \qquad [A.2]$$

where χ is the radial position measured from the external surface toward the center, ρ_p is the pellet density, C_{CO} is the CO concentration in the liquid-filled pores and r_{CO} is the intrinsic rate of reaction on the active sites. The shape factor, s, is equal to two for a sphere and to unity for a cylinder; the treatment can be extended to other pellet shapes.

The boundary condition on the external surface is:

$$C_{CO} = P_{CO,b}/H_{CO} \qquad [A.3]$$

where $P_{CO,b}$ is the CO partial pressure in the bulk gas phase and H_{CO} is the Henry's Law constant. The other boundary condition can be defined for two cases as:

$$\text{inert core} \quad dC_{CO}/d\chi = 0 \quad \chi = \chi_i \qquad [A.4]$$

$$\text{hollow core} \quad C_{CO} - P_{CO,b}/H_{CO} \quad \chi = \chi_i \qquad [A.5]$$

This derivation assumes that external mass transfer resistance is negligible and that the pellet is isothermal. Experimental data verified that these are valid assumptions.

The intrinsic rate expression (small particle, diffusion free case) for cobalt or ruthenium on titania or silica support is

$$r_{CO} = k_1 \exp(-E_1/RT)[\, P_{CO}{}^{a} P_H{}^{b} /(1 + k_2 P_{CO} + k_3 P_H)_c] \qquad [A.6]$$

where k_1, k_2, k_3, E_1, a, b, and c are calculated from experimental rate data. [In this and other Exxon patents there are many typos that are usually obvious but sometimes cause concern. Thus, in the above equation we have modified the equation given in the patent by replacing 1 in the original with a and 2 with c to produce equation [A.6].] The inventor indicates that the kinetic parameter, k_1, usually depends only on the metal concentration on the support; presumably the dispersion must also be included. The inventor indicates that in certain cases such as cobalt on titania, it is also a function of water partial pressure:

$$k_1 = A[(1 + k_4 P_{H_2O})/(1 + (k_5 P_{H_2O})^2)] \qquad [A.7]$$

where A is the activity of the catalyst.

Henry's Law can be used to express equation [A6] in concentrations of CO and H_2:

$$C_{CO} = P_{CO}/H_{CO} \;;\; C_H = P_H/H_H \qquad [A.8]$$

Integrating equation [A1] allows the expression of the hydrogen concentration in terms of the carbon monoxide concentration:

$$C_H = [P_{H,b}/H_H] - [\beta D_{e,CO}/D_{e,H}][(P_{CO,b}/H_{CO}) - C_{CO}\,] \qquad [A.9]$$

or

$$H_H C_H/P_{H,b} = 1 - \gamma[1 - (H_{CO} C_{CO}/P_{CO,b})\,] \qquad [A.10]$$

where

$$\gamma = (\beta D_{e,CO}/D_{e,H})(H_H/H_{CO})(P_{CO,b}/P_{H,b}) \qquad [A.11]$$

Substituting equations [A6] and [A7] into equation [A8] and expressing in dimensionless form yields

$$\phi = (\chi_s - \chi_C)[\rho k_1 \exp(-E_1/RT)[\, P_{CO}^{\,a} P_H^{\,b} / D_{e,CO}(k_2 P_{CO,b})^c\,]^{1.2} \qquad [A.12]$$

The Thiele modulus, ϕ, is the ratio between the maximum rate of reaction and the maximum rate of diffusion. Likewise, γ expresses the ratio between the maximum rate of diffusion of the two reactants; when $\gamma = 1$ the ratio C_{CO}/C_H remains constant and when it is less than one the ratio decreases.

Equation [A.2] is solved to yield the concentration profiles in the pores of the catalyst pellet. This concentration profile is then integrated over the volume of the pellet and this is used to calculate the effectiveness factor which is the ratio of the actual reaction rate (global rate) averaged over the pellet and the maximum reaction rate calculated for the surface conditions:

$$\eta_{CO} = [1/V \int_{VP} r_{CO} dV]/[R_{CO}(P_{HP_{CO}} P_{H_2O}) \qquad [A.13]$$

The effectiveness factor for methane can also be obtained in a similar manner using the rate of methane production, r_{CH_4}:

$$\eta_{CH_4} = [1/V \int_{VP} r_{CH_4} dV]/[R_{CH_4}(P_{HP_{CO}} P_{H_2O}) \qquad [A.14]$$

and r_{CH_4} is obtained from kinetic measurements:

$$r_{CH_4} = k_4 \exp(-(E_2 - E_1)/RT)\ [P_H/(1 + k_2 P_{CO} + k_3 P_H)] r_{CO} \qquad [A.15]$$

Assuming an isothermal reactor for simplicity, η_{CO} and η_{CH4} are used in a reactor mass balance to calculate the carbon monoxide conversion and methane selectivity:

$$y_{CO,i}(G_f/M_i)(dX_{CO}/dZ) = \eta_{CO}\,\rho_B\,r_{CO} \qquad [A.16]$$

$$y_{CO,i}(G_f/M_i)(dX_{CH_4}/dZ) = \eta_{CH_4}\,\rho_B\,r_{CH_4} \qquad [A.17]$$

where $Y_{CO,i}$ is the carbon monoxide mole fraction in the feed, G_f is the mass velocity, M_i is the molecular weight of the feed, ρ_B is the bed density and X_{CO} and X_{CH_4} are the carbon monoxide and methane conversion, respectively.

Using a 6% Co/0.5% Re catalyst of different pellet sizes and a feed with H_2/CO = 2, the CO conversion and CH_4 selectivity were measured. These conversion data were used to estimate the CO and H_2 diffusivities using the following procedure:

a. values of $D_{e,CO}$ and $D_{e,H}$ were assumed;

b. effectiveness factors η_{CO} and η_{CH_4} were calculated from equations [A.9] and [A.10] and the solution of equation [A.2] given the inlet conditions of the reactor;

c. the CO conversion and conversion to methane were calculated by integrating equations [A.16] and [A.17]; since the effectiveness factors are functions of the partial pressures of CO, CH_4 and H_2O they must be recalculated along the length of the reactor taking into account of the changes in the partial pressures;

d. methane selectivity was calculated from the ratio of conversion to methane, X_{CH_4} and carbon monoxide conversion, X_{CO};

e. the calculated carbon monoxide conversion and the methane selectivity were compared with the experimental values for the various pellet sizes; and

f. the effective diffusivities are adjusted to give the best fit of the experimental data.

An example of the agreement between the calculated and the experimental data for catalysts with a range of diameters is shown in figure A.1.

In one example the experiments were performed in a 3'x0.5" reactor that was packed with 1 mm diameter spherical particles uniformly loaded with 6%Co-0.5%Re. Data were obtained as the reaction temperature and the H_2/CO ratio were varied and the CO conversion and CH_4 selectivity obtained as described above. When the initial H_2/CO ratio is less than 2, the ratio will decrease along the catalyst bed and, since methane selectivity depends upon this ratio, it will decrease down the bed.

Simulations of carbon monoxide conversion and methane selectivity were made for various thickness of the rim loaded metals. As shown in figure A.2, both conversion and methane selectivity increase with increasing rim thickness. However, the important point is that these two factors increase rapidly from a low to high value and that the rim thickness where this increase occurs is different for the two factors.

In another simulation, the carbon monoxide conversion and methane selectivity were determined for two pellet shapes: ring and cylinder. As shown in figure A.3, the rim thickness needed to obtain the maximum CO conversion and a low methane selectivity depends upon the pellet shape. Thus, the cylindrical shape provides a much greater difference between the rapid increase in the two factors than the ring shape does.

The inventor claims a method for making a catalyst by determining the rim thickness which optimizes both the rate of carbon monoxide hydrogenation and the reduction of methane selectivity.

Long (A.2,A.3) claims a substantially once-through hydrocarbon synthesis process which comprises reacting in a first reactor or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst. The effluent is treated to recover the product from the first reactor by condensing the liquids and then reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shift activity, producing and recovering additional products.

A basis for this invention is that "The shift reaction can, however, be suppressed if the feed contains higher amounts of CO_2 relative to CO, and CO_2 is known to be added to H_2 + CO synthesis gas feeds for hydrocarbon synthesis. Synthesis gas feeds can contain up to 10% CO_2, that is, about 0.1-10% CO_2." The feed to the first stage(s) has H_2/CO in a 1.5:1 to 1.5:1 mole ratio, preferably 1.9: to 2.3:1, and CO_2 in the range 1.0-10 mole%, preferably 5-10 mole%. This mixture is subjected to synthesis with a non-shifting catalyst, preferably cobalt on alumina, silica or titania (preferred), and preferably promoted by metals as Ru, Rh, Ce or Hf, most particularly Rh (A.4). Conversion of CO in the first stage(s) are preferably at least 90%. Following conversion by the non-shifting catalyst, the liquid products, containing C_5+ hydrocarbons, water, oxygenated compounds and small amounts of dissolved gases.

The feed for the stage 2 reactor(s) with shift catalyst is illustrated in Table A.1. Based on our calculations, the mole fraction of water in the feed is 0.0024 (1.83 mm if operating at 20 atm). For a water-vapor saturated stream, we estimate the temperature of the separation to be -10 to -15°C, a surprisingly low temperature. The gas shown in Table A.1 is fed to a stage 2 reactor(s) where subsequent hydrocarbon synthesis produces a product with an olefin:paraffin ratio of 1.5:1 to 4:1, the lower ratios being favored for higher hydrocarbons and the higher ratios favored for the lower carbon number hydrocarbons. The H_2/CO ratio entering the stage 2 reactor(s) will be essentially the same as the stage 1 reactor(s) because of the non-shifting character in the stage 1 operations. However, because of the conversion in stage 1 reactor(s), less gas will enter stage 2 reactor(s) with the result that the relative concentration of CO_2 will be higher in stage 2 than in stage 1 reactors. Sufficient hydrogen must be present in the feed to stage 2 reactor(s) to react with both CO and CO_2. Reaction conditions in stage 2 reactor(s) will be similar to those in stage 1 reactor(s); e.g., 10-35 bar, 220-340^o, SHSV 200-2000 dry feed (water less than 5 vol% of feed).

Slurry Reactor

Herbolzheimer et al. (A.5) claim the use of a second solid in a slurry phase hydrocarbon synthesis process. A gas is injected at or near the bottom of the bubble column containing a slurry liquid, a catalytically active first solid and at least a second solid. The energy to maintain the dispersion of the solids is supplied by the gas in the absence of liquid recycle. The second solid is added in sufficient quantity to increase the bed height by at least 10%.

The authors state that slurry phase reaction, particularly those occurring in bubble columns, are well-known and do not need to be discussed. In column 6, line 23, the authors state that, "Slurry reactors are well known..." This is surprising since it would appear to imply that at the time of filing this patent [February 25, 1991] the use of slurry reactions are well known and, since bubble column reactors are also well known, only specific improvements to the operation of slurry bubble column reactors should be patentable inventions. Catalyst settling is a problem that can be encountered in bubble column reactors. Particles tend to settle to the bottom because of the influence of gravity. Opposing the settling tendency is the dispersion forces created by the rising bubbles of gas injected at or near the bottom of the reactor. The balancing effect of these two forces results in an exponential distribution of catalyst solids concentration.

The authors utilize the data employing a dispersion coefficient and the settling velocity. D, the dispersion coefficient, depends on the superficial gas velocity through the system and on the effective diameter of the reactor column. The authors do not define this term in more detail, and presumably are considering the dispersion coefficient for the solids. The settling velocity of the catalyst particles, U_s, is given as

$$U_s = U_o(1 - c)^n \qquad [A.18]$$

where

$$U_o = dp^2(\rho_s - \rho)g/18\mu \ [\rho_s \text{ is given as } \rho s \text{ in the patent}] \qquad [A.19]$$

where c is the volume fraction of solids in the slurry, d_p is the particle diameter, ρ_s is the density of the solids, g is the gravitational constant, μ is the viscosity of the suspending liquid, and n is a constant ranging from 4 to 8.

In the description, they indicate that most reactors operate in a regime somewhere between plug-flow and fully-backmixed (or CSTR) conditions. A plug-flow condition can be attained by using fixed-bed catalyst or a very large L/d (where L and d are the length and effective diameter of the reactor, respectively). In the plug-flow reactor the concentration (or partial pressure) of hydrogen and carbon monoxide, the reactants for Fischer-Tropsch Synthesis, decrease along the path of reactor flow due to reaction, and this decreases the driving force of the reaction. On the contrary, complete backmixing results in the same concentration of reactants along the entire length of the reactor resulting in a constant driving force and reflects the relatively low driving force at exit conditions.

Productivity is generally favored in plug-flow systems and selectivity is favored in backmixed systems. Later Exxon patents pertain to the operating conditions for plug-flow bubble column slurry reactors .

In the preferred mode for this patent, there ia an absence of liquid throughput; thus, in the preferred mode, all of the energy from maintaining solids as a dispersion in the liquid is provided by the injection of gas at or near the bottom of the slurry reactor.

The catalysts utiliized in the examples are typical of those described in many Exxon, and other, patents. The preferred catalyst is cobalt supported on titania and promoted with rhenium. The preferred catalyst particle size is in the range of 20 to 100 microns.

The data described in the examples were obtained in a 5 meter tall, non-reactive bubble column with 15 cm internal diameter (i.e., the L/d ratio was greater than 20, corresponding to nearly plug-flow conditions). Nitrogen gas was injected vertically into the column through a half inch hole at the bottom of a conical insert. This cone was used to insure fluidization of all the particles charged to the system. Pressure and temperature were monitored at 1 meter intervals along the column length, and slurry samples were withdrawn at these locations. The slurry liquid was C_{20}-C_{40} paraffinic wax produced by Fischer-Tropsch synthesis using a cobalt catalyst. The solid was either TiO_2 or glass beads. No liquid was added during the measurements.

The solids distribution of 80 micron glass beads in FT product was determined at a temperature of 400°F (204°C) and 280 psig (for gas velocities below 8 cm/sec) or 150 psig (for gas velocities above 8 cm/sec). The decay length of the particle concentration profile was obtained by taking the slope of a line segment joining the data points when plotted as the logarithm of the solids concentration versus height. In figure A.4, the decay length in each zone is plotted versus the average concentration in the zone for superficial gas velocities of 2-16 cm/sec.

They correlated the data by

$$D/U_s(\text{feet}) = 0.2(1 + 20c^2 + 3000c^4)/U_o(\text{cm/sec}) \qquad [A.20]$$

for $U_g < 4$ cm/sec and

$$D/U_s(\text{feet}) = 1.2(1 + 3c^2 + 500c^4)/U_o(\text{cm/sec}) \qquad [A.21]$$

for $U_g < 4$ cm/sec.

U_o is Stokes settling velocity and c is the volume fraction of solids in the slurry.

The results of the above experiment with glass beads was then used in models to predict solids distribution for several examples of various solids combinations. For catalyst and inert solids of the same density (2.7 g/cm^3) and diameter (50 microns) that are (1) dispersed in a solvent with a liquid viscosity of 0.9 cp and density of 0.7 g/cm$_3$, (2) with an average catalyst loading of 0.05 by volume (gas-free basis), (3) an expand bed height of 30 feet, (4)a gas inlet velocity of 8 cm/sec, and (5) an overall conversion of 0.8, they obtained catalyst distributions with 0, 0.05, 0.1, 0.2 and 0.3 volume fraction of inert solids added.

The data in figure 5.A show that with only catalyst the effective bed height is about 13 feet, and with the catalyst more heavily concentrated at the bottom of the reactor. The addition of even a small amount of inerts increase the bed height. As the inert solids content is increased the bed expands further in height and the catalyst concentration profile becomes flatter.

In another example, they use the same catalyst and inert solid except the inerts are 1 micron in size. This example would be approximated by the use of 80 micron iron catalyst spheres made up of 1 micron particles that, because of attrition, produce individual 1 micron fines. Effects similar to those of equal sized particles are obtained. A similar calculation was made using an active catalyst of density 2.7 g/cm^3 and lower activity catalyst with a density of 1.0 g/cm^3. They also made calculations for the case when the original activity is decreased by factors of 2, 4, and 6. The use of the less active component also causes the bed to expand.

In the examples provided, the authors do not provide an identification of the meaning of the curves for volume fraction of catalyst vs. height in figures A.2-A.5 of the patent or in the figure legend. Thus, the reader must assume the identity of the curves.

It appears that this patent is the basis for the several patents that pertain to inert solids. For example, a structurally modified alumina prepared by incorporating a Group IIA metal or metals, particularly Mg or Ba, is claimed to have increased resistance to sintering and agglomeration (A.6). These materials are considered as aiding catalyst fluidization, as a catalyst support, and as heat transfer agents in syngas production or utilization in the slurry phase (A.7-A.12).

Stark (A.13,A.14) was issued a patent to cover the use of pentane (or similar light hydrocarbon) to remove the exothermic heat of reaction of the Fischer-Tropsch process and to expand the pentane to recover the energy to drive air plant compressors. Steam/water is the usual material for heat removal, and is utilized in the commercial reactors at Sasol. However, Stark indicates that it is desirable to have a coolant that has a boiling point and vaporizes at a pressure higher than the reaction pressure; this will ensure that no problem will arise if a leak allows coolant to enter the reaction zone. In order for vaporization to occur with pentane, it is necessary that the coolant side be below the critical conditions (197^{o}C; 44.1 atm. (679 psi)).

Stark (A.13,A.14) claims a method for removing heat from a hydrocarbon synthesis process reaction zone. A cooling medium is passed through the reactor zone in an indirect heat exchange, thereby vaporizing the cooling medium. The cooling medium is chosen so that it possesses the properties of inertness, condensable and vaporizes at a pressure which is at least as great as the pressure in the reaction zone.

Water/steam is frequently employed as the heat transfer medium. However, the authors claim that there is a reasonable expectation of leaks in a F.T. reactor because of the presence of numerous tubes and welds. In the case of water/steam, the reactor pressure is higher than the water/steam side so that F.T. products will leak into the cooling section whenever a leak occurs. The accumulation of products in the cooling side will eventually require the unit to be shut down for cleaning and/or repairs. In this instance, the cooling medium is chosen to have a higher vapor pressure than inside the reactor so that any leakage will be from cooling side to reactor. An appropriate cooling medium is n-pentane, a product of the F.T. synthesis.

The high pressure energy is recovered from the cooling medium through an expander. Preferably a substantial portion of the energy recovered from the expander is used to drive compressors for an air plant which separates oxygen from nitrogen.

The U.S. patent, but not the European patent application, indicates that the F.T. synthesis is carried out in a slurry phase system.

Hydrocracking and Hydroisomerization

Davis et al. (A.15) claim a hydroisomerization process for the conversion of a C_{5+} paraffinic feedstock to middle distillates. This involves contacting and reacting the feedstock and hydrogen at hydroisomerization reaction conditions with a catalyst comprising a Group IB, VIB or Group VIII metal component, or two or more metals, supported on an acidic particulate solid with an average particle diameter of the size range 30 to 150 µm which is dispersed in a paraffinic liquid hydrocarbon.

Davis et al. (A.15) report that in normal hydrocracking with large catalyst particles, secondary reactions, arising from diffusional limitations, produce large amounts of gas and naphtha, and decrease the yield of the desirable middle distillate fractions. To overcome this limitation, staged fixed-bed reactors are operated at relatively low space velocities. They cite an earlier process [U.S. Patent 5,378,348] utilizing a separation into two boiling range fractions (500^{o}F^{-} and 500^{o}F^{+}) and separately hydroisomerizing to make middle distillates.

The hydroisomerization of the present invention is conducted in a slurry phase, preferably with greater than 25% catalyst slurry of particles in the micron size range (preferably 40-60 micron). The catalyst is bifunctional, possessing metallic hydrogenation and acidic functions. The metal oxide support, preferably a silica-alumina material, is prepared as described in reference -[U.S. Patent 3,843,509].

It is reported that one slurry reactor can be used to obtain approximately as much conversion as in three packed bed reactors in series under similar reaction conditions. An additional advantage of the slurry reactor is that a water-steam cooling coil can be used to remove the exothermic heat of reaction and to control the temperature. Using a packed fixed-bed reactor, a complex system of traps and quenching techniques are required to control the heat that is released during the reaction.

Data for the conversion of n-hexane show that the conversion decreases with increasing hydrogen pressure. At a given temperature, the fraction of single methyl branches decreases with increasing feedstock conversion; significant amounts of multi-methyl branched compounds appear at higher feedstock conversion. In contrast, in a fixed bed reactor undesirable cracked products result at higher conversion levels. Even with the slurry technology, the fraction of cracking increases with feedstock conversion at levels above about 80%.

The kinetics of the Fischer-Tropsch wax cracking with a Pd/silica-alumina catalyst was obtained to design a reactor for a commercial scale process. They report that conversion followed zero order kinetics with an apparent activation energy of 30-35 kcal/mole for the conversion range of 30-70%.

Davis and Ryan (A.16) claim a process for producing middle distillate transportation fuels from a waxy product of a hydrocarbon synthesis process. The process consists of:

1. separating the product into a heavier (500^oF^+) and at least one lower (500^oF^-),
2. catalytically isomerize the heavier products in the presence of hydrogen,
3. catalytic hydrotreat the lighter fraction to remove heteroatoms (primarily O), and,
4. catalytically isomerize the product from step (3) to a product with a freeze point of -30°F or lower.

The authors indicate that a cobalt catalyst tends to produce heavier products, e.g., containing C_{20+}, whereas ruthenium tends to produce more distillate type products, e.g., C_5-C_{20}. A typical product slate for a cobalt catalyst is given as (the values may vary by ±10% for each fraction) is given in Table A.2.

Surprisingly, they found that hydrotreatment of the heavier fraction (containing about 0.45 wt% oxygen) prevents the production of a product with the excellent cold flow properties that was formed by hydroisomerization of the untreated material. They indicate the need to limit the conversion for the 700°F+ to the 700°F- products to the 35-

80% range as a measure to limit cracking to produce gases and thereby a lower yield of distillates.

The lighter fraction can be the 320-500°F or, preferably, the entire liquid fraction boiling below 500°F. Following a conventional hydrotreatment, the naphtha is flashed off and the remaining material is hydroisomerized using a catalyst appropriate for light fractions, such as the ones described in reference A.17.

The most active catalysts were those materials containing a surface silica additive. However, it is stated that selectivity is more important than activity. Activity was improved when a 4% surface SiO_2/CoNiMo/10%SiO_2-Al_2O_3 catalyst was used at 700 psig rather than 1,000 psig. Increasing the LHSV to 3.0 and increasing the temperature to provide activity similar to that of LHSV = 0.5 to 1.0 dramatically effected the products; the yield of jet fuel was decreased in favor of gas and naphtha production and the jet fuel had an increased freeze point. The cause for this was not understood but it was speculated that diffusional problems were the major factor.

An international patent application (A.18) claims the production of a high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to C_{20}. The solvent has a molar ratio of iso-/n-paraffins ranging from about 0.5:1 to 9:1 and the isoparaffins of the mixture contain greater than 50% of the mono-methyl species. This patent application employees catalysts and processing schemes that are included in reference (A.19).

The Fischer-Tropsch product was obtained from the conversion of a synthesis gas (H_2:CO = 2.11-2.16) with a titania supported cobalt-rhenium catalyst. The reaction conditions were in the range of 422-428°F, 287-289 psig and feed linear velocity of 12 to 17.5. The alpha of the Fischer-Tropsch synthesis was 0.92.

The 700°F+ boiling fraction was hydroconverted over a Pd-silica-alumina catalyst (0.5 wt.% Pd, 38 wt.% Al_2O_3) to produce 39.4 wt.% conversion of the 700°F+ to 700°F- materials (Table A.3).

Wittenbrink et al. (A.20) describe a processing scheme whereby some oxygenates (primary alcohols) remain in the finished fuel. These oxygenates function to improve the lubricity of the diesel fuel.

The process scheme illustrated in their figure A.6 leads to some confusion. Shown leaving the Fischer-Tropsch reactor (vessel 2) are two streams: 3 (700°F+; 370°C) and 4 (700°F-). It is reported that the reactor is operated in the range 422-428°F (217-220°C) and 287-289 psig using a titania supported cobalt/rhenium catalyst (A22). The syngas had a composition of H_2/CO = 2.11-2.16. The alpha for FTS was 0.92. The FTS products were separated into three fractions having approximate boiling ranges: (1) C_5-500°F (designated F-T cold separator liquids); (2) 500-700°F (F.T. hot separator liquids) and 700°F+ (F.T. reactor wax). It appears that streams 3 and 4 in figure A.6 must be sent to a fractionator (not shown in the figure) to generate three streams.

The hydroisomerization and recombining of fractions are the same, or essentially the same, as described by Davis et al. (A.15) above.

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A.15. S. M. Davis, J. W. Johnson, C J. Mart, D. F. Ryan and R. J. Wittenbrink; European Patent Application EP 0 753 563 A1, filed April 7, 1996.

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A.17. U.S. Patent 5,187,138]

A.18. WO 97/21787

A.19. U.S. Patent 5,378,348

A.20. R. J. Wittenbrink, R. F. Bauman, P. J. Berlowitz and B. R. Cook, International Publication No. WO 97/14769, April 24, 1997.

A.21. U.S. Patent 4,568,663.

Table A.1

Reactor Simulation Results

		Stage 2 Product	
	Stage 2 Feed	Shifting Catalyst	Non-shifting
Component Rates, Moles/Hr			
H_2	11584	3021	6781
CO	2823	564	524
CO_2	16324	15065	16326
H_2O	113	4887	2400
Hydrocarbon + Alcohol	13701	14045	13924
Inert	2434	2434	2434
Moles Converted			
CO		2259	2299
CO_2		1259	-2
Total		3518	2297
% ($CO+CO_2$) Converted		18.4	12.0
Hydrocarbon + alcohol		344	223
Yield, Moles/Hr			

Table A.2

Typical Product Slate from FT Process Liquids Produced with a Cobalt Catalyst (from ref. A.17)

Fraction	Wt.%
IBP-320°F	13
320-500°F	23
500-700°F	19
700-1050°F	34
1050°F+	11
TOTAL	100

Table A.3 Fischer-Tropsch Synthesis conditions	
Operating Conditions	
Temperature, °F	638
LHSV, v/v/h	1.2
Psig	711
H_2 treat rate, SCF/B	2,100
Yields, Wt.%	
C_1-C_4	0.97
C_5-320°F	10.27
320-500°F	14.91
500-700°F	29.99
700°F+	43.86
TOTAL	100
700°F Conversion, Wt.%	39.4
15/5 Distillation Yields, Wt.%	
IBP-650°F	50.76
650°F+	49.24

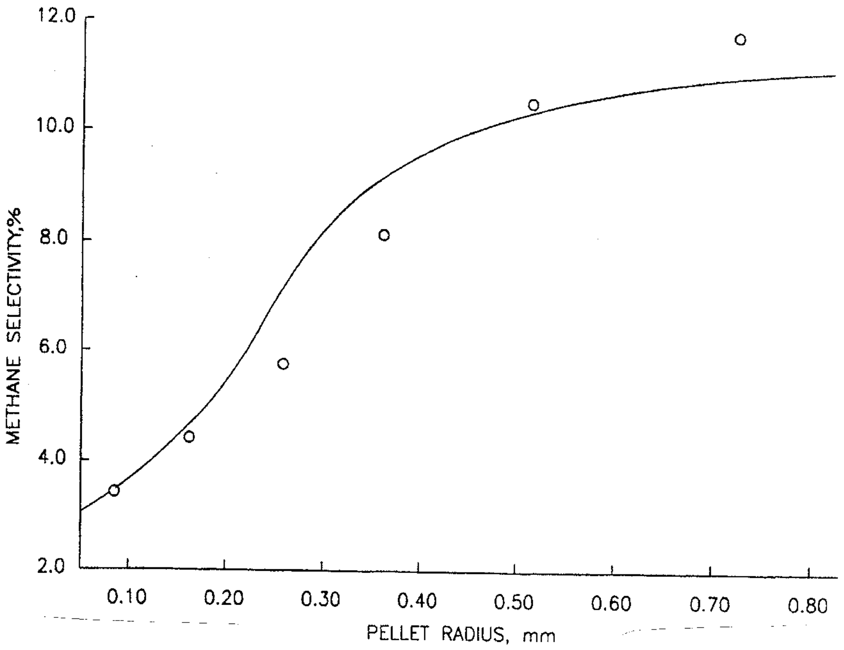

Figure A.1. Model predictions for methane selectivity as a function of pellet radius compared to experimental data (6% CO-0.5% Re catalyst; T = 200°C; $(P_{H_2}/P_{CO})_{feed}$ = 2.0; P_t = 19 atm) (from ref. A.????).

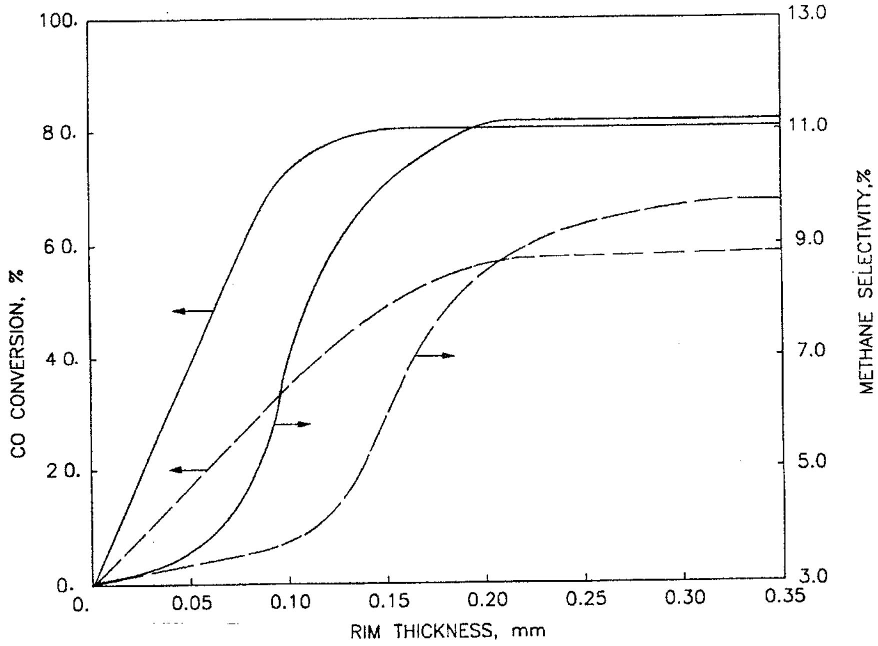

Figure A.2. CO conversion and methane selectivity as a function of rim thickness for spherical particles (d_p = 1.0 mm; T = 200°C; GHSV = 770 v/v/hr; --- A = .6 x 10^{+5} mole/s/s•g•atm^2;))) A = 1.2 x 10^{+5} mole/mole/s/s•g•atm^2) (from ref. A.1).

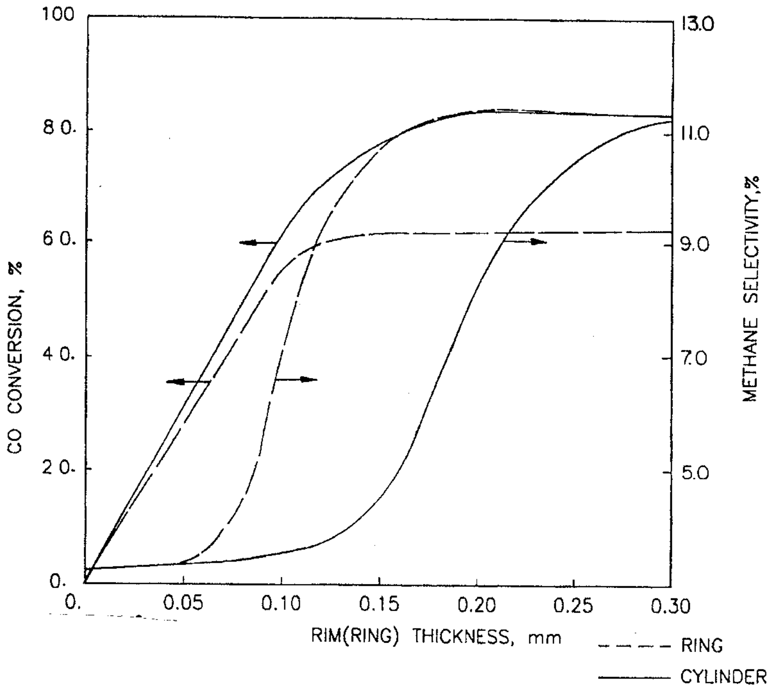

Figure A.3. CO conversion and methane selectivity as a function of rim thickness for ring (---) and cylinder ( )))) pellets (d_p = 1.0 mm; T = 200°C; GHSV = 770; A = 1.2 x 10^5 mole/s•g•atm^2 (from ref. A.1).

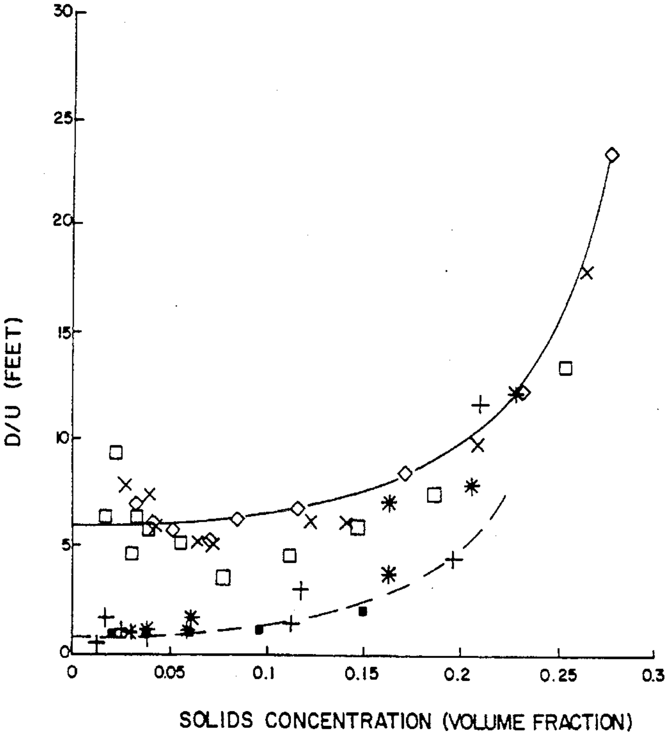

Figure A.4. Plot of decay length versus volume fraction solids concentration (#, 2 cm/sec; G, 8 cm/sec; +, 4 cm/sec; X, 12 cm/sec; *, 6 cm/sec; ◊, 16-18 cm/sec).

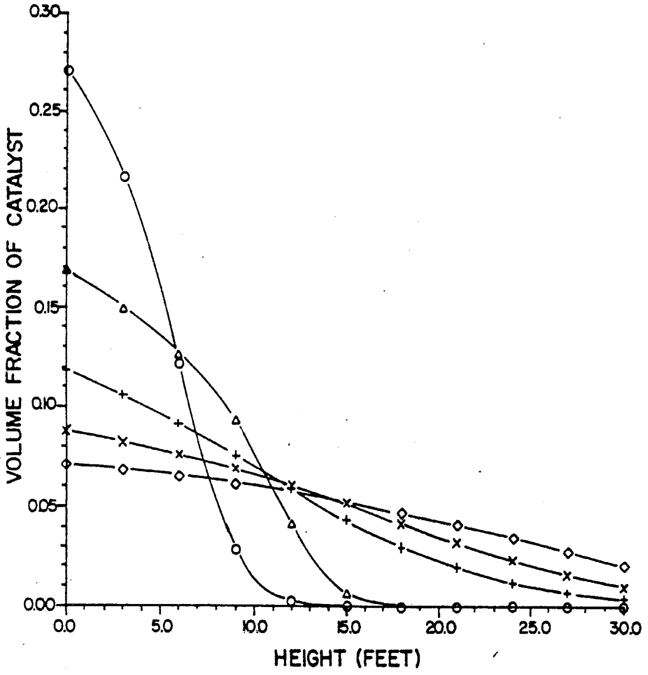

Figure A.5. A plot of volume fraction versus bed height when a second inert solid to a first catalytically active solid in a bubble column, the inerts being of the same density and diameter as the catalytic solid.

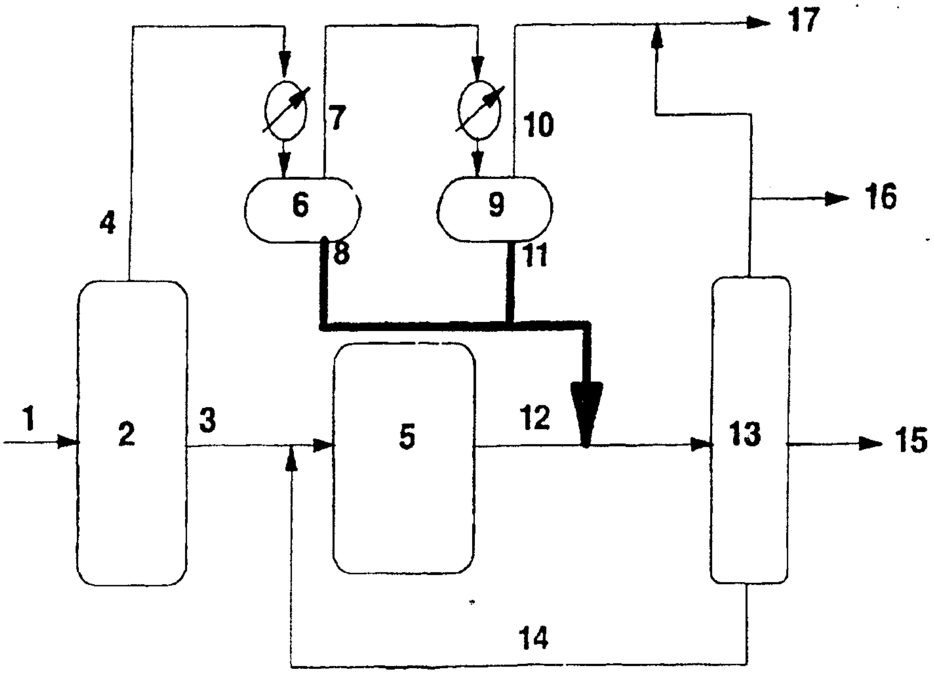

Figure A.6. Schematic of the process (from ref. A.21).

ATTACHMENT XI

Listing of Open Literature Description of Exxon FT Work

A listing of papers by Exxon personnel, and including two by E. Iglesia identified by * that were published after he left Exxon but covering work that was conducted at Exxon. The synopsis will be brief since the results and conclusions in these papers are reviewed in papers XI.1, XI.12, XI.15 and XI.26.

The polymerization of the C_1 monomer produces a distribution described by the Anderson-Schulz-Flory (ASF) distribution. Thus, each carbon number surface species has a probability of continuing the chain growth or terminating the polymerization to produce a product. The ASF mechanism assumes that the ratio of chain propagation r_p, and termination, r_t, are independent of they hydrocarbon chain length. The resulting hydrocarbon selectivity predicted is described as:

$$m_i = \alpha\, m_{i-1} = (1 - \alpha)\, \alpha^{i-1} \qquad [1]$$

where m_i is the mole fraction of hydrocarbon containing i carbon atoms and α is the probability for chain growth and is related to the probability for chain growth and termination as

$$\alpha = r_p / (r_p + r_t). \qquad [2]$$

According to the ASF mechanism, a plot of the logarithm of the mole fractions of the hydrocarbons produced versus the number of carbon atoms in the hydrocarbon should result in a straight line with a single slope given by the chain growth probability, α. Much of the data generated, both in small and large reactor systems, exhibit two values of α. Recently an explanation has been given for this deviation of the hydrocarbon selectivity from that predicted by the ASF reaction mechanism has been offered by workers at Exxon (XI.1,XI.15,XI.18,XI.26). The explanation termed as the Transport-Enhanced Olefin Re-adsorption (TEOR) model is briefly outlined below.

The normal ASF chain growth scheme is outlined in Figure 1. This mechanism for hydrocarbon production has been modified by the Exxon workers first as shown in figure 2 and later as shown in figure 3. The modified mechanism is claimed to be applicable for iron, cobalt and ruthenium catalysts, although date for iron has not been included.

This mechanism distinguishes between paraffins and olefins formed by termination of the hydrocarbon chain on the catalyst surface. Further, the olefins formed can re-adsorb back onto the catalyst surface and re-enter the chain growth process. This process of re-adsorption is quantified by a re-adsorption rate (r_R). Finally, the olefins formed can be hydrogenated, at least partially on other catalytic sites (rate given by r_S) to paraffins. The effective rate of chain termination is then

$$r_t = r_o + r_H - r_R \qquad [3]$$

where r_o is the rate of termination to olefins and r_H is the rate of termination to paraffins. Thus olefin re-adsorption serves to decrease the effective rate of termination.

The rates of chain growth, olefin termination, paraffin termination, hydrogenation and olefin re-adsorption are assumed to be independent of chain length, i.e., the number of carbon atoms in the hydrocarbon. The value of the chain growth parameter, α, is then

$$\alpha = r_p/(r_p + r_o + r_H - r_R) \qquad [4]$$

Note that due to the independence of the rates with chain length, this modified mechanism by itself cannot predict two or more values of the chain growth probability with increasing number of carbon atoms in the hydrocarbon.

The pores inside a catalyst particle are filled with the heavier hydrocarbon products (presumably liquid under reaction conditions) from the FTS. In the TEOR model it is assumed that this limits or exerts a strong influence on the diffusion of the FTS hydrocarbon products (both olefins and paraffins) out of the pores. The effect of diffusion resistance is to increase the time spent in a catalyst pore by the FTS hydrocarbon products. The diffusivity of individual hydrocarbons is dependent on their molecular weight or chain length or the number of carbon atoms. In the TEOR model, the dependence of diffusivity is assumed to be an exponential function of the number of carbon atoms:

$$D = D_o e^{-0.3i} \qquad [5]$$

where D_o is a constant.

As the diffusivity increases with chain length, the time spent inside a catalyst pore is longer for a hydrocarbon containing, for instance, 20 carbon atoms than for a hydrocarbon containing 10 carbon atoms. Thus the olefins containing 20 carbon atoms have a greater chance to re-adsorb on to the catalyst surface and re-enter the chain growth process than olefins containing 10 carbon atoms. Hence, the rate of re-adsorption for a C_{20} olefin is greater than the rate of re-adsorption of a C_{10} olefin, i.e., the re-adsorption rate for heavier olefins is enhanced by transport limitations. Then, according to equation [4], the probability for chain growth, α, should increase with the number of carbon atoms in the hydrocarbon.

The diffusivity of light olefins (C_2-C_{10}) in the liquid-filled catalyst pores is fairly high so that the re-adsorption rate of these olefins is relatively unaffected. Thus, a single value of the chain growth probability, α, is obtained for these hydrocarbons. For hydrocarbons containing higher than 10 carbon atoms, the rate of diffusion becomes increasingly significant. Hence, the rate of re-adsorption, and thus the chain growth probability (α), increases with the hydrocarbon chain length. The increasing rate of olefin re-adsorption with hydrocarbon chain length finally reaches the rate of olefin termination, i.e.,

$$r_R = r_o \qquad [6]$$

at a sufficiently high value of the number of carbon atoms (C_{25} or greater) in the olefin. At this point no more olefins are desorbed from the catalyst surface and the resulting probability for chain growth becomes

$$\alpha = r_p/r_p + r_H \text{ for } C_{25}\text{+ olefins} \qquad [7]$$

Thus, for C_{25}+ hydrocarbons, the chain growth probability does not depend on the hydrocarbon length and once again approaches a constant value.

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ATTACHMENT XII

Review of Fischer-Tropsch Work by Gulf Oil

The Gulf-Badger process leads from the catalysis research work on Fischer-Tropsch synthesis work and the reaction engineering analysis conducted by Gulf Oil, and later the process and engineering design provided by Badger (XII.1). A simplified process scheme is shown in Figure XII.1 (XII.2). The process was first discovered from exploratory work conducted by Gulf in the early 1970s. As Gulf continued to discover large reserves of natural gas, the need to convert remote natural gas to transportation fuels became important (XII.1). Since the exploratory research was successful, fundamental engineering and development work were undertaken, in the early 1980s. Because of its experience with others in the Fischer-Tropsch Synthesis, the Badger Company was invited to participate in some of the experimental work on reactor development and later provided the process engineering as well as the basis for the process economics (XII.2).

The initial involvement by Badger was because they had experience with fluid bed reactors and already had two of them set up in their lab. Gulf management wanted rapid development and did not want to delay to build their own reactors. Gulf researchers apparently advised against using the cobalt catalyst in a fluidized bed reactor but the work progressed to the point where 100 g batches of catalysts were prepared. The catalyst proved to be so active they had to strip insulation off the reactors when the reaction started to go out of control.

More money was spent on the fluid bed work in six months than Gulf had spent in the previous six years. With the result, of course, that the catalyst behaved just as Gulf researchers had predicted. The unit ran fine for half a day or so but then it began to be difficult to keep the catalyst suspended. The catalyst had to be hydrogen-stripped once or twice a day, and the methane make was so high during those stripping periods that the overall selectivity to liquids was rather poor.

At the same time, the go-ahead for fixed bed development was given, and Gulf continued with Badger because they were already familiar with the catalyst and process. The scale-up of the fixed bed process of the catalyst manufacture by Davison were successfully accomplished.

Two types of reactors - two fluid-phase fixed bed and fluidized bed - were seriously considered. Because of the high molecular weight products that are produced by Gulf's most promising catalysts and thermal instability of the reactor, the fluidized bed reactor design concept presented real problems. Therefore, the Gulf Oil reaction engineering staff selected a fixed bed reactor. Its design and operation were critical, but success was quickly achieved.

The proprietary catalyst (in 1983) was inherently stable when combined with the proper reactor design and operation. Catalyst activity decay was avoided when stable, parametrically insensitive conditions and operation were achieved. The catalyst could be regenerated to the original activity by controlled oxidation and reduction.

The catalyst activity is an important property. It has a direct impact on the reactor design and operation as well as on capital and operating costs. The catalysts activity and selectivity in the developed reactor determine the reactor size that is required to produce a given quantity of desirable product, and to convert a given volume of synthesis gas, per day.

Operating conditions also influence the catalytic conversion and selectivity, and thereby the product distribution. An increase in temperature increases the reaction rate whereas decreasing the H_2/CO ratio at constant temperature and pressure decreases the rate with the Gulf catalyst (XII.2). It was found that a 10°C increase in temperature would just about compensate the rate loss for a decrease in H_2/CO ratio from 2 to 1.5. A substantial increase in reaction rate results from increasing the total pressure. The results for increasing pressure and temperature are illustrated in Figures XII.2 and XII.3 (XII.2). Representative data are summarized in Table XII.1 (XII.2). The Gulf-Badger reactor design has a constrained range of performance and acceptable operation.

Production of C_5+ products depends upon both the activity and selectivity of the catalyst, and is a product of these two factors. Thus, some of the effects that increase activity may decrease productivity.

Pilot plant data for a reactor, consisting of a single, commercial-size reactor (1" x 40') tube show that reasonable temperature control can be achieved. Conditions that are representative of those used at Gulf are (XII.2):

Temperature	200-225°C
Pressure	250 psig
H_2/CO feed ratio	1.5-2
Feed space velocity	500-1,000/hr.
CO conversion	40-60% per pass
Selectivity to C_5+	*ca*. 70-75% of carbon converted

A typical product make from a reactor operating under such conditions are illustrated in Table XII.2.

Two reactor concepts were tested during the pilot plant work - a tubular fixed bed and a fluidized bed at Badger. The latter was not satisfactory. Details on only the fixed bed reactor were given in reference XII.2. Gulf's pilot plant consisted of two reactor sections in series (Figure XII.4, ref. XII.2). After initial operation, temperature of the hot spot in the Gulf Oil reactor did not exceed that of the average temperature by more than 5^{o}C. The illustrated CO conversions depended linearly upon temperature, as did the relative rate (Figures XII.5 and XII.6; ref. XII.2). The productivity of C_5+ hydrocarbons did not increase linearly with temperature due to the relative increased production of light (C_1 - C_4) gaseous products (Figure XII.7; ref. XII.2).

A demonstration unit was designed (in 1983) that would produce approximately 15 b/d of naphtha, 15 b/d of diesel fuel and 7 b/d of wax from 350,000 scf of natural gas (Figure XII.7; ref. XII.2). Natural gas was compressed to the reformer pressure and mixed with recycle CO_2, heated and passed through a zinc oxide bed to remove sulfur compounds. The natural gas was obtained by drilling a well at the laboratory site. It then entered a steam-methane reformer and was converted to synthesis gas. Carbon dioxide was removed in an amine scrubber after the gas was cooled and compressed. The gas then passed through a membrane separation system to adjust the H_2/CO ratio. Hydrogen would be used as fuel in the demo plant but could be utilized for upgrading in a commercial operation.

Gulf-Badger Process - Patent Literature

A series of catalysts was prepared that demonstrated a beneficial effect of a minor amount of ruthenium on a catalyst containing a major amount of cobalt for the low pressure synthesis of higher hydrocarbons from synthesis gas (XII.3).

A standard reference cobalt catalyst was prepared according to a published procedure (XII.4) whereby solution I (49.4 g. $Co(NO_3)_2 \bullet 6H_2O$; 11.0 g. $Mg(NO_3)_2 \bullet 6H_2O$ and 1.5 g. $Th(NO_3)_4 \bullet 4H_2O$ dissolved in 250 ml water) and solution II (35 g. K_2CO_3 in 250 ml water) were heated to boiling. Solution I was added rapidly with vigorous stirring to solution II, and immediately thereafter, 20 grams of dry powdered kieselguhr was admixed with stirring which continued for 10 minutes. The mixture was filtered and washed with distilled water until no evidence for nitrate ion was observed in the wash water. The solid was dried at 120°C for 16 hours, calcined in air at 350°C for 16 hours, then reduced in flowing hydrogen at 350°C for 3 hours. A second catalyst was prepared following the same procedure except that 0.35 g. of $RuCl_3$ was added to solution; this catalyst had the following composition: Co (31.6 wt.%); Mg (3.25 wt.%); ThO_2 (1.98 wt.%); Ru (0.53 wt.%); and kieselguhr (62.64 wt.%).

These two catalysts were subjected to synthesis runs using the same experimental conditions (H_2/CO = 2; upflow reactor with preheater for feed gas; atmospheric pressure; gas hourly space velocity based on the total amount of charge gas was 250; g.c. analysis). A series of experiments were conducted at various reaction temperatures with the CO conversion levels shown in Figure XII.9. It is seen that a measurable conversion is obtained only at a temperature of about 125°C or higher. On the other hand, the same catalyst except that it contains Ru, exhibits appreciable conversion at 50°C and maintains this superiority with increasing reaction temperature. The products from the runs at 220°C with the standard Co catalyst and the Ru containing catalyst were analyzed. The products from the standard catalyst exhibited an ASF distribution, with an alpha value of 0.85 (Figure XII.10). The products from the Ru containing catalyst exhibited a product distribution that contained significantly heavier hydrocarbons; the alpha value, based on the curve in Figure XII.10, was 0.98. Thus, the addition of Ru to the standard catalyst resulted in a significant increase in the catalytic activity as well as producing a significantly heavier products. The data indicated that the presence of Ru essentially eliminated the production of methane and ethane (however, this conclusion is on a relative basis). In addition, the C_{9+} product from the standard catalyst contained 29% of olefinic product compared to 4% with the Ru containing catalyst. The gaseous products were found to contain about 15 volume percent CO_2 for the standard cobalt catalyst but only traces of this gas were obtained with the Ru containing catalyst. While it is not stated how the samples were collected, the low value for the C_{9-11} product fraction, relative to lower and higher carbon number products (Figure XII.10), suggests that the products consisted of gaseous and liquid fractions that were subsequently analyzed separately, resulting in loss of some C_{9-11} hydrocarbons.

Similar catalysts were prepared. For catalyst 3, about equal amounts of alumina and magnesia were added to replace kieselguhr in the above Ru containing catalyst (31.6 wt.% Co, 2.0 wt.% thoria, 0.5 wt.% Ru, 32.9 wt.% alumina and 32.9 wt.% magnesia). The other catalyst (4) contained a lower amount of Co and no thoria; at the same time alumina was substituted for the kieselguhr and the amount of magnesium oxide was increased. This catalyst (XII.4) contained 17.77 wt.% Co; 0.70 wt.% Ru, 40.77 wt. % alumina and 40.77 wt.% MgO.

The three catalysts were compared for methane production at various reaction temperatures; these results are compiled in Table XII.3. Referring to Table XII.3, it is apparent that the presence of Ru significantly decreased the amount of methane produced at all reaction temperatures. All Ru containing catalysts produced only traces of CO_2. Substituting gamma-alumina for kieselguhr had little, if any, effect on methane production; likewise, the removal of thoria and an increase in magnesia had little effect on methane production.

As shown in Table XII.4, it is noted that the "% selectivity for C_{9+} fraction" increased, and the % olefin in the fraction decreased, when Ru was present in the catalyst.

It appears that another Gulf worker later repeated Kobylinski's work with precipitated Co and CoRu catalysts, as well as one with the $20Co-0.5Ru-1La_2O_3$ composition. Ru was found to confer better dispersion and activity, just as it did for the impregnated catalysts, but that there was no appreciable change in product distribution in standard week-long tests. Apparently a problem with the GC analysis, such as getting drops of liquid product in with the vapor phase products impacted the reported data. The precipitated catalysts were found to have activities per unit weight of metal that were intermediate between those of catalysts made by aqueous impregnation and those made by nonaqueous impregnation.

High octane gasoline and diesel fuel are produced from synthesis in a two stage process (XII.5). In the first stage, synthesis gas is converted to straight chain paraffins that have a boiling range that falls mainly in the diesel fuel range. A cobalt catalyst, preferably containing a Group IIIB or IVB metal oxide, is supported on gamma- or eta-alumina, or a mixture of these two aluminas. The C_5-C_9 straight chain portion of the product from the first stage is converted in the second stage to highly aromatic plus branched chain paraffinic gasoline using a platinum group metal catalyst. The most preferred metal oxide for use in the catalyst for the first stage is thoria. The support should have low acidity, meaning a Brønsted acidity with $H_o \leq 1.5$, which is less than 5 micromole per gram (about 10^{16} acid sites per m^2 of surface area). The deleterious effect of acidity is the isomerization and cracking of intermediate alkenes, removing them from chain growth and producing a low molecular weight product. **This latter**

statement implies that higher molecular weight alkenes readsorb on the catalyst to react with synthesis gas (or other alkenes) to produce higher alkenes. In addition, the production of low molecular weight products requires either that low molecular weight alkenes do not readsorb to undergo subsequent chain growth or that the low molecular weight products produced by cracking are alkanes, and not alkenes.

The catalyst for the first stage was defined by hydrogen chemisorption and should adsorb at 25°C from 125 to 300 micromole per gram of total catalyst. The chemisorption of hydrogen is illustrated in Figure XII.11 and shows a maximum for a catalyst that is receded in flowing hydrogen at 350°C. The maximum hydrogen adsorption corresponds to a dispersion, d, of cobalt of 0.066; that is, 6.6% of the Co atoms are located on the surface of cobalt metal crystallites.

The support must be of high purity and have a surface area in excess of 50 m^2/g, and preferably in the range of 150 to 225 m^2/g. High purity means that the support will contain negligible amounts of sodium, sulphate, silicon, phosphates or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbons.

The preparation of the catalyst was accomplished using a nonaqueous, organic impregnation solution containing the soluble cobalt and Group IIIB or IVB salts in order to achieve the necessary metal loading and distribution. The alumina was calcined in air prior to impregnation, preferably in 5h 400 to 600°C range. Suitable solvents include ketones, such as acetone or methyl ethyl ketone; the lower alcohols; amides, amines, ethers, hydrocarbons or mixtures thereof. A mixture of ethanol and acetone (4 parts acetone; 1 part ethanol) is preferred and is used in an amount that will fill the pore volume; a maximum amount would be equivalent to five times the total pore volume.

The impregnated material is dried (25 to 45°C) to remove solvent to "dryness" and the material is then calcined in air, preferably 225 to 275°C. The impregnation, drying and calcination steps are repeated until the desired metal loading is obtained. The catalyst is slowly reduced in hydrogen. In the first reduction step, the catalyst is heated slowly (0.5 to 5°C/min) to a maximum temperature of 180 to 220°C and held at this temperature for about 24 hours. The second reduction step is accomplished by heating at a rate of 5 to 20°C per minute to the optimum temperature. Initially the reduction step is accomplished in a diluted hydrogen stream (e.g., 5% hydrogen in nitrogen); gradually the hydrogen concentration is increased to provide pure hydrogen.

While it is stated that the reactor type utilized is not critical, a fixed bed, with gas downflow, was preferred.

The catalyst for the second stage could be a typical naphtha reforming catalyst; that is, a platinum group metal supported on alumina using halogen to impart acidity.

The catalyst which gave the hydrogen adsorption data that is shown in Figure XII.11 contained the following composition by weight: $100Co/18ThO_2/200Al_2O_3$. This catalyst was evaluated for activity using a flow of 240 cm^2/g/hr of CO and the same flow of H_2. Data were obtained for the above catalyst and are summarized in Tables XII.5 and XII.6.

The conversion depends upon temperature as is shown in Figure XII.12 (the numbers in parentheses are the total gas flow rate (cm^2/g/hr)). Thus, at a flow rate of 1:1 synthesis gas of 1.22 NL/g/hr; the conversion of CO was 6.5%. The activation energy was calculated using the data in Figure XII.12 to be 15 kcal/mole. The product distribution changed slightly to favor lower weight products as the temperature increased (Figure XII.13). The product distribution did not adhere to the ASF plot except perhaps for the lowest temperature run; in all instances the C_2-C_4 products were much too low to approach fitting an ASF plot. It was not possible to fit the data in Table XII.2 with an ASF distribution.

This patent covers the activation of a promoted or unpromoted supported cobalt catalyst (XII.6). The catalyst is prepared using cobalt carbonyl and the support is either silica or alumina. The activation procedure comprises three steps: (1) reduction in hydrogen, (2) oxidation in an oxygen-containing gas, and (3) reduction in hydrogen, all three steps conducted at temperatures less than 500^{o}C. This activation comprising reduction, oxidation and reduction has been called "ROR". It has been found that the addition of promoter, such as lanthanum or manganese (and oxides of the lanthanides and actinides), reduces the activity of the unpromoted catalyst. However, if in addition to the above promoters, ruthenium is also incorporated the ROR activation results in an increase in activity above that of the unpromoted cobalt catalyst.

The cobalt carbonyl is added by an impregnation technique using a non-aqueous solvent. If desired, the addition of promoter can be accomplished by co-impregnation along with cobalt. In the preferred procedure, the promoters (metal oxide and/or ruthenium) are added prior to the cobalt carbonyl.

Thus, the promoter is added to the calcined support as described in ref. XII.5. The impregnated catalyst, preferably using the incipient wetness technique, is dried slowly in air. The slow drying procedure is used so as to spread the metals over the entire support. After drying in air, the catalyst is calcined by heating slowly in flowing air to, preferably, 250 to 300^{o}C. The drying and first calcination can be accomplished separately, or done in a combined step. The calcination step is accomplished at a slow heating rate, preferably 0.5 to 1.0°C/min., and held at the final temperature for up to 20 hours (2 h. is preferred). If necessary, the impregnation, drying and calcination steps are repeated to provide the optimum metals loading.

Following the calcination, the catalyst is impregnated with an organic solution containing cobalt carbonyl. Prior to impregnation, the catalyst is not exposed to the atmosphere sufficiently for the support to be rehydrated. If more than one impregnation is required, the catalyst must be subjected to a reduction-reoxidation treatment, the first two steps of the ROR procedure.

The preferred procedure for the ROR process is:

(1) Slowly heat to about 200°C and hold at this temperature for about 20 hours (starting with about 5% H_2 in nitrogen and increase gradually to pure H_2), then heat to the optimum reduction temperature (about 350°C) and hold for about 24 h. Reduction should be slow enough to prevent the volatilization of cobalt carbonyl and to prevent the water vapor from exceeding 1% in the exit gas. Passivation is effected at room temperature using diluted air.

(2) The oxidation step is conducted as described in ref. XII.5.

(3) The oxidized catalyst is reduced as described in step (1) above.

The advantage of the ROR technique was illustrated by the preparation of three catalysts: (A) cobalt carbonyl was impregnated onto Ketjen gamma-alumina; (B) impregnating gamma alumina with cobalt and ruthenium nitrates (20 wt.% Co and 0.5 wt.% Ru); and (C) impregnating gamma-alumina with nitrate salts to give a material containing 25 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% lanthanum oxide. The three catalysts were tested at 185°C; H_2/CO = 1.85 (atmospheric pressure), producing the results shown in Table XII.7.

The ROR treatment of the cobalt carbonyl catalyst provided a more active catalyst than the other two preparations and the selectivity of the cobalt carbonyl catalyst for C_5+ hydrocarbon is comparable to the ruthenium-promoted cobalt catalyst.

Hydrogen adsorption studies showed that the ROR treatment produced lower dispersions of Co than just hydrogen reduction. Thus, catalyst A had a metal dispersion of 0.29 following a reduction in hydrogen, but only 0.13 following the ROR treatment. Thus, the activity per metal site increased rather than the number of sites.

The activity of a silica-supported catalyst prepared using cobalt carbonyl is higher than that of an alumina-supported catalyst; however, the selectivity for C_5+ hydrocarbons is lower. The ROR treatment of the silica-supported material improves the C_5+ hydrocarbon selectivity.

This patent provides additional data to support the view that the reduction-oxidation-reduction, "ROR", technique provides superior activity over the same catalyst when it is just treated with hydrogen (XII.7). Data is also presented to show the improvement in activity when ruthenium is incorporated into the cobalt catalyst. The data shown in Table XII.8 was obtained at 1 atm pressure with [the patent gives the gas composition as weight percent but it surely is molar percent] a 35% CO and 65% H_2 synthesis gas mixture.

As shown in Table XII.8, the use or ruthenium significantly improved the catalyst activity as compared to the test of a catalyst that did not contain ruthenium. Even when the Co/Ru molar ratio exceeded 200/1, the catalyst activity increased in excess of 100 percent over that in which ruthenium was absent. Likewise, the ROR activation led to a catalyst that exceeded the activity of a hydrogen treated material by 24-34 percent.

Data were also presented to show the benefit of Ru for a catalyst prepared by precipitation of cobalt, ruthenium and lanthanum oxide onto an alumina support by the addition of potassium carbonate. In this case the use of the ROR treatment improved the catalyst activity. However, when the amount of ruthenium exceeded 0.5 wt.%, the activity showed a decline of 4%.

A method of catalyst preparation is given which consists of an aqueous impregnation using a solution of a cobalt salt, drying the impregnated material and then employing a nonaqueous, organic impregnation solution of salts of ruthenium and a Group IIIB or IVB metal (XII.8).

A supported catalyst was prepared using a microspheroidal gamma-alumina commercially available from Harshaw; this alumina had an average particle diameter of about 60 microns. After calcination at 600°C, the alumina was impregnated with a cobalt nitrate solution. The material was dried at 120°C and then impregnated with thorium nitrate and ruthenium acetylacetonate dissolved in an acetone-ethanol (=2:1 ratio) solution. Excess solvent was removed at reduced pressure at room temperature in a rotary evaporator. The catalyst was then dried by heating to 90°C with the nitrate salt melting with evolution of water in the temperature range of 50-60°C. Prereduction and passivation was conducted using a hydrogen flow of 720 ml/g/hr. The catalyst was heated to 100°C at 1°C/min and maintained at this temperature for 1 hr and then heated at the same rate to 200°C. After holding at the latter temperature for 2 hr., the catalyst was heated at 10°C/min to 360°C and held at this temperature 16 hrs. After cooling below 200°C, the catalyst was flushed with nitrogen and the temperature lowered to room temperature. Air was then bled into the nitrogen (1:50 air:nitrogen with flow of 50 mL per minute per 5 g catalyst for 16 hr). The final reduced catalyst contained 21.9 wt.% Co, 0.5 wt.% Ru, 2.2 wt.% Tho_2 and 75.4 wt.% alumina.

The activity of the catalyst was obtained using a 1/2" fluid bed reactor where 50 grams of catalyst was heated to a temperature of 350°C in a flow of hydrogen (N L/g/hr) and held at this temperature overnight. The hydrogen flow was reduced to 0.3-0.4 L/g/hr and an equal flow of CO was introduced (if $H_2/CO = 2$, the hydrogen flow was doubled). The results of runs are summarized in Table XII.9.

The results show that, for similar conditions, an increase in the H_2/CO ratio from 1 to 2 caused a decrease in the C_5+ hydrocarbon yield and an increase in the amount of methane. An increase in pressure from 15 to 30 psia caused an even greater decrease in the C_5+ hydrocarbons and increase in methane; an increase in temperature had a similar effect.

A recent paper by Haddad and Goodwin (XII.16) on the CoRu catalyst claimed to obtain no change in activity from a ROR treatment. Looking at their catalyst preparation, they claimed to add 20% Co as the nitrate apparently in one step. This would appear to require the use of a supersaturated cobalt solution. In most catalysts, the alumina does not have enough pore volume to accommodate that much cobalt nitrate. The fact that they saw no ROR effect could be taken to mean that they had not produced an alloy catalyst whereas measurements of Curie point changes showed that the Gulf workers had done so. Goodwin reports TGA studies after a wide range of precalcination and reduction temperature, but none for an RO-treated catalyst. Gulf workers usually found a 100°C lowering in the reduction temperature for an RO-treated catalyst, compared to a fresh one - more evidence of a drastic change in properties.

The best proof of the advantage of ROR was obtained ona large scale - after one year of operation and several hydrogen strippings, the catalyst in the demo plant was regenerated (mainly for experience with recalcination). It was then 50% more active than it had been after initial startup and this made operation with the regenerated catalyst even more difficult. After the plant was shut down Gulf workers tested catalysts from about 20% of the reactor tubes and the catalysts, except for one tube, had the expected catalytic properties.

This patent relates to the use of a mixture of a catalyst active for the Fischer-Tropsch synthesis and one that effects alkene isomerization and/or cracking to produce gasoline from synthesis gas (XII.9). The Fischer-Tropsch synthesis catalyst is any one of the many examples that are comprised of cobalt alone or promoted by ruthenium and/or Group IIIB or IVB metal oxides. The acid cracking/isomerization catalyst is a silicalite-1 type (see XII.10 - XII.12).

An example utilized a catalyst containing 50 wt.% silicalite and 50 wt.% of a catalyst with the composition $100Co/18ThO_2/200Al_2O_3$ (example of conversion data given above). The particles were separately ground to give a particle size 100 mesh, mixed and then wetted, and then comminuting and sieving the resultant mixture to provide uniform 30-40 mesh particle size. Tests were conducted using 0.5 g samples of the prereduced catalyst by reducing in hydrogen at 360^oC in hydrogen 2.4 L/g/hr at one atmosphere. The hydrogen flow was then reduced to 0.48 L/g/hr and an equal flow of CO ($H_2/CO = 1:1$). The tests were effected at 185^oC and one atmosphere pressure to provide the data in Table XII.10.

The impact of the addition of silicalite to the Fischer-Tropsch catalyst is apparent (Figure XII.14). The ASF plot shows that alpha = ~1 for the C_3+ hydrocarbons; however the amount of methane is much above and the C_2 products much below the values expected for conformity to the ASF plot. When silicalite is added to the Fischer-Tropsch catalyst, the data do not fit the ASF distribution. Methane and the C_2-products are slightly higher than was obtained with the Fischer-Tropsch catalyst alone. More importantly, the C_3-C_{10} hydrocarbon products significantly deviate from the ASF distribution. Thus, it is apparent that the acid catalyst has effected a significant amount of isomerization and cracking of heavier hydrocarbons to lighter, gasoline range hydrocarbons.

The fraction of n-alkane in each carbon number hydrocarbon fraction provides a surprising distribution (Figure XII.15). When the catalyst contains only the Fischer-Tropsch component, the amount of n-alkane drops from about 75% for C_2 to about 20% for C_3 and then slowly increases with increasing carbon number to approach 60% for the C_{10} carbon number fraction. In this respect, the cobalt catalyst, when operated at 1 atmosphere, exhibits a distribution that is very similar to the one obtained for an iron catalyst at 1 atmosphere or at intermediate pressure levels (XII.13). However, when the silicalite catalyst is present, the alkane fraction deviates from the one obtained for Fischer-Tropsch synthesis. Up to carbon number 6, a similar trend is obtained for both catalysts; however, above carbon number 6 there is significantly less n-alkane when the silicalite is present. The apparent explanation for this is that the products have increasing fractions of isoalkanes, isoolefins and internal olefins as the carbon number increases above C_4, thus lower fractions of n-alkanes and 1-olefins. Isomerization to iso or internal olefins is not possible with C_2 and C_3. The degree of olefin reincorporation may be strongly influenced by the degree of substitution at the double bond. Ethylene readsorbs the most readily because it has two free CH_2 groups. Among the 1-olefins, readsorption and chain initiation declines slowly with carbon number. Internal olefins readsorb poorly because they have no free CH_2 group, but they can isomerize back to 1-olefins and that gives them a small path towards readsorption. Isoolefins are also relatively unreactive. Although some have a free CH_2, if they have two substituents on the adjacent carbon that appears to be enough to make readsorption difficult.

All that is needed then to lower the effective chain growth probability among C4+ chains is for the 1-olefins, produced as primary products, to be isomerized to internal olefins or isoolefins. That removes them from the F-T reaction. With a catalyst that does this (almost any acidic catalyst), one can observe a large drop in chain growth probability between C_3 and C_4.

The isomerization to isoolefins requires a strong acid site and it was found that this reaction declined fairly quickly with time over silicalite or ZSM-5. However, the isomerization to internal olefins, which requires only moderate acidity, persisted for as long as any of the composites were run, and it was sufficient to alter the ASF distribution.

A layered aluminosilicate (montmorillonite-type structure) containing cobalt substituted into the crystal lattice was activated for the Fischer-Tropsch reaction using a sequential reduction-oxidation-reduction (ROR) technique (XII.14). A Group VIII noble metal, such as ruthenium, is also added by impregnation prior to the final reduction step.

The hydrothermally produced cobalt aluminosilicate has the following general formula prior to its activation:

$$Al_{4\text{-}n\text{-}x3}Co_{3/1n}O_8(OH,F)_4Si_{8\text{-}y}Al_yO(3x\text{-}y)NH_4^{+}zH_2O$$

[it is 3x-+y in the patent]

where n is between 0.02 and 4 (prefer 2 to 3); x is up to about 1 (prefer 0.1 to 0.1); n+x between 0.02 and 4 (prefer 2 to 3); y is between 0.05 and 2 (prefer 0.5 to 2); and z is up to about 10. In the above the predominant amount of Al, Co, OH, and F are in the octahedral layers, and the Si and minor amounts of Al are in the tetrahedral layers. Ammonia and water are located between the layers. Water and ammonia are lost in the pre-activation calcination. The reduction is carried out in hydrogen (or other reducing gas) and the oxidation process is preferable accomplished in air or diluted air. The activation is accomplished in three steps - the ROR process described earlier.

A catalyst is prepared using a saturated aqueous solution of 161 g of $AlCl_3•6H_2O$ in two liters of water that is slurried with 1.84 g of a silicic acid solution providing a Si/Al=4.7 ratio. The silica-alumina gel was precipitated by adding the slurry to 1 L of ammonium hydroxide with a pH of 8. The gel was washed with distilled water to remove chloride. A 50 g sample of the washed gel was slurried with 225 ml of water containing 60 g of cobalt acetate, 0.78 g of ammonium fluoride, and 0.42 g of HF while stirring and maintaining the pH at 8.-0 by adding ammonium hydroxide as needed. The mixture was heated at 300^oC in an autoclave (1,240 psig) for four hours. After drying at 120^oC, the gel was calcined at 500^oC for 4 hrs and produced a hard, wine-red solid with SiO_2/Al_2O_3 = 0.30. The catalyst was reduced at 400^oC for 2 hr in hydrogen and then reoxidized at 500^oC. A hydrogen reduction at 600^oC (16 hr.; 8.5% wt. loss) then reoxidized in air at 500^oC (8.1% wt. gain). A final reduction was effected at 400^oC for 16 hours.

This catalyst was utilized at 1 atm. in a 0.5 g. catalyst bed using a hydrogen:carbon monoxide = 1:1 with a feed of 0.48 l/g/hr. Three temperatures were utilized following activity stabilization to produce the results shown in Table XII.11.

The major products in the C_5+ hydrocarbons were found to be isoalkanes and isoalkenes. The alkenes contained a high fraction of internal alkenes.

The catalyst is a rare earth promoted layered complex metal silicate composition characterized as having repeating units with a structural formula

$$[(1-x)Ni^a + xRu^b]_n(OH)_4Si_2O_5 \bullet wH_2O$$

where x is a number from 0 to 1 (fraction of Ru in Ru+Ni); a is the valence of nickel, b is the valence of ruthenium; n is a number defined by

$$6/[a(1-x) + bx]$$

and w is a number ranging from 0 to 4 (XII.15). The preferred catalyst is a rare earth promoted nickel chrysotile.

These catalysts produce much methane in addition to higher carbon number hydrocarbons. Typical examples, using H_2/CO = 2.5; 350 GHSV; 210°C; and atmospheric pressure, are shown in Table XII.12.

Low concentrations of thoria are needed but higher (30% or more) are not beneficial, and may have a slight detrimental effect. The inclusion of low concentrations of thoria greatly increase the amount of C_2+.

Typical examples, using H_2/CO = 2.3; 400 GHSV; 204°C; and atmospheric pressure, to define the differences in rare earth promoters, if any, are shown in Table XII.13.

The results show that there is a synergistic benefit in conversion when a mixture of two rare earth promoters are used. Thus, thoria incorporation provides a CO conversion of 31.5% and lanthana 25%; rather than the expected intermediate value for CO conversion when a mixture of thoria and lanthana are incorporated, the CO conversion is 71.5%. A similar result is obtained when thoria and praseodymium is utilized.

Slurry Phase Synthesis

A patent (XII.17) claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support. In subsequent claims the support was identified as alumina or silica. Another subclaim indicated that the fluid is a liquid medium which could be a synthetic hydrocarbon liquid or a hydrocarbon conversion product. The activation known as ROR (reduction in hydrogen, oxidation, reduction in hydrogen) was claimed. A promoter could be selected from the group consisting of Rh, Pt, Pd, Ir, Os, Ag and Au. The use of these catalysts produced a product with less than 16 wt.% methane. The catalyst cobalt concentration covered was from about 5 to about 25 wt.% and the promoter in an amount from about 0.01 to 0.5 wt.% based upon the total catalyst weight.

The patent contains examples of conversions in fixed-bed reactors with a catalyst prepared to have various particle sizes. A catalyst was prepared that had a particle size that one normally encounters in fixed-bed operations (1/16th inch (0.16 cm) extrudate) and then this catalyst was ground to produce average particle sizes of 0.28 and 0.54 mm. The found that both catalyst activity and product selectivity changed with particle size. In particular, the fraction of methane decreased and the amount of C_5+ increased with decreasing particle size of the catalyst (Figures XII.16 and XII.17); over the particle sizes tested it appears that both selectivities change linearly with particle size. It appears that the methane production of the three catalyst sizes extrapolates to a common value of about 4 wt% at very small particle size (Figure XII.16). Likewise, the C_5+ selectivity appears to approach about 87 wt.% at very small particle size. This means that the C_2-C_4 yield is about 9 wt.% for the very small particle size catalyst. As expected, the rate of reaction increased as the particle size was decreased (Figure XII.18). For the smallest particle size (0.24 mm) the reaction rate increased by a factor of 1.94 for an increase in temperature of 10.5^{o}C, a factor close to the rule of thumb of a doubling in reaction rate for every 10^{o}C increase in temperature. At 195^{o}C, the rate decreased by 27% when the H_2/CO ratio was decreased from 2.0 to 1.5.

The authors indicate that the catalyst prepared using an organic solvent has higher activity than one prepared in the same manner but using an aqueous solution. The authors indicate that the catalyst may contain Group IIIB or IVB metal oxide as a promoter, with oxides of the actinide and lanthanide series being preferred. Especially preferred metal oxides are La_2O_3, CeO_2, ZrO_2, TiO_2, HfO_2, or ThO_2. MnO_2 and MgO are also listed as preferred promoters. The amounts of these promoters can be from about 0.05 to 100 parts by weight to 100 parts by weight of cobalt. It appears that the patent covers only catalysts using these oxides as promoters, and not as the support material.

The support should have low acidity. Its surface area should be at least about 40 to 50 m^2/g but not so high that "permit reactant materials to enter the interstices of the catalyst." A preferred surface area is in the range of 150 to 225 m^2/g. The support should be high purity, meaning having low concentrations of components having deleterious effects on the cobalt catalyst.

The process is outlined in figure XII.19 and does not differ significantly from one used by Kölbel and coworkers (XII.18). In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present from about 2 to 40 wt.%. The catalyst density can be in the range of 0.25 to 0.90. The gas flow enters at a rate sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Figure XII.19. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone (54) before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. The catalyst for the fixed bed reactor was supported on 1/16 inch extrudate alumina which contained about 20 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides. The synthesis gas (H_2/CO = 2.03:1 with methane diluent of 19.1 mole %) passed through the 1" i.d. reactor at a maximum stable temperature of 215°C with a pressure of 275 psi (18.7 atm., 1895 kPa). For the slurry reactor, alumina which contained about 12 wt.% Co, 0.3 wt.% Ru and 0.6 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides was in the form of 20-105 microns (less than 140 mesh; average particle size 52 microns). A liquid with a viscosity of 8 centistokes (8×10^{-6} m^2/s) was composed mainly of C_{40}-C_{50} isoparaffins. Gas entered at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (10.7 atm) and the gas flow with $H_2/CO = 1.95$ was 1826 cm/s. Initially the temperature was 225^oC but was increased and held at several higher temperatures to obtain additional conversion data.

The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol) (Figure XII.20). This value of the activation energy is surprisingly close to that reported for a fused iron catalyst (20.0 kcal/mol; 83.6 kJ/mol) and a precipitated iron catalyst (20.9 kcal/mol;87.4 kJ/mol) (XII.19). At 225^oC, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240^oC. As the temperature increases, the C_5+ fraction gradually decreases (Figure XII.21) and the C_5-C_{20} fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table XII.14).

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Table XII.1

Evaluation of G-B Catalyst in Pilot Fluid Bed Reactor
Data Taken at 25 Hours on Stream (from XII.2)

Run	Temp., ^oC	Pressure, (psig)	H_2/CO	Syngas Space Velocity, $cm^3/g/h$	Per Pass CO Conversion, %	Selectivity to C_5+^a
First	195	15	2.0	600	25	74
Second	195	30	2.0	1200	22	82
Third	195 215	30 30	2.0 2.0	1200 1200	16 44	74 71
Fourth	215	60	2.0	1950	41	72
Fifth	205	30	1.5	1200	17	72
Sixth	215	30	3.0	1200	76	55
Seventh	205	30	2.0	1200	23	67
Eighth	205	30	2.0	1800	25	73
Ninth	215	40	1.5	1600	25	72

a. C_5+ expressed as percent of carbon selectivity basis.
b. At some point, every run had one or more reactor "run aways." They all failed.

Table XII.2

Typical Data from Fixed Bed Pilot Plant (XII.2)

Temperature, ^oC	210
Yields, Wt.% of Hydrocarbon Product	
CH_4	13.7
C_2H_4 to C_4H_{10}	11.6
C_5-C_8 (naphtha)	25.4
C_9-C_{20} (distillate)	33.4
C_{21}+ (wax)	14.2
Oxygenates	1.7

Table XII.3

Influence of Ru on Catalyst Performance (from ref. XII.3)

Experimental Conditions: H_2:CO = 2:1, GHSV = 380

		% Selectivity to CH_4 Catalyst from Example			
Ex. No.	Temp., °C	1 (Co)	2 (Co + Ru)	3 (Co + Ru)	4 (Co + Ru)
18	200	9.8	0[a]	0	0
19	300	27.5	0	0	0
20	400	48.0	0	1.2	0.5
21	450	87.0	10.1	21.0	25.0

a. The low selectivities (zero) are most likely not real.

Table XII.4

Influence of Ru on the Production of C_9^+ (from ref. XII.3)

		% Selectivity to C_9+ Fraction Catalyst from Example Number in Table XII.3				% Olefins in C_9+ Fraction Catalyst from Example Number in Table XII.3			
No.	Temp., °C	1	2	3	4	1	2	3	4
22	200	41	88	87	--	29	4	5	3
23	300	30	75	71	73	32	10	9	7
24	400	18	41	38	34	48	30	26	21

Table XII.5

Products Using a Prereduced Co-Th-Alumina Catalyst (from ref. XII.5)

Example No.	2	3	4	5[2]	6[3]
Temp., °C	175	185	195	205	194
H_2/CO	1:1	1:1	1:1	1:1	2:1
CO Flowrate (cm^3/gram/hour)	155	155	270	610	270
CO Conversion Rate (cm^3/gram/hour)					
To CO_2	0.2	1.1	1.6	2.9	(1.3)
To Hydrocarbons	19	41	61	79	(120)
CO Conversion (Percent)	13	27	23	13	44
Product Distribution (Carbon Atom %)					
CH_4	4	5	6	8	9
C_2-C_4	6	7	8	10	9
C_5-C_8	23	25	29	34	24
C_9-C_{20}	62	59	50	44	49
C_{21}+	5	4	7	4	9

[2] Separate run.
[3] Not aged at 205°C.

Table XII.6

Alpha Values for Runs Shown in Table XII.5 (From ref. XII.5)

Run Number	Alpha, Based on C_5-C_8/C_9-C_{20}
2	0.89
3	0.82
4	0.83
5	0.79
6	0.74

Table XII.7

Impact of ROR (reduction-oxidation-rereduction) of a Co Catalyst (from ref. XII.6)

	CO Conversion Rate (cc/gram Co/hour)		C_5+ Liquid (Wt.%)	
Catalyst	R350	ROR	R350	ROR
A	1230	1485	73	81
B	790	1190	80	79
C	690	960	81	--

Table XII.8

Influence of Ru on Activity of a Co Catalyst (from ref. XII.7)

		Co/Ru Ratio		195°C CO Conversion Rate (cc/gram metal/hour)	
Test No.	Ru (Wt.%)	(Wt.)	(Molar)	R350 (F)	ROR (G)
1	0.0	---	---	382	476
2	0.05	400	693	780	968
3	0.10	200	346	879	1093
4	0.50	40	69	1034	1415
5	1.00	20	35	930	1286

Table XII.9
Influence of Temperature on a Co-Th-Alumina Catalyst (from ref. XII.8)

Example No.	2	3	4	5	6
Temp., ^oC	195	195	195	205	215
Pressure, psia	15	15	30	30	30
H_2/CO	1:1	2:1	2:1	2:1	2:1
CO Flowrate (cm^3/gram/hour)	310	310	735	735	735
CO Specific Rate (cm^3/gram/hour)	70	95	102	200	257
C_5+ Synthesis Rate (mg/gram/hour)	38	48	47	83	97
Product Distribution Carbon (Atom %)					
CH_4	6	10	15	19	22
C_5+	88	79	73	64	58
C_9-C_{20}	57	45	41	32	25
C_{21}+	9	5	6	4	1
CO_2	2	2	1	2	2

Table XII.10
Influence of Silicalite on the Product Distribution (from ref. XII.9)

	$Co/ThO_2/Al_2O_3$		$Co/ThO_2/Al_2O_3$ + Silicalite	
Carbon No.	Carbon Atom %	Wt.% n-Paraffin in Fraction	Carbon Atom %	Wt.% n-Paraffin in Fraction
1	4.7	(100)	11.3	(100)
2	0.7	50	1.8	75
3	2.5	15	8.4	24
4	3.5	20	23.2	25
5	5.0	25	23.1	35
6	6.1	33	14.9	45
7	6.8	46	9.0	38
8	7.5	56	4.8	22
9	8.5	58	2.3	13
10	9.4	62	0.9	5
11+	45		1	

Table XII.11

Products from the Conversion of Syngas with a Co-Silica-Alumina Catalyst (from ref. XII.14)

	Temperature, °C		
	175	185	195
Yield, Wt.%			
C_1-C_4	22	25	34
C_5-C_{11}	54	60	57
C_{12}+	24	15	9
Relative Rate, mg/g/hr[a]			
C_1-C_4	0.3	0.5	1.1
C_5-C_{11}	0.7	1.2	1.8
C_{12}+	0.3	0.3	0.3

[a] The units or the numerical values are probably in error. They may be specific rates (mg/g cat/hr) but if this is the case, the magnitude of the values are questionable. In any event, it appears that the rates are only about one-tenth that of a good Co-Al_2O_3 catalyst. The low activity may be due to the difficulty of reducing Co in the above catalysts.

Table XII.12

Effect of Thoria Concentration on Product Composition (from ref. XII.15)

			Mol % Selectivity to	
Example No.	Wt.% ThO_2	% CO Conversion	CH_4	C_{2+}
30	0.5	31.1	92.0	8.0
31	1.5	29.0	55.0	45.0
32	2.0	30.5	57.0	43.0
33	3.0	33.2	57.5	42.5
34	5.0	31.0	54.3	45.7
35	10.0	28.6	55.5	44.5
36	20.0	21.4	58.2	41.8
37	30.0	11.2	50.3	49.7

Table XII.13

Relation of Catalyst Composition to Conversion and Product Selectivity (from ref. XII.15)

Example No.	Catalyst	Wt.% Rare Earth	% CO Conversion	% Selectivity to C_{2+}
11	Ni-Chrysotile	0	17.0	0
38	Th-Ni Chrysotile	2	31.5	43.0
39	La-Ni Chrysotile	2	25.0	39.0
40	Ce-Ni Chrysotile	2.5	32.5	32.1
41	Pr-Ni Chrysotile	2	35.3	35.0
42	Th + La-Ni Chrysotile	2 + 2	71.5	49.0
43	Th + Pr-Ni Chrysotile	2 + 2	69.1	48.0

Table XII.14

Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. XII.17)

Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, ^{o}C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C_5-C_{20} (mg/g/h)	67	325	400	478	560
C_5+, wt.%	60.0	79.0	78.0	76.0	73.0

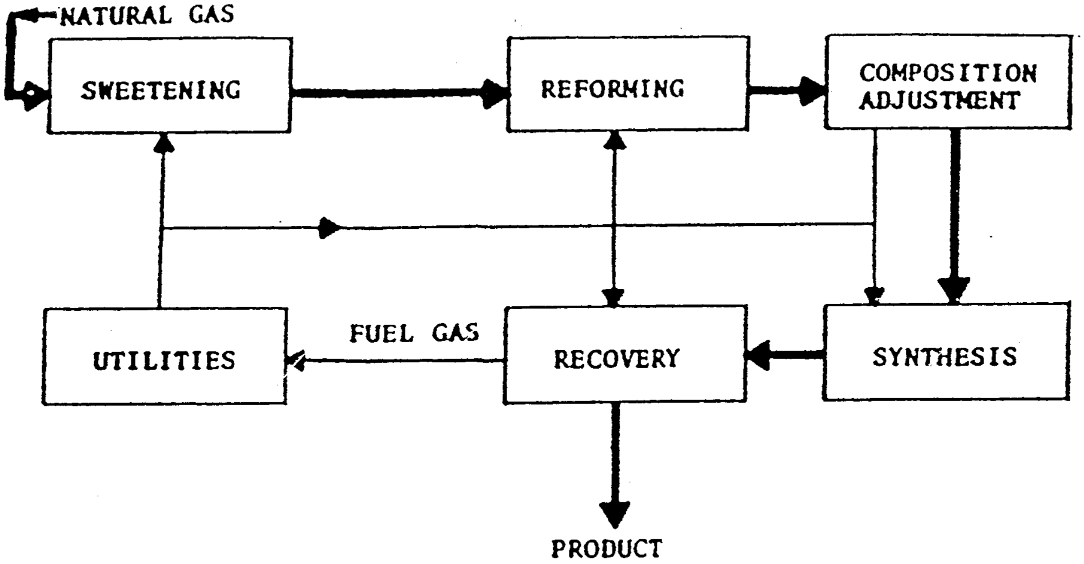


Figure XII.1. G.B. process, remote natural-gas conversion (from ref. XII.2).

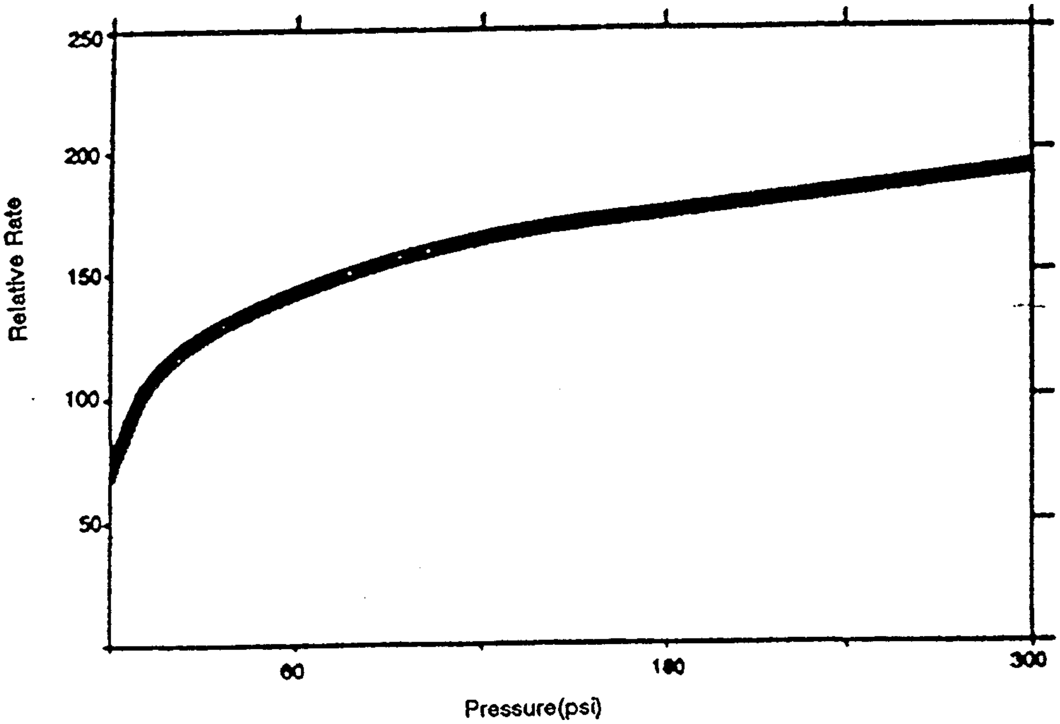


Figure XII.2. Effect of pressure on catalyst activity (relative rate based on data as given in Table XII.1) (from ref. XII.2).

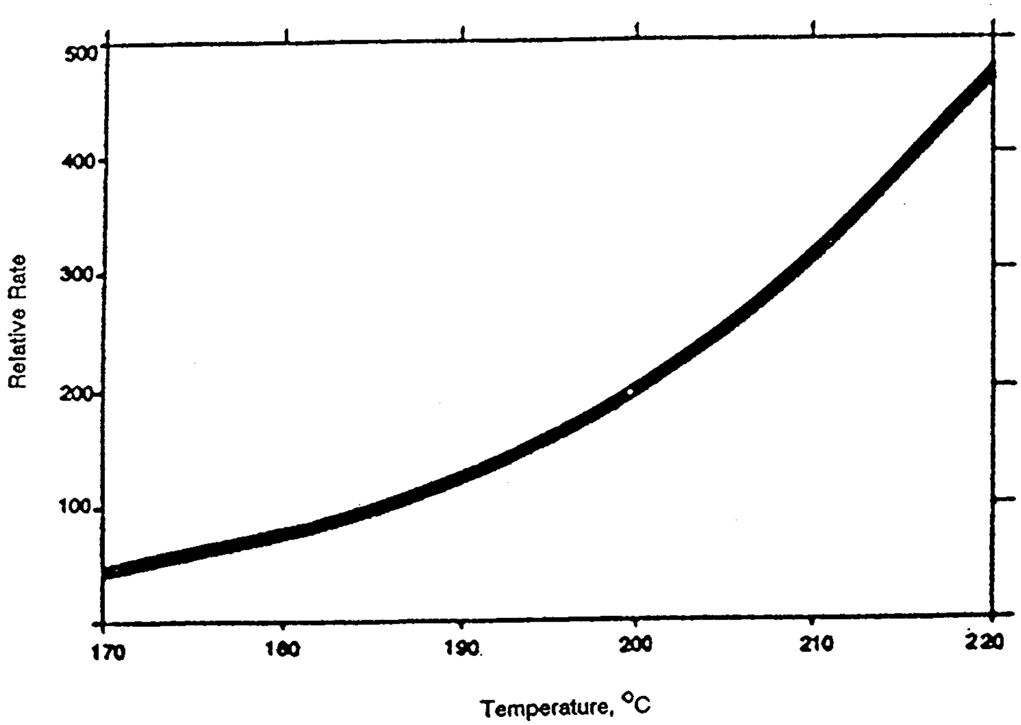


Figure XII.3. Effect of temperature on catalyst activity (relative rate) (from ref. XII.2).

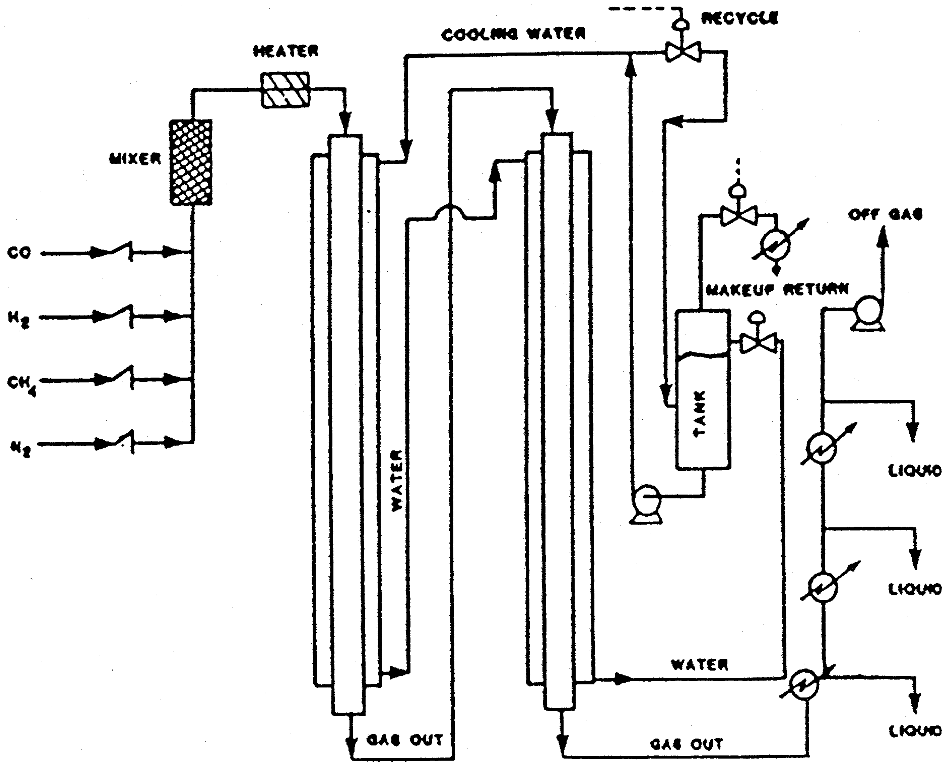


Figure XII.4. Schematic diagram of the pilot plant remote-gas-to-diesel fixed-bed process (from ref. XII.2).

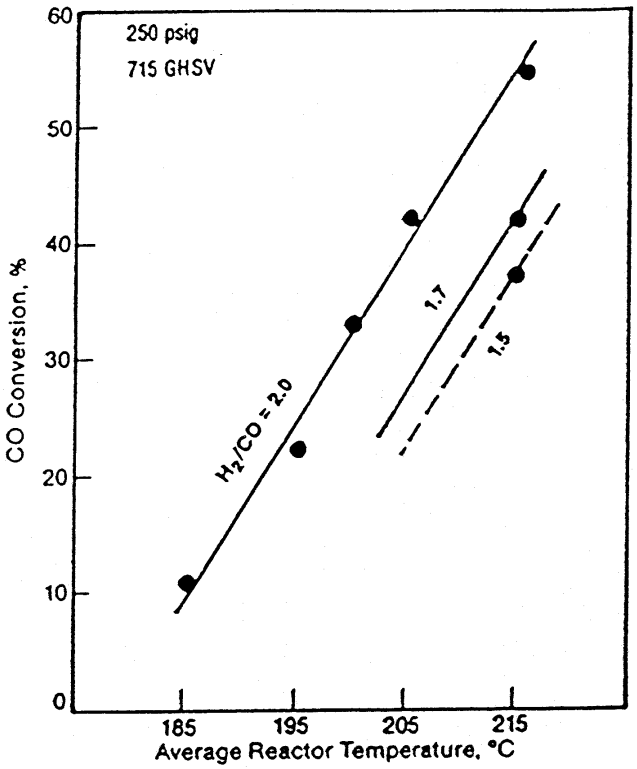


Figure XII.5. Effect of temperature and H_2/CO on carbon monoxide conversion (from ref. XII.2).

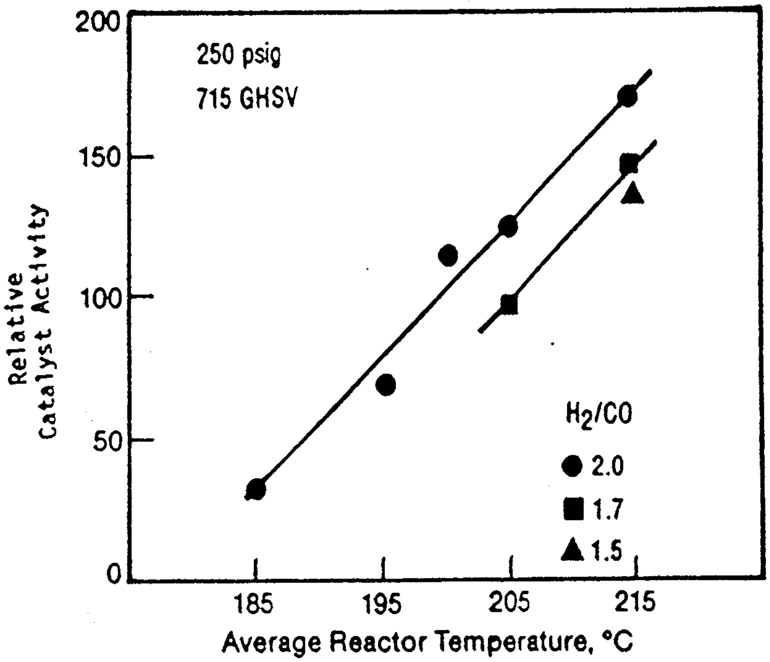


Figure XII.6. Catalyst activity (from ref. XII.2).

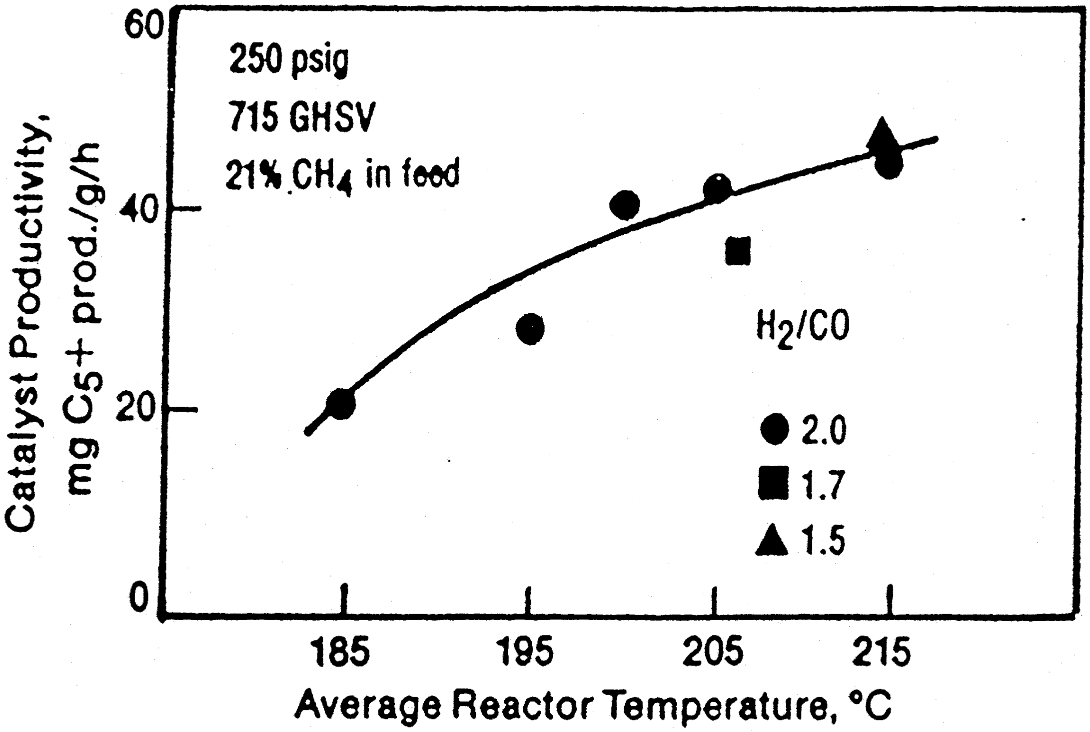


Figure XII.7. Catalyst productivity (specific rate) (from ref. XII.2).

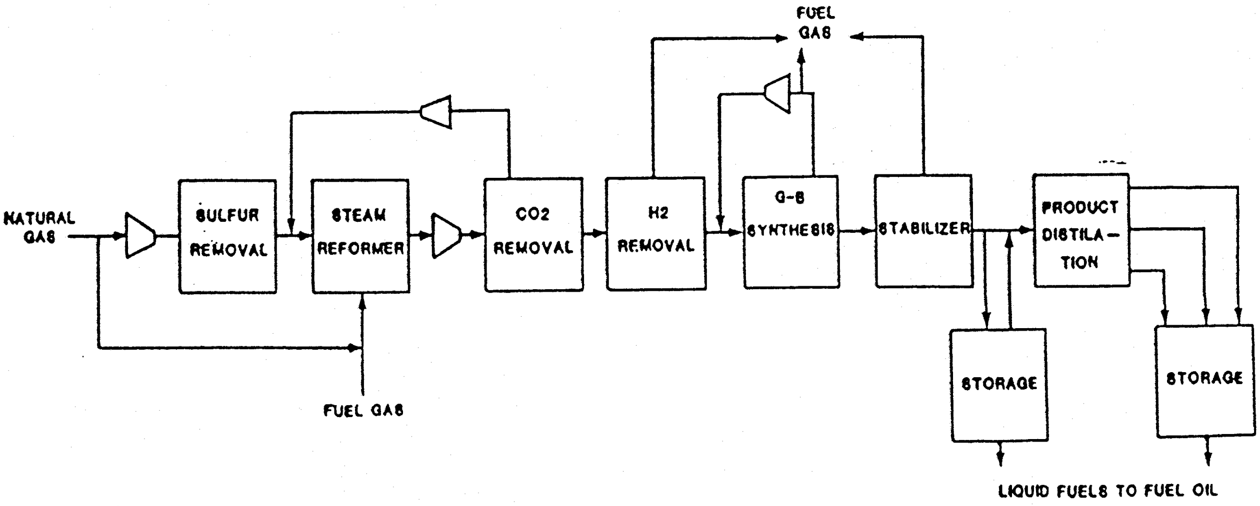


Figure XII.8. G.B. demonstration plant, block-flow diagram (from ref. XII.2).

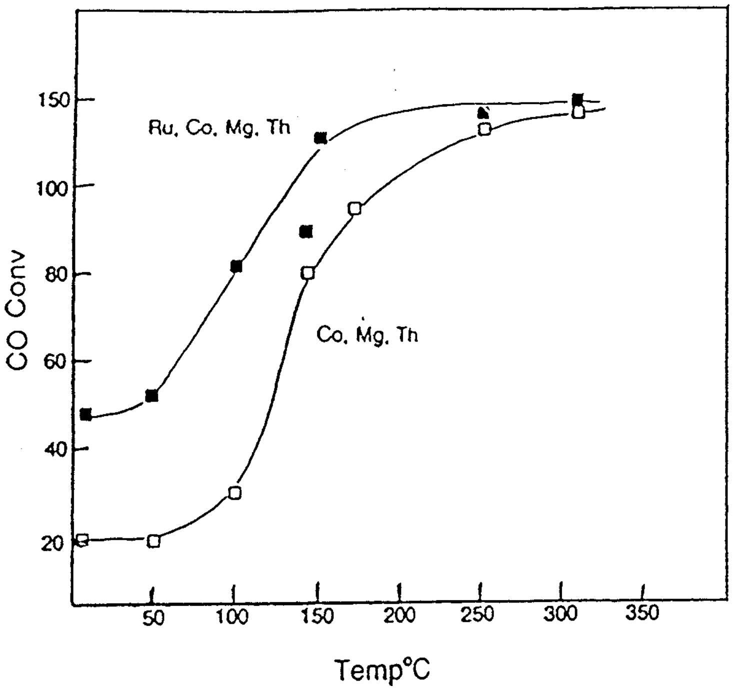


Figure XII.9. The impact of Ru (# data points) on a Co ($MgThO_x$) catalytic conversion as a function of temperature (data from XII.3).

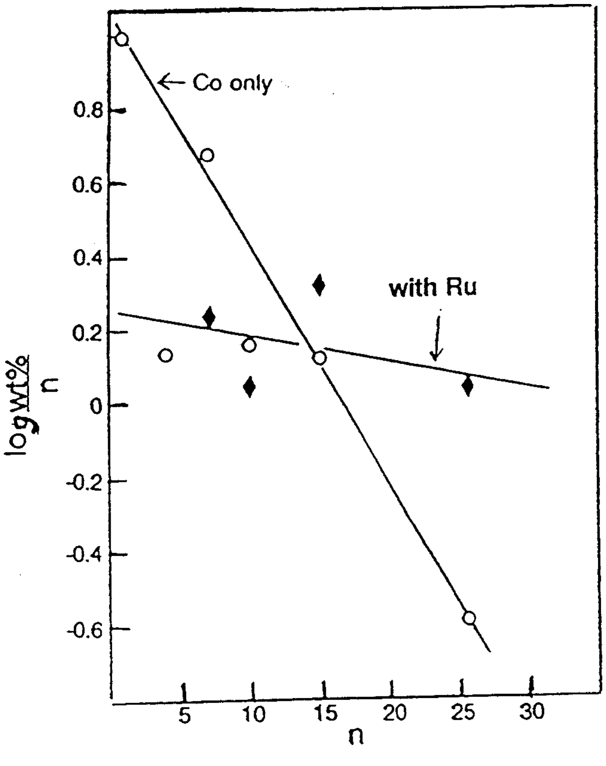


Figure XII.10. Anderson-Schulz-Flory plot of the products from the synthesis using a Co catalyst and one also containing Ru, Mg and Th) (data from XII.3).

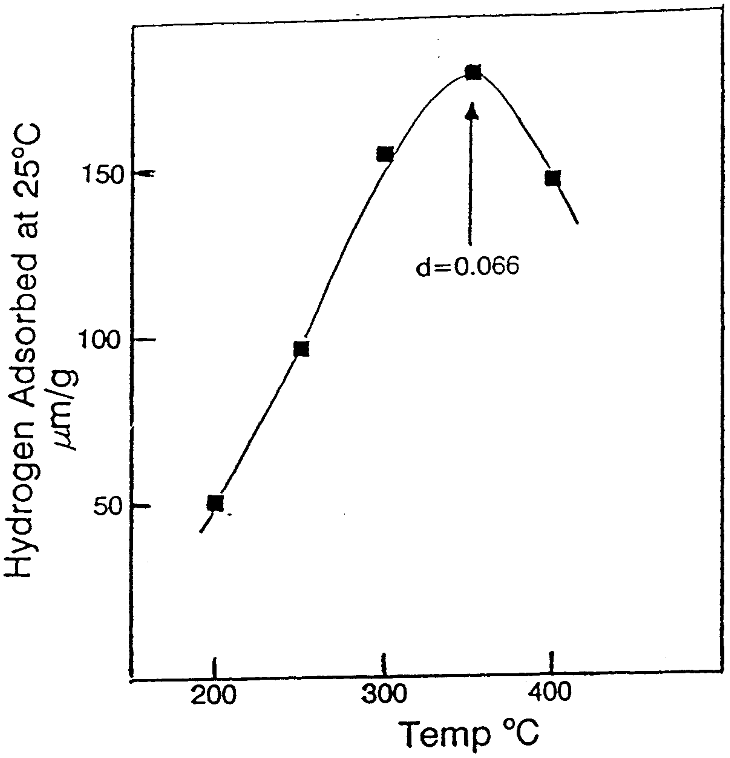
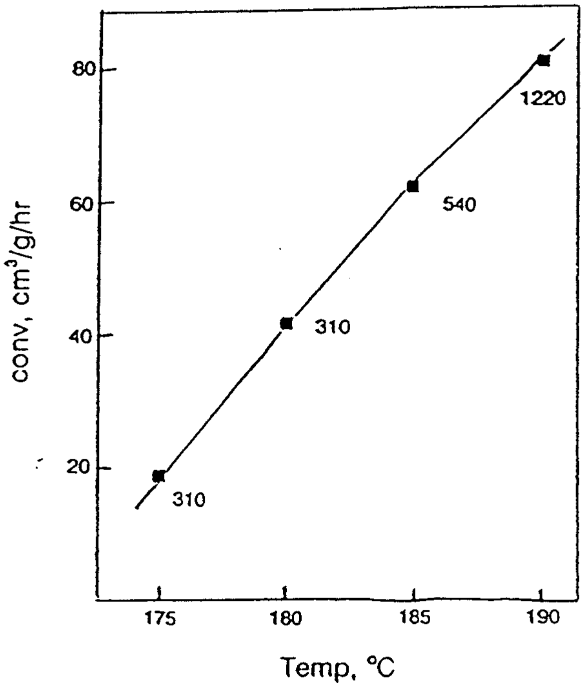


Figure XII.11. Co dispersion measurements as a function of temperature (data from XII.5).



igure XII.12. Dependence of CO conversion on the temperature (numbers in figure are the GHSV) (data from ref. XII.5).

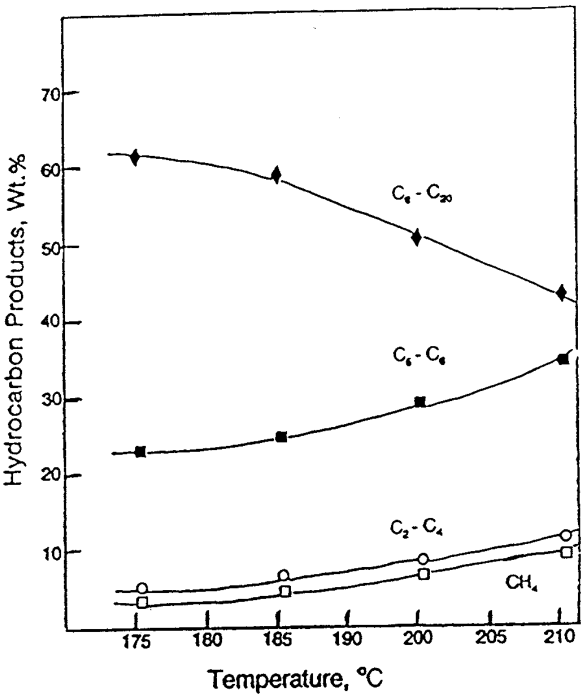


Figure XII.13. Hydrocarbon product distribution for a cobalt catalyst as a function of temperature (data from XII.5).

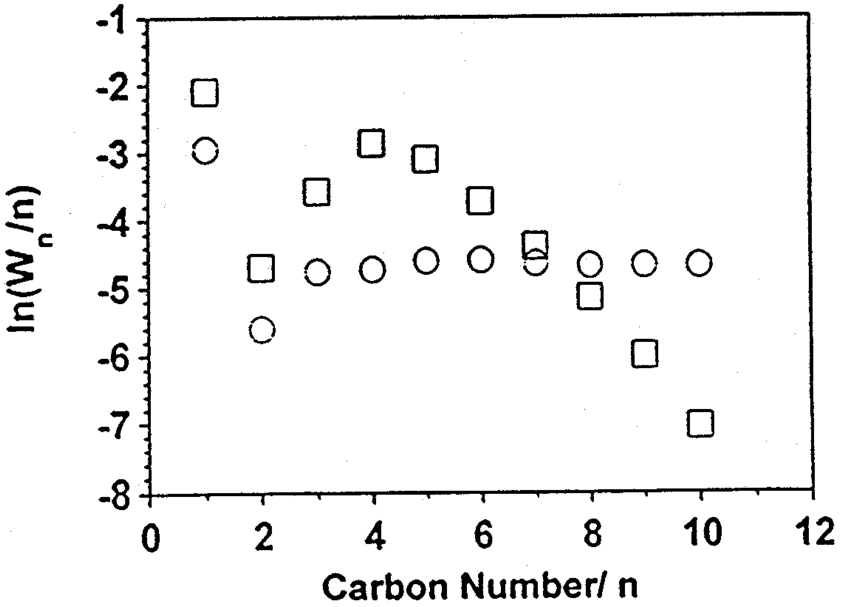


Figure XII.14. Anderson-Schulz-Flory plot of the products from the Fischer-Tropsch synthesis with a cobalt (Th, Al_2O_3) catalyst alone (F) and physically admixed with a silicate zeolite catalyst (G) (data from XII.9).

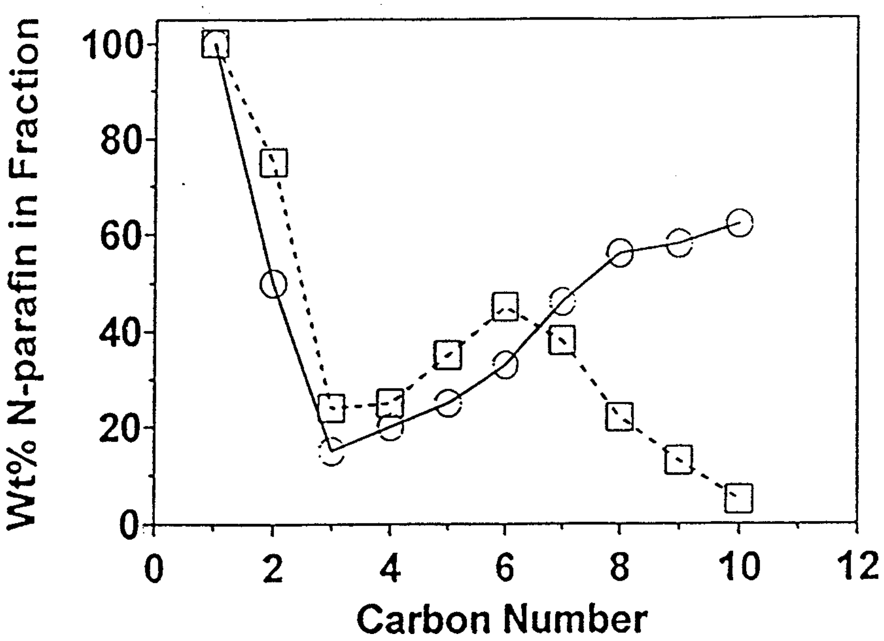


Figure XII.15. Wt% N-alkane in the carbon fractions of the products from Fischer-Tropsch synthesis with cobalt (Th, Al_2O_3) catalyst (F) and physically admixed with silicate zeolite (G) (data from XII.9).

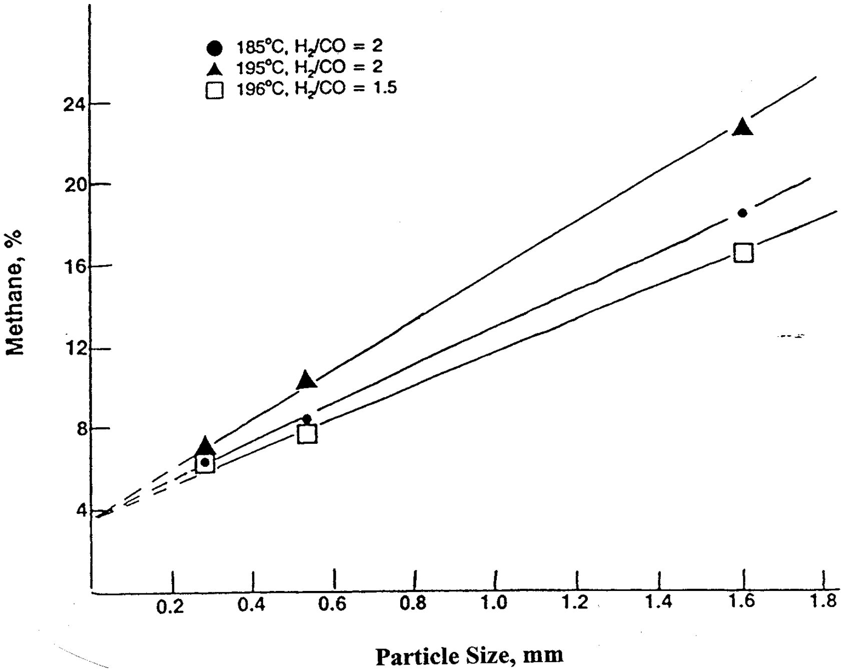


Figure XII.16. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

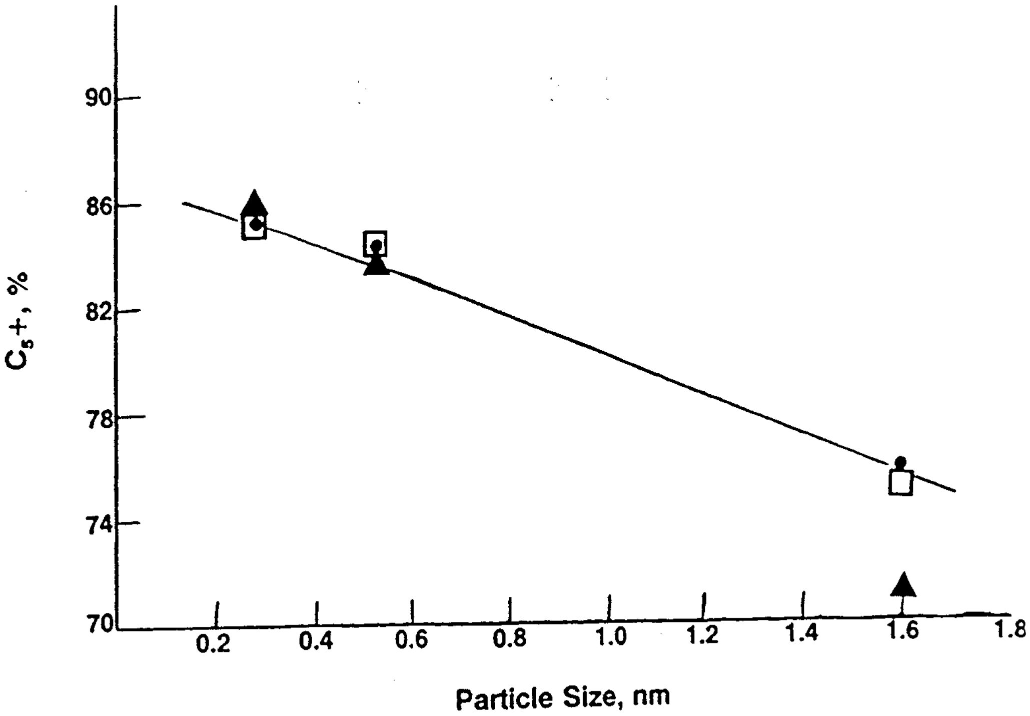


Figure XII.17. C_5+ product selectivity for three particle size catalysts in fixed-bed reactor (! , 185^{o}C, H_2/CO = 2; ▲, 195^{o}C, H_2/CO = 2; G, 195^{o}C, H_2/CO = 1.5) (from XII.17).

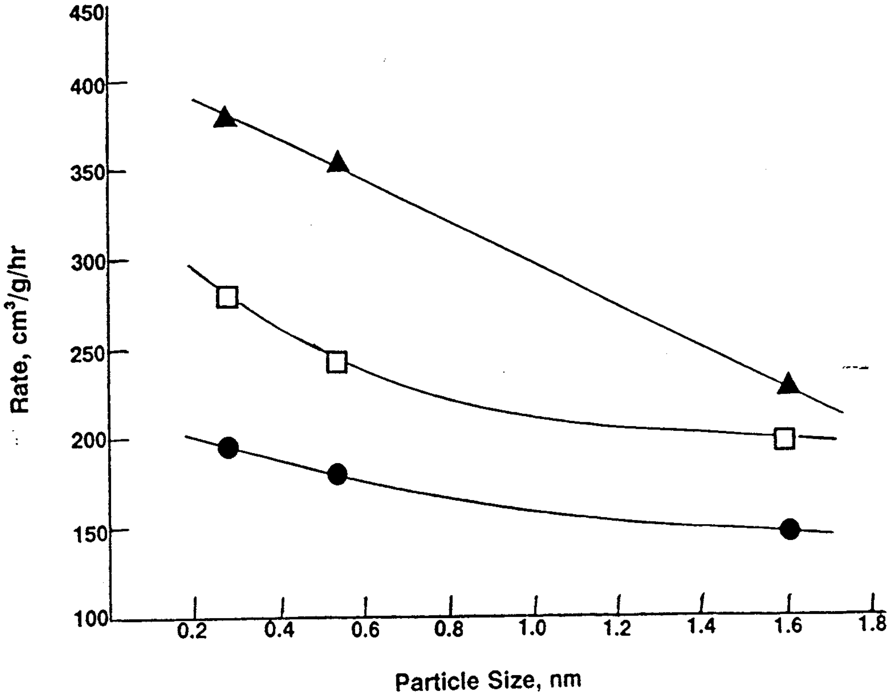


Figure XII.18. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (! , 185^{o}C, H_2/CO = 2; ▲, 195^{o}C, H_2/CO = 2; G, 195^{o}C, H_2/CO = 1.5) (from XII.17).

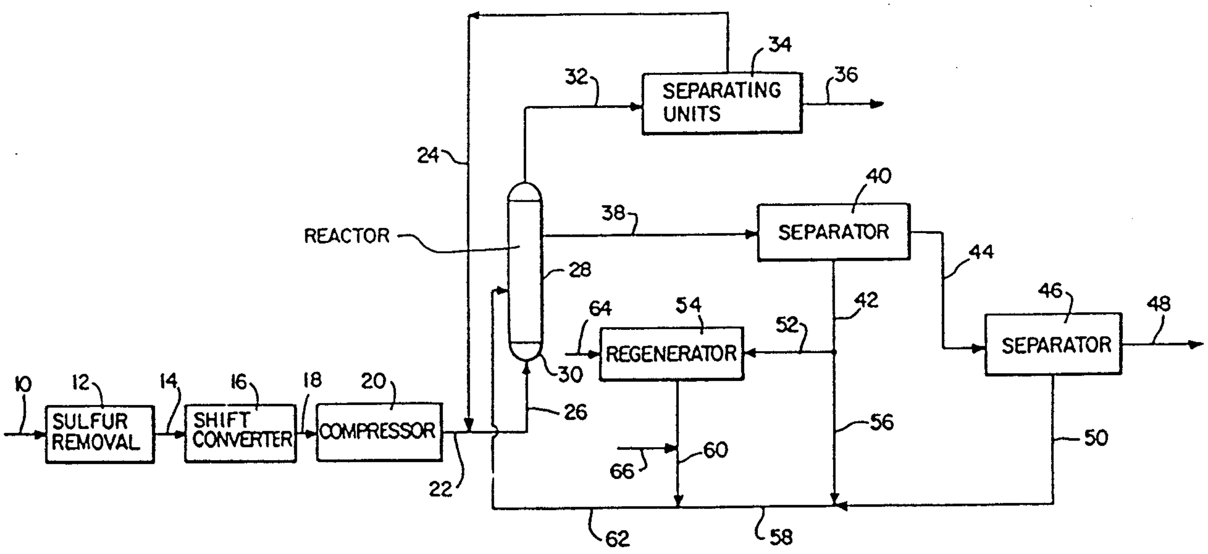


Figure XII.19. Process schematic for slurry reactor system using cobalt catalyst (from XII.17).

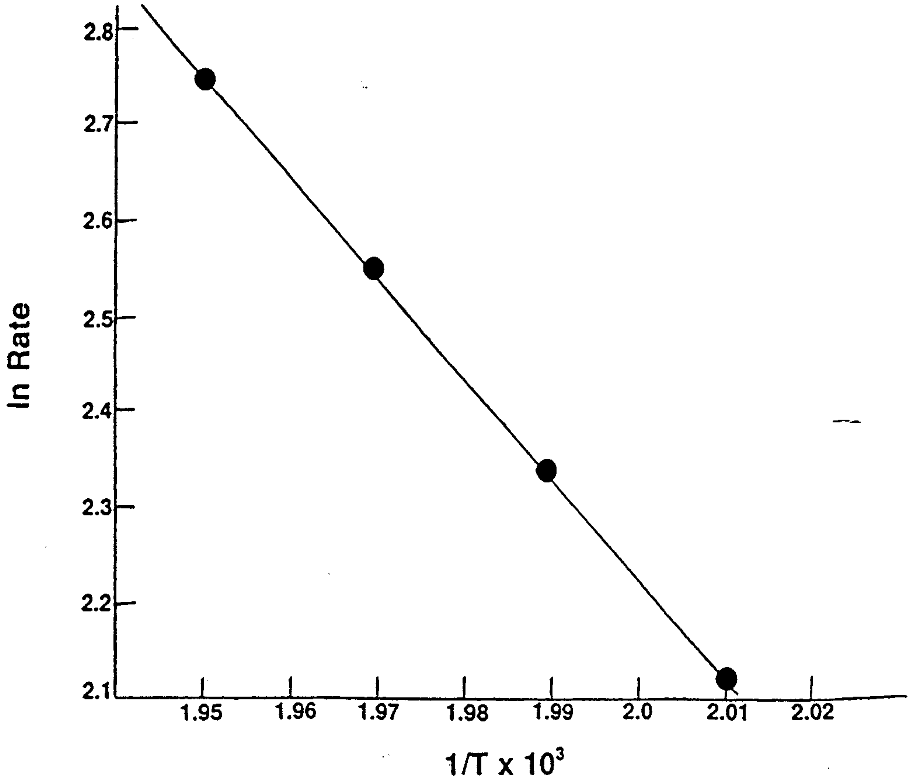


Figure XII.20. Arrhenius plot for CO conversion in slurry reactor with Co catalyst (data from XII.17).

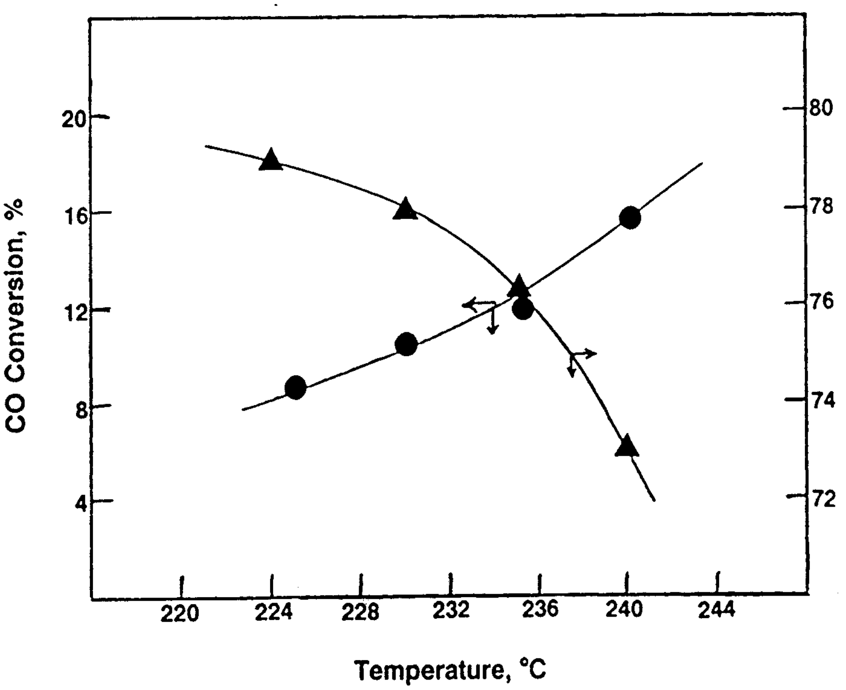


Figure XII.21. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

ATTACHMENT XIII

Review of Fischer-Tropsch Work by Statoil

Three patents on Fischer-Tropsch synthesis catalysts assigned Den Norske Stats Olijeselskap A.S., Norway by Norwegian and U.S. investigators are summarized below (XIII.1-XIII.3). These individuals summarize the background for their invention. Anderson's book (XIII.4) is taken as the main background for the inventions and consider this book to indicate that the common Fischer-Tropsch (FT) catalysts are nickel, cobalt and iron. Nickel is considered to be active but it produces mainly methane. Among the Group VIII metals (old U.S. Periodic Table nomenclature), ruthenium is a very active catalyst and produces mainly hydrocarbons. Ruthenium is considered to have higher activity than Fe, Co or Ni at low temperatures. Other metals which possess high activity are considered to produce oxygenates and the patentees cite rhodium as an example (XIII.5). Osmium is considered to have moderate activity and Pt, Pd and Ir to have low activity (XIII.4,XIII.6,XIII.7).

These investigators recognize that others have used various combinations of metals for Fischer-Tropsch Synthesis (FTS). For example, nickel-doped cobalt has a higher productivity of methane that cobalt alone (XIII.8). On the other hand, Kobylinski taught that the addition of small amounts of ruthenium to a cobalt catalyst provided a material with a higher activity and with lower methane production than a similar catalyst comprised of cobalt without the ruthenium (XIII.9). Other work has documented that the activity is higher when ruthenium is added to the catalyst but the lower methane make is not as well documented.

These investigators indicate that, "In general, the catalysts [of combinations of metals] of these [prior] teachings have activities and selectivities which are within the ranges of the individual components." They also note that the combination of a metal with certain oxide supports may lead to higher productivity of products, presumably due to the increase in surface area of the active metal component. The authors cite the case of using titania to support cobalt or cobalt-thoria (XIII.10) with a resulting increase in activity for the production of hydrocarbons and, by implication, attribute this beneficial effect to strong-metal-support-interactions (SMSI) (XIII.11).

Statoil investigators also indicate that a patent (XIII.12) teaches that combinations of cobalt, rhenium and thoria or cobalt and rhenium supported on titania are useful for hydrocarbon production. The patent indicates that similar improvements in activity can be obtained when using other inorganic oxide supports; however, the inventors indicate that titania is the only support specifically discussed in reference 12. These workers indicate that, "The typical improvement [reported in reference 12] in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2."

The major teaching of the Statoil patent is that the choice of support for Co is critical, "and the addition of a small amount of rhenium to an alumina—supported cobalt catalyst gives a much greater improvement in activity than the addition of rhenium to cobalt supported on any other inorganic oxide. To be effective as a support for cobalt, the alumina should possess low acidity, high surface area and high porosity. The method of adding the active metals to the alumina support is, according to the inventors, not critical.

Included in inventions by the Statoil investigators is the finding that it is beneficial to include a small amount (0.1 - 5%, preferably 0.1 to 2 wt.%) of a metal oxide promoter in addition to cobalt and rhenium. The inventors conclude that the most preferable metal oxide is La_2O_3 or a mixture of lanthanides rich in La.

After preparation, the catalyst is calcined in a specified manner ultimately to attain a preferred temperature between 250 and 350^oC for 2-5 hours. To activate the catalyst, it is reduced in hydrogen, again using a specified heating ramp to attain a preferred temperature of 300-400^oC and holding at this temperature for 6-24 hours. Catalyst passivation and rereduction cycles may be carried out.

Catalyst testing was accomplished with a $H_2/CO = 2$ synthesis gas. A fixed-bed reactor (0.5 g catalyst) was utilized at atmospheric pressure and temperatures of 185, 195 and 205^oC [a standard testing procedure involved 9.82 hr at 195^oC, 4.3 hr at 205^oC, 4.5 hr at 185^oC and 9.5 hr at 195^oC]. The flow rate of synthesis gas was 1.68 L/g catalyst/hr. Catalysts were compared using results obtained during the period of 10 and 30 hours-on-stream.

A series of identical catalysts (12 wt.% Co, 1 wt.% rare earth oxide), except for the content of rhenium, were prepared. For the alumina supported catalyst, there was a greater than 3-fold increase in CO conversion as Re content increases to about 1 wt.% and then a gradual decline in CO conversion was noted for further increases in Re content Figure XIII.1). The incorporation of these amounts of Re did not substantially increase the production of either methane (10-14%) or CO_2 (0.6-1.3%).

Two series of catalysts were prepared in which the Co loading was increased, one series with and one without rhenium. Re was added so as to keep the wt.% Co/wt.% Re constant at 12 for 3, 6 and 9 wt.% Co; for the 20 and 40 wt.% Co formulations, the ratios were 0, 4, 20 and 0, 8, 20 and 40, respectively. The impact of Re is evident in Figure XIII.2 (apparently the data for the 20 and 40% Co are for Co/Re ratio of 20 samples in Table V of reference XIII.1). This patent indicates that the improvement in activity due to the addition of rhenium increases as the cobalt content increases.

The Statoil investigators report that,

> "The catalysts in Table VII (Table XIII.1 of this report) were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII (Table XIII.2 of this report) leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity."

Some may question the conclusion that a selectivity that includes 13-18 wt.% methane is a commercially attractive catalyst.

The MgO and Cr_2O_3 supports provide catalysts with very low activity. The zirconia and silica-alumina supported catalysts showed improved but low activity and poor selectivity for C_2^+. For silica and titania supports, the cobalt only catalysts exhibited activities similar to an alumina supported cobalt catalyst. However, for the addition of rhenium to the alumina, titania and silica cobalt catalysts, a significant improvement was observed **only** for the material employing alumina as a support. The authors report that, "This [latter] result is surprising and would not have been predicted based on teachings in the prior art." [This does not appear to be in complete agreement with some Exxon patents.]

The "Weisz Window" provides a rule-of-thumb estimation of the productivity needed for commercial operation as 10^{-5} - 10^{-6} mole sec^{-1} (cm^3 reactor)$^{-1}$ (XIII.13). In the following we assume: (1) a fixed-bed reactor, (2) the density of the alumina supported catalyst as 2 g/cm^3, (3) the flow of syngas as 1.88 NL/hr/g and (4) H_2/CO = 2. From Table XIII.2 for the Re containing catalyst (example 8), the CO conversion is 33%. Thus we calculate that the conversion of CO is 0.209 NL/hr/cm^3. Using this value, we calculate that the conversion of CO is 0.52 x 10^{-5} mole/cm^3/sec; this is close to the value of the Weisz Window. If the rate increases directly with pressure, then the conversion is in the Weisz Window at 10 atm.

The incorporation of alkali in the cobalt catalyst impacts both the activity and hydrocarbon product distribution. For a catalyst containing Co, Re and rare earth oxide, the incorporation of alkali caused (1) a decrease in CO conversion and (2) an increase in the alpha value of the products (Tables XIII.3 and XIII.4; Figures XIII.3 and XIII.4). However, the conclusion that the alpha value depends upon the K/Co ratio depends entirely upon the two data points obtained for the lowest to K/Co ratios. If these two points are not reliable (or are not considered), the K/Co ratio has no impact upon the value of alpha. The question of promotion changing activity and selectivity is complicated for a cobalt catalyst. Anderson pointed out that selectivity changes can be effected by changing reactor pressure (XIII.14).

van Berge and Everson (XIII.15) point out that the data in reference 1 were obtained at different conversion levels, and thus different reactor partial pressures, and that the chain of chemical promotion by K, Na, Cs and Rb could not be regarded as conclusive. Studies performed at Sastech (XIII.16) are reported to confirm the ineffectiveness of chemical promotion of cobalt Fischer-Tropsch catalysts.

The loss of activity with increasing alkali content allows one to calculate, assuming one K eliminates 1 site, that only 4.5 atomic % of the Co is catalytically active. At first glance, it appears that the data are consistent with each potassium eliminating one catalytic site, or some constant fraction of a site (Figure XIII.4). However, it must be realized that the addition of alkali causes an increase in $\ell n\ \alpha$, and a corresponding increase in the average molecular weight of the products. The average number of growing chains, and the average number of catalytic sites, is directly proportional to the average molecular weight of the growing chains (e.g., the average molecular weight of the products). Hence,

$$\overline{No.\ of\ Sites}\ \alpha\ \overline{M.W.} = 1/(1-\alpha).$$

When this is taken into account, the catalytic sites decrease more rapidly than the increase in K, or at least those catalytic sites that initiate chain growth must do so (Figure XIII.5).

During the past few years, Statoil has obtained patents related to a catalytic multi-phase reactor, and specifically to catalyst wax separation (XIII.17-XIII.21). An example of such a reactor is illustrated in Figure XIII.6 (XIII.17). "This is a solid/liquid slurry reaction apparatus which comprises: a reaction vessel **(11)**, a filter member **(13)** in contact with the slurry **(16)** defining a filtrate zone which is separated from the slurry and having an outlet **(23)** for filtrate product **(32)**; means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry (XIII.17)."

One of the claims is for a filter element **(22)** which comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles (XIII.17). The hydrostatic pressure preferably results from the filter member being submerged in the slurry.

The pulsating pressure can be applied directly to the filtrate or to the gas space above the filtrate, preferably by the action of a reciprocating piston in a cylinder. The pressure fluctuation may be of the order of 10 to 200% differential (preferably 2 to 5 mbar).

The filter element material and catalyst are preferably selected so that the <u>maximum</u> hole or pore size of the filter element is of the same order of the catalyst particle size. It might be expected that catalyst would plug the filter but this is found not to be the case. Of course, the particle size of the catalyst may be much larger than the maximum hole or pore size of the filter.

In operation, products pass through the filter element **(12)** to form a product filtrate **(32)** which is free of catalyst. Any gaseous products and unconverted reactants that pass through the filter element can be vented through outlet **(31)** and subsequently through **(17)**. The product filtrate **(32)** leaves through level device **(23)** and outlet **(24)** to collect in **(25)** for regulated continuous or periodic removal.

In an example, a reactor of 4.8 cm x 2 m dimensions was filled with approximately 10 wt.% of a Co on alumina catalyst (30 to 150 µm). The gas (H_2, CO and N_2) was fed at a superficial gas velocity of 4 cm/s. The temperature was 230^{o}C and pressure was 30 bar.

The filter unit was located in the upper part of the reactor and comprised of Sika stainless steel sintered metal cylinder Type R20 produced by Pressmetall Krebsöge

Gmbh. The filter had an outer diameter of 2.5 cm, a height of 25 cm and an average pore diameter of 20 µm.

The slurry was effected using a poly-α-olefin liquid. Fischer-Tropsch product **and a poly-α-olefin that was fed to the reactor** were both withdrawn through the filter unit (ratio of Fischer-Tropsch and poly-α-olefin not specified). Liquid withdrawal rate varied from 2.5 to 320 g/hr, depending on Fischer-Tropsch synthesis rate and feed rate of poly-α-olefin. The experiment lasted for about 400 hrs and approximately 30 liters was withdrawn through the filter unit. Most would therefore conclude that the test was of a short duration compared to the length of time that a commercial unit must operate. Furthermore, the product was diluted with start-up solvent that was added during the run. Thus, it appears that this example is applicable to a limited process scheme, and not for all process schemes.

A solid/liquid slurry reaction apparatus with a filtration section has been submitted for patent coverage (XIII.22) and is illustrated in figure XIII.7. The teachings of this patent application is based upon a recent report identified only as "a report issued by the United States Department of Energy." The DOE report addressed the question of catalyst/wax separation in Fischer-Tropsch slurry reactor systems and concludes:

> "Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature

termination of the run, and commercial plants are not allowed to take chances."

The patent applicants have discovered that, contrary to the teachings of the DOE report, "...it is possible to provide a continuous reaction system for a Fischer-Tropsch synthesis in which it is not necessary to perform the solid/liquid separation in an external filter unit. Furthermore, a sufficiently high flow rate of filtrate for commercial operation can be achieved."

The description in the patent application indicates that the filter screen and the catalyst are similar, or identical, to those described in the previous patent application (XIII.17). In this instance, however, the filter screen has been made a part of the slurry reactor wall or, as shown in figures XIII.8 and XIII.9, it may be incorporated in multiple locations of the slurry reactor wall. In the example shown in figure XIII.7, a conical section **(15)** is included as an expansion chamber to prevent the slurry from foaming over and to define a gas space **(16)** above the reaction zone. The cone-shaped portion **(15)** may contain additional means (that are not shown nor specified) for breaking up or reducing foam formation.

The invention was described and was then further illustrated with the following example. Experiments in a laboratory using an apparatus similar to that shown in figure XIII.7 were carried out. The length and diameter of the unit were 1250 mm and 55 mm, respectively. The filter member had a mean pore size of 30 µm and a length of 200 mm. A heat transfer oil (diethyl benzene (95%) and minor amounts of other alkyl benzenes) and 20 wt.% alumina were used as the slurry phase. The alumina particles initially had a cut-off at 53 µm. The experimental conditions in the example were: 1 bar pressure, 20-25^{o}C and 6 cm/s superficial gas velocity. After an initial start-up period, the separation capacity became approximately constant at a level of 750-800 kg/m^{2}h. The calculated pressure differential was approximately 5 mbar. After 40 days of operation, there was only a slight decrease in separation capacity.

The section of the DOE report that was quoted above was concerned with an operating slurry bubble column reactor for Fischer-Tropsch synthesis at a commercial scale operation. The example provided by the patent applicants was for a cold model with only an alumina solid and without Fischer-Tropsch synthesis. It would appear that the patent applicants have not shown by their example anything that would be contrary to the teachings of the DOE report since the patent applicants did not operate at any of the conditions necessary for a commercial Fischer-Tropsch plant that is currently being operated successfully.

Another patent application (XIII.19) relates to a vessel that contains a number of vertical reaction tubes, each suitable for multi-phase catalytic conversions (figure XIII.10). In this application, the above DOE report is quoted and the teaching that the applicants have provided a means of accomplishing this. Each reactor tube has essentially the features of the reactor described in the previous reference XIII.ref. 18). In operation, the gas is preferentially fed to each multi-phase catalytic reactor. These reactors are held in place by plates **(18)** and **(14)**; in effect these two plates and the vessel wall **(12)** provide the vessel to hold the heat transfer liquid/vapor.

The filter section of each reactor tube is located above the top plate **(14)**, which serves to hold a level of the wax following separation from the catalyst slurry. In another version, a sieve **(34)** surrounds each filter and is utilized to maintain a minimum wax level for each reactor tube so that the tube does not lose liquid level so that the reactor tube is depleted of liquid. Thus, the sieve extends above the level of the wax filtrate that is maintained on plate **(14)**.

The heat exchange medium is preferably a liquid at its boiling point; water is the preferred medium since the heat of reaction can be recovered as steam to be used to generate electricity or provide heat for plant operations.

In the only example of the patent application, a slurry bubble column Fischer-Tropsch reactor **is simulated** using a two phase quasihomogeneous one dimensional model. They use typical catalyst performance data contained in US 4,801,573. The simulations are utilized to **calculate** optimum values for the reactor and its operation. **Experimental data of an operating Fischer-Tropsch reactor are not provided in the application**. Since the DOE report was for an operating reactor that actually effects a separation of wax and catalyst, it is difficult to understand how the applicants can show that they have provided a solution to the problems enumerated in the DOE report.

A patent application (XIII.20) describes a separation device that has as its main object the prevention of gas from being entrained in the liquid phase in cases where it is desirable to separate gas and liquid or immiscible liquids.

A recent patent application describes a method of regenerating a catalyst in a Fischer-Tropsch synthesis reaction (XIII.21). Examples of regeneration procedures are reviewed and the conclusion is that "These arrangements all suffer the drawback that a separate source of H_2 gas must be provided to achieve regeneration." The present invention (XIII.21) is to overcome this drawback. While the use of hydrogen could be a drawback, it would appear to be so only from an operational viewpoint. For example, Sasol produces a nearly pure hydrogen stream by a pressure swing adsorption process.

It would be a disadvantage to utilize a stream of pure CO since this stream is not available in a normally operating Fischer-Tropsch plant.

Schematic sections through a slurry reactor (figure XIII.12) and a slurry reactor with a separate regeneration vessel (figure XIII.13) are shown. Details of the slurry reactor (figures XIII.12 and XIII.13) are not provided in this patent. To effect regeneration, the feed parameters of the synthesis gas are adjusted to increase the conversion of CO in the synthesis gas until the H_2/CO ratio of the gas leaving the reaction zone exceeds 10:1 and then maintaining this conversion level during the regeneration mode for some period of time to effect regeneration to a desired level. Preferable, the CO conversion is between 95 and 100%, most preferable 100%. Thus, the preferred H_2/CO ratio is 20/1, and most preferably, greater than 30/1. To achieve this high hydrogen/CO ratio, the flow is decreased, preferably slowly, so that the conversion increases to attain the desired level. Alternatively, hydrogen could be increased in the synthesis gas by modification of the generation step of the synthesis gas.

At the high conversion level, the reaction changes from synthesis to a regeneration mode. The regeneration mode is characterized by: high H_2/CO ratio, low C_{5+} selectivity and high CO_2 selectivity. This is taken to indicate a high water gas shift rate due to the high hydrogen partial pressure. Experimentally, it has been found that a few hours of regeneration is normally sufficient; however, it may take longer for more severely deactivated catalysts.

When a separate regeneration vessel is used, "normal" conditions for synthesis are maintained on the synthesis side and the high hydrogen (100% CO conversion) condition is maintained on the regeneration side. Preferably, there is a flow of deactivated and regenerated catalyst between the two sides.

Two examples are given for the regeneration. In the first example, a catalyst containing 12% Co and 0.5% Re on alumina are used at 220°C and 20 bar (2 MPa) total pressure in a continuous slurry stirred tank reactor (CSTR). The reactor volume is 2 L and is half-filled with slurry. The H_2/CO inlet synthesis gas ratio was 2; the exit gas was also close to this value. The initial stable hydrocarbon activity is set relative to 1; note that this is based on hydrocarbon production. The CO conversion was 63% at this hydrocarbon production level of 1.

After the catalyst had operated for a few days, the catalytic activity had declined so that the relative hydrocarbon productivity activity number had declined to 0.69. At the relative activity number of 0.69, the CO conversion was 68% at a flow rate of 2100 NL/kg cat./hr. It is not clear whether this flow rate is for synthesis gas or for CO only; in the following we shall **assume that the flow is for CO only**. The C_{5+} selectivity was 89.4%. At this stage of catalyst deactivation, a decrease of the flow rate to 1050 NL/kg cat/hr resulted in an increase in CO conversion to 88% with a C_{5+} selectivity of 89.9%.

To establish a regeneration mode at this point (0.69 relative activity), the flow rate was reduced to 750 NL/kg cat/hr and the CO conversion was 99%. The exit H_2/CO ratio was 14/1. This regeneration mode was maintained for 10 hours and was then brought back to the Fischer-Tropsch mode by increasing the flow rate to 2100 NL/kg cat/hr. The reaction continued to produce a C_{5+} selectivity of over 88%. The relative activity at these final Fischer-Tropsch conditions was 0.77. This value is above the value of 0.69 for the deactivated catalyst but still considerably below the value of 1.0 for the fresh catalyst.

Example 2 is for a catalyst that contains 20% Co and 1% Re on alumina; however, the data are less extensive than for example 1. They report that the 20 wt.% Co catalyst was brought back to the initial level following 24 hours of the regeneration mode whereas 10 hours for the 12 wt.% Co catalyst only restored the activity to 77% of the initial activity.

The hydrocarbon production of the deactivated catalyst (relative activity of 0.69) in Example 1 corresponds to 0.983 g hydrocarbon/g cat/hr. For the fresh catalyst (relative activity of 1.0) the hydrocarbon productivity is calculated by us to be 1.29 g hydrocarbon/g cat/hr. For the reactivated catalyst (relative activity 0.77) the productivity is 1.16 g hydrocarbon/g cat/hr.

If it is assume that the catalyst productivity is linear in Co content, the productivity of the deactivated 20 wt% Co catalyst would be 1.49 g hydrocarbon/g cat/hr and that of the fresh and regenerated catalyst would be 2.15 g hydrocarbon/g cat/hr.

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Table XIII.1 (from ref. XIII.1)

			Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, Wt.%	
Example No.	Support	Weight of Support, g	$Co(NO_3)_2$	$HReO_4$*	Co	Re
28	Silica	20	13.47	---	12	---
29	Silica	20	13.62	0.38	12	1.0
30	Titania**	25	16.84	---	12	---
31	Titania**	24.64	16.78	0.46	12	1.0
32	Titania***	25	16.84	---	12	---
33	Titania***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	---	12	---
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	---	12	---
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica-alumina	20	13.47	---	12	---
39	Silica-alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	---	12	---
41	Zirconia	20	13.62	0.38	12	1.0

* Weight of 82.5% perrhenic acid solution.
** Calcined at 500°C.
*** Calcined at 600°C.

Table XIII.2 (from ref. XIII.1)

Example No.	Co %	Re %	Support	CO Conversion %	C_2^+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
1	12	---	Al_2O_3	12	90.0	8.9	1.1
8	12	1	Al_2O_3	33	87.7	11.4	0.9
28	12	---	SiO_2	11	90.1	8.7	1.2
29	12	1	SiO_2	12	88.1	10.7	1.2
30	12	---	TiO_2*	11	87.6	11.8	0.6
31	12	1	TiO_2*	17	86.5	12.8	0.7
32	12	---	TiO_2**	11	87.6	11.7	0.7
33	12	1	TiO_2**	17	85.8	13.5	0.7
34	12	---	Cr_2O_3	1	83.5	15.5	1.0
35	12	1	Cr_2O_3	2	80.8	12.3	6.9
36	12	---	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	---	SiO_2/Al_2O_3	5	76.3	22.2	1.5
39	12	1	SiO_2/Al_2O_3	6	78.6	19.8	1.6
40	12	---	ZrO_2	4	80.9	16.3	2.8
41	12	1	ZrO_2	7	78.8	18.7	2.5

* Support calcined at 500°C.
** Support calcined at 600°C.

Table XIII.3 (from ref. XIII.1)

			Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst, Wt.%			
Example No.	Wt. of Al_2O_3, g	Type of Alkali	(a)	(b)	(c)	(d)	Co	Re	RE	Alkali
42	300.0	---	1039.65	17.21	13.99	---	40	2.0	1.0	0.0
43	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
44	75.0	K	256.36	4.25	---	0.67	40	2.0	---	0.2
45	175.0	K	609.03	10.08	8.20	1.59	40	2.0	1.0	0.2
46	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
47	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
48	60.0	Na	205.49	3.40	---	0.93	40	2.0	---	0.24
49	60.0	Cs	209.55	3.47	---	2.12	40	2.0	---	1.36
50	65.0	Rb	225.38	4.23	---	1.71	40	2.0	---	0.87
51	20.0	---	13.78	0.38	0.62	---	12	1.0	1.0	---
52	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
53	20.0	Li	13.64	0.38	---	0.11	12	1.0	---	0.05
54	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
55	20.0	Cs	13.67	0.38	---	0.10	12	1.0	---	0.3
56	20.0	Cs	13.83	0.38	0.62	0.10	12	1.0	1.0	0.3

(a) $Co(NO_3)_2$! $6H_2O$
(b) 82.5% $HReO_4$ solution, except for example 50 which was 72.9% $HReO_4$
(c) Rare earth nitrates (RE) (see example 1)
(d) $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$ or $CsNO_3$

Table XIII.4 (from ref. XIII.1)

	Alkali				
Example No.	Type	Content Wt.%	CO Conversion %	CH_4 Selectivity %	Product Alpha*
42	---	---	52.5**	14.2**	0.75**
43	K	0.1	52 50	8.6 11.1	0.86 0.79
44	K	0.2	43	9.3	0.83
45	K	0.2	51 44 41	9.5 11.6 9.4	0.84 0.84 0.81
46	K	0.4	30 35	7.3 7.8	0.87 0.85
47	K	1.0	12 9 6	7.0 7.9 6.2	0.88 0.85 0.87
48	Na	0.24	21	8.3	0.82
49	Cs	1.36	14	8.5	0.86
50	Rb	0.87	11	7.3	0.86
51	---	---	31.7***	10.9***	0.77***
52	K	0.1	19 22	7.6 9.8	0.78 0.84
53	Li	0.05	31	11.7	0.78
54	Li	0.05	27	12.0	0.78
55	Cs	0.3	21	11.1	0.83
56	Cs	0.3	21	10.3	0.84

* Calculated by plotting $\ln(W_n/n)$ vs. n, where n is carbon number and W_n is the weight fraction of the product having a carbon number n, and determining the slope of the line.

** Average of 21 tests.

*** Average of 6 tests.

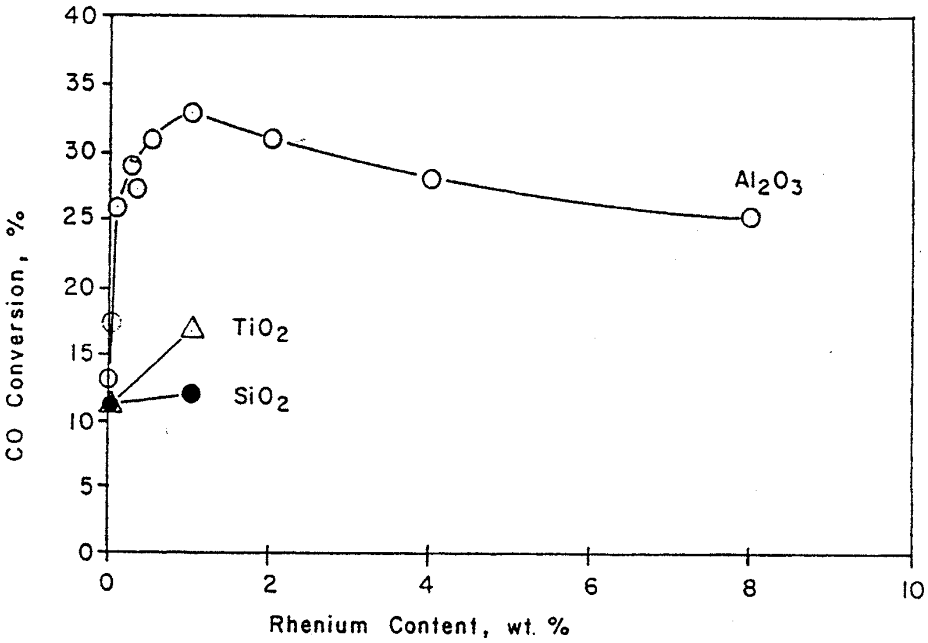

Figure XIII.1. Effect of rhenium on CO conversion catalysts containing 12% cobalt (from ref. XIII.1).

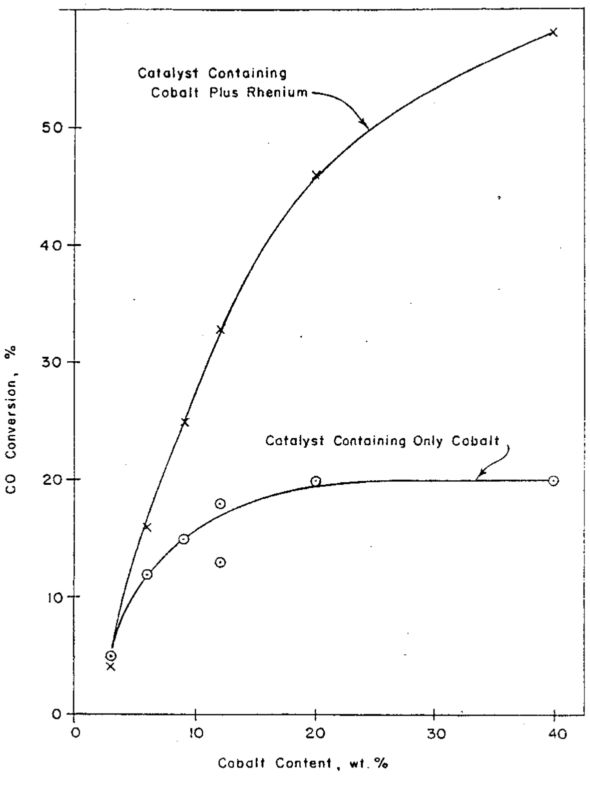

Figure XIII.2. Effect on conversion of adding rhenium to cobalt on alumina catalyst (from ref. XIII.1).

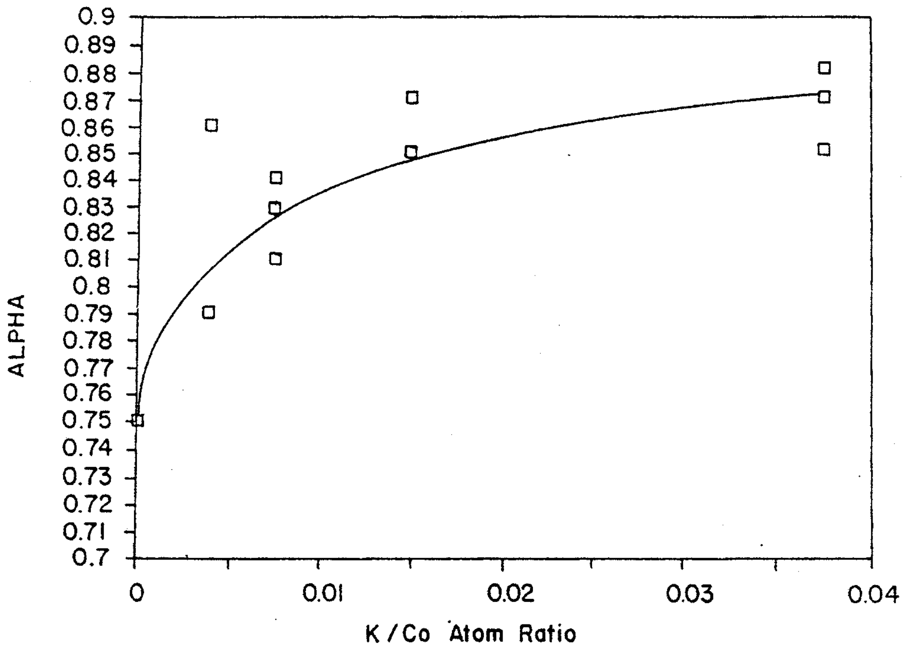

Figure XIII.3. Alpha versus K/Co (from ref. XIII.1).

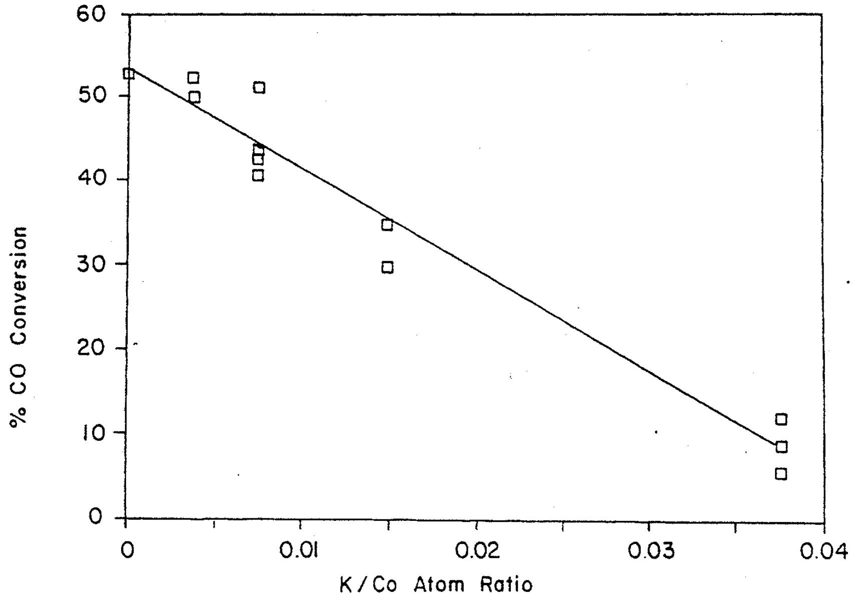

Figure XIII.4. Percent CO conversion versus K/Co (from ref. XIII.1).

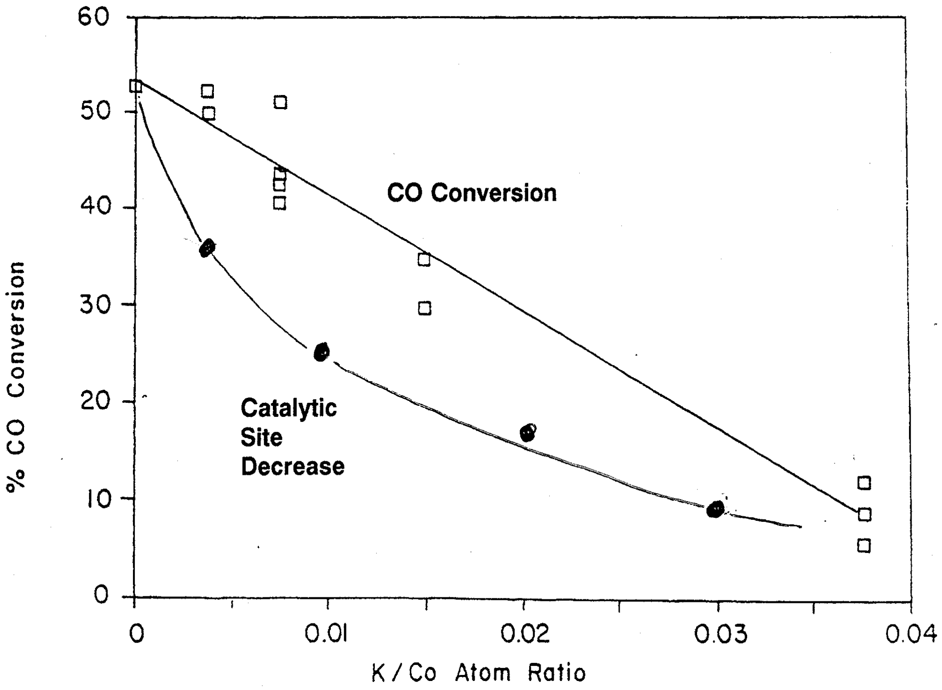

Figure XIII.5. Percent CO conversion versus K/Co (from ref. XIII.1) and our decrease calculated assuming α is related directly to the site density.

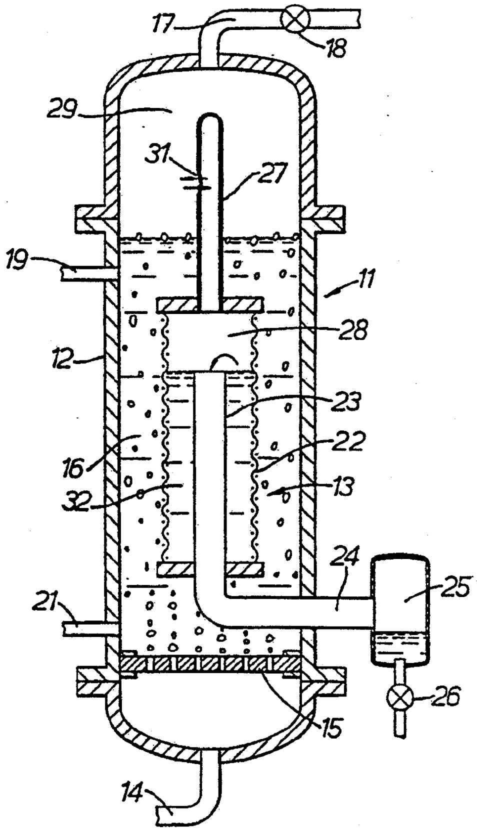

Figure XIII.6. Slurry reactor with internal filter for wax/solids separation from ref. XIII.17).

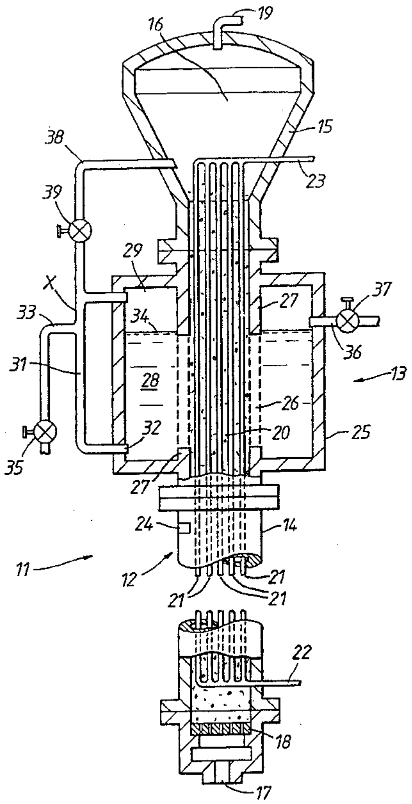

Figure XIII.7. Slurry reactor incorporating a filtration system into the reactor wall (from ref. XIII.22).

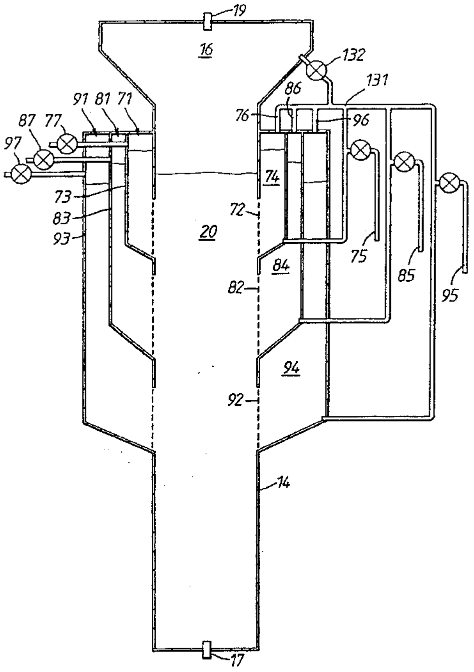

Figure XIII.8. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

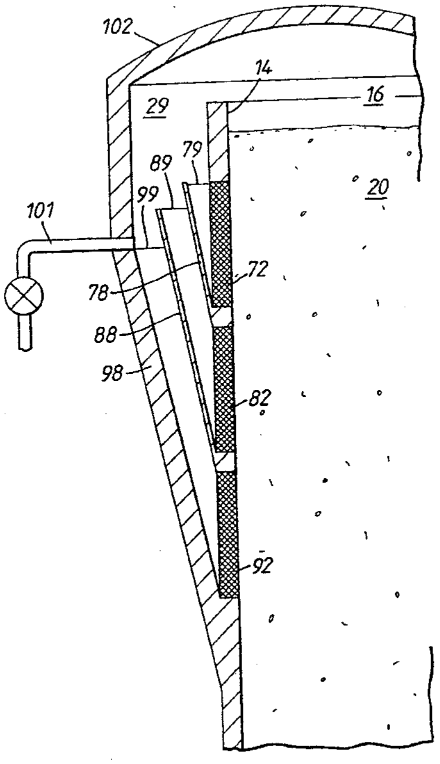

Figure XIII.9. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

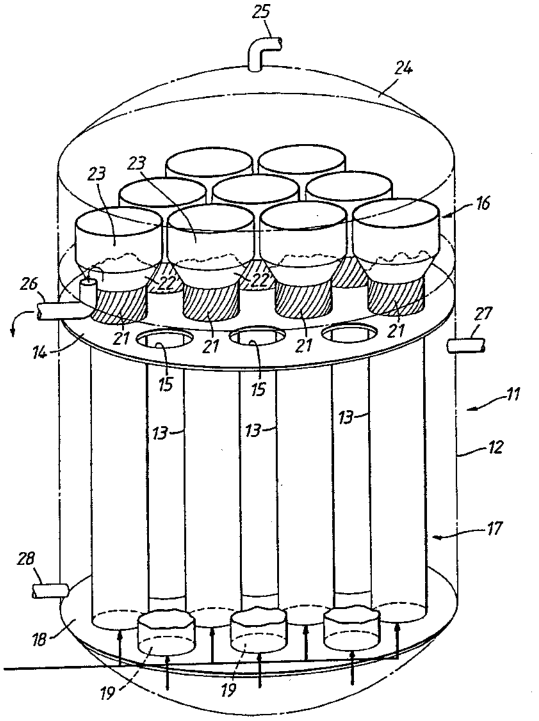

Figure XIII.10. A multi-phase catalytic reactor with multiple tubes for slurry phase reactor systems (from ref. XIII.19).

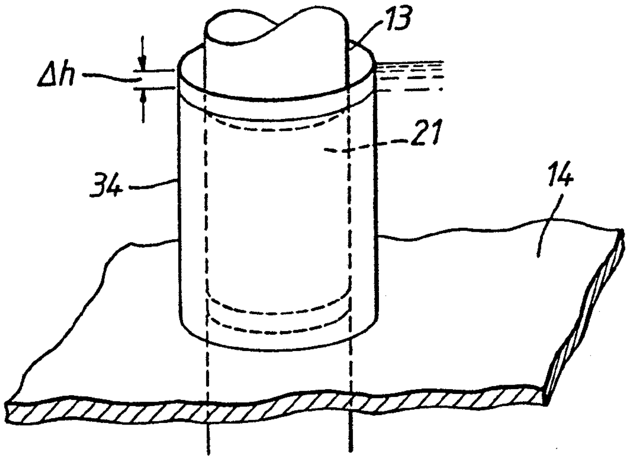

Figure XIII.11. Schematic of sleeve on reactor tube in Figure 10 to maintain slurry level in each reactor tube (from ref. XIII.19).

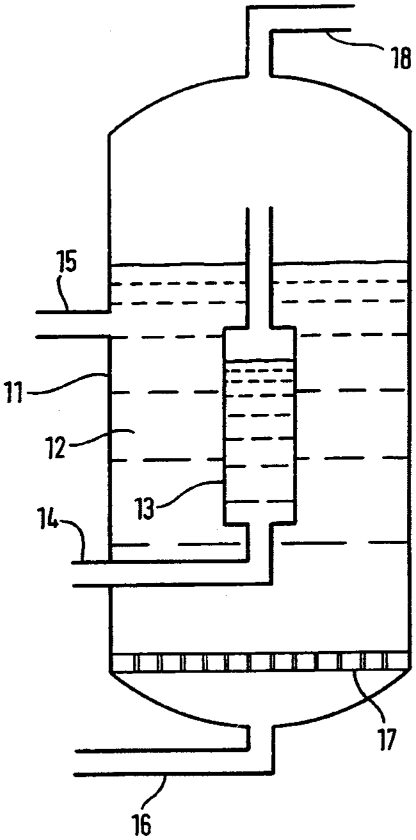

Figure XIII.12. Schematic of slurry phase reactor with internal wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

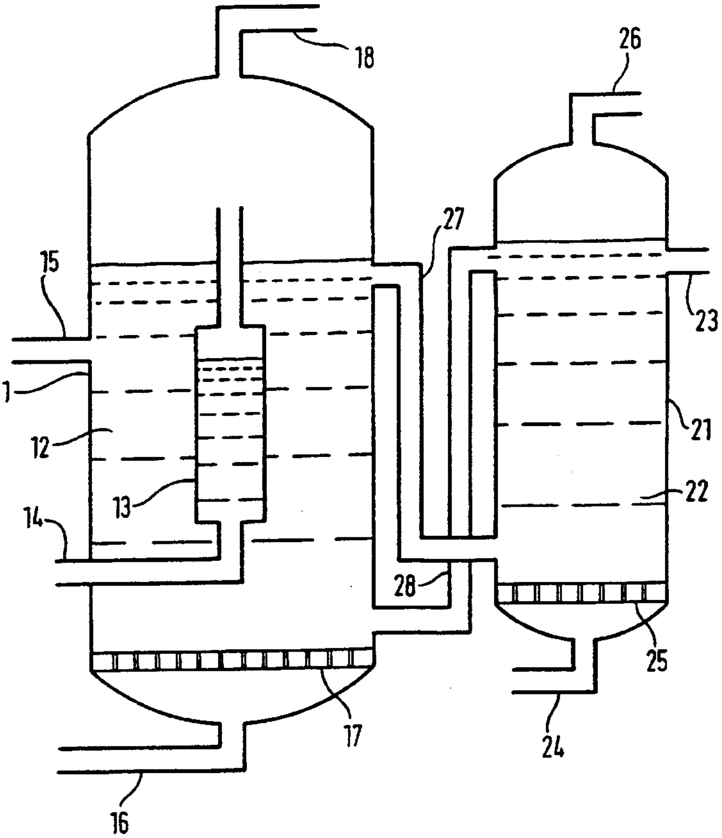

Figure XIII.13. Schematic of slurry phase reactor with external wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

ATTACHMENT XIV

Review of Fischer-Tropsch Work by Rentech

Rentech has obtained eight patents to date [October 10, 1996] [XIV.1-XIV.8]. The drawings, background of the invention and objectives of the invention are identical [except for combining some paragraphs and minor changes in a few paragraphs such as "A further object ..." rather than "It is yet another objective..."]

The background provides a brief description of earlier work [XIV.9-XIV.14]. They indicate that today there are two primary methods for producing syngas from methane: steam reforming and partial oxidation. The primary advantage of partial oxidation over steam reforming is indicated to be that the reaction is self-sustaining and the only heat that must be added is the initial preheating of the reactants. Another advantage is that a lower ratio of H_2/CO is produced, and that it more nearly matches that needed for the FTS. In addition, the CO_2 and/or hydrogen need not be removed from the syngas prior to the synthesis.

The authors indicate that "...the Fischer-Tropsch reactor must typically be able to convert at least 90% of the incoming carbon monoxide."

They discuss the advantages of the two materials they consider to be attracting the most attention: cobalt and iron based catalysts. They indicate that, theoretically, a cobalt catalyst can produce higher conversion yields than an iron based-catalyst since the cobalt catalyst can approach 100% carbon conversion efficiency but that an iron catalyst tends toward 50% carbon conversion to hydrocarbons due to the extent of the water-gas-shift (WGS) reaction. They indicate that cobalt is much higher in cost, and this is likely to increase even further if the demand for cobalt increases to meet widespread development of Fischer-Tropsch synthesis (FTS).

It is indicated that recycle of the tail-gas is usually utilized to achieve 90% conversion of CO. Too much water is considered to be an inhibitor for FTS and the maximum attainable in single-pas operation is 70% CO conversion. On the other hand, the WGS activity of the iron catalyst permits operation at 90% conversion per pass without difficulty. It has been reported, contrary to this view, that even with an iron catalyst, the rate of CO conversion may decline rapidly at CO conversions above about 60% [XIV.15].

The present inventions are claimed to "...include a solution to the problems of reducing the formation of excess hydrogen from the reformer or partial oxidation unit and increasing the conversion efficiency for the entire carbon input to the system when using specifically prepared promoted iron catalysts." The patents demonstrate the use of recycle of the carbon dioxide produced during the FTS to the reformer in order to control the excess hydrogen and to improve the carbon conversion efficiency problems.

It is stated that olefins, alcohols and aldehydes are readsorbed on the catalyst and thereby participate in further chain growth. Naphtha and light diesel fractions are considered to be rich in olefins and to contain relatively large amounts of alcohols. Thus, the authors indicate that it is possible to force the reaction toward higher molecular weight by recycle of olefins, alcohols and aldehydes.

It is also proposed to convert the excess hydrogen as well as the carbon dioxide that is produced through the WGS reaction in a second FTS reactor.

A schematic of one of the process schemes is provided in figure 1. Indicated in this process is the recycle of carbon dioxide and/or recovered gas (streams 9 and 19).

The preferred catalyst is a precipitated iron catalyst that is promoted with a predetermined amount of potassium and copper. The amount of promoters depends upon the desired extent of chain growth and the product molecular weight distribution.

The preferred catalyst is unsupported. To accomplish catalyst preparation, iron and copper metal is dissolved in nitric acid. However, to minimize the emission of oxides of nitrogen, oxygen is bubbled through the solution while the metals are being dissolved.

The catalyst precursor was prepared by precipitation by the addition of ammonium hydroxide (ambient temperature) to the hot (up to 150°C copper/iron solution to produce a pH of 7.4. After cooling to 80°F, the pH is adjusted to 7.2. The slurry is pumped to a holding tank, the solid settles and the solution is removed; subsequent washings to remove ammonium nitrate are with "high quality water free of chloride". A drum filter, with water spray bars, is used to complete the washing and collection of the slurry. Aqueous potassium carbonate of the desired amount is added to the slurry and it is then thoroughly mixed. Drying, such as in a spray drier, is used to produce spherical catalyst in the size range of about 1 to 5 up to about 40 to 50 microns. The last step is heating to 600°F in a fluidized bed to remove residual moisture and to convert the hydrous iron oxide to hematite (Fe_2O_3).

The authors report that "Determining the "best" activating procedure for a catalyst is difficult at best..." In their study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure used carbon monoxide at 325°C at 0.1 atm. pressure. The authors indicate that it may be preferable to activate in synthesis gas, and give a recipe for doing this in a controlled manner. They heat the catalyst precursor in an inert gas to 500°F and then to 540°F in synthesis gas until the heat of reaction becomes sufficient to heat the catalyst bed at a faster rate than the applied external heat; at this point heating is terminated and cooling is effected to keep the temperature at 540°F until the CO conversion is 90%. At this point the temperature is lowered to the desired reaction temperature (450 to 525 °F) and the reactor pressure is raised from the activation pressure of 150 psig to below about 450 psig. The flow rate is adjusted to a space velocity in the range of 240 to 300 per hour.

It was reported that the activity and selectivity of the iron catalyst is improved by exposure to a hydrogen-rich synthesis gas at elevated temperature and pressure. The production of water is believed to prevent over-carburization of the catalyst, and thereby inducing the improved activity and selectivity [XIV.16].

The authors prefer a reactor design similar to that utilized by Bureau of Mines workers [XIV.17]. The gas distributor may consist of orifices or of porous metal spargers. Preferably a design using concentric rings of manifolds arranged to conform to the reactor; i.e., the largest diameter ring is at the highest and the smallest diameter at the bottom of the reactor. The reactor diameter should be selected to give a superficial velocity (actual volumetric flow rate of feed gases divided by empty reactor cross-sectional area) between about 0.02 to 0.2 meters per second. This flow should expand the bed by 30 to 45% over that of no flow conditions.

The authors prefer between 5 and 15 wt.% by weight of iron in the slurry, more preferably between 7.5 and 12.5, and most preferably 10 wt.% iron. This corresponds to 30 to 90 grams of iron per liter of expanded bed, and the most preferred is 60 g/L.

Heat removal utilizes heat exchanger tubes that commence about 1 meter above the gas distributor and extends to the top of the expanded slurry. Pressurized steam is the preferred heat transfer medium.

The preferred iron catalyst particle is between 10 and 40 microns, with 30 microns being most preferred. The preferred ratio of potassium (as carbonate) to iron is about 0.010 (0.005 and 0.015). The copper to iron ratio is preferably about 0.010.

The means of removing wax from the catalyst employed a cross flow filter. The advantage of this means is that the flow velocity of the slurry through the porous filter tubes is about 10 feet/sec and this slows down the rate of building a catalyst layer on the tube wall. When the flow has declined to a predetermined level, an inert gas is used to pressurize the shell side to remove the layer of catalyst into the slurry stream, which flows back to the reactor. They described rates for a cross-flow filter from Mott Metallurgical Corp., a filter and procedure which were found to be unsuitable for the operation at the LaPorte, Texas plant.

Catalyst can be removed from the reactor periodically by employing a slipstream.

The gaseous product stream (20, figure 1) can be used directly for process heat.

The quality of the diesel obtained from the Fischer-Tropsch synthesis are illustrated in Tables XIV.1 and XIV.2.

According to the data, the material contains 3.05 wt.% oxygen and the average carbon number is C_{14}. Assuming that the oxygen is distributed on the same basis as the hydrocarbons, then we calculate that the F/T diesel must contain about 38 wt.% alcohols in order to contain 3.05 wt.% oxygen. This value for the alcohol content appears consistent with the composition included at the bottom of Table V of U.S.

Patent 5,324,335. This would appear to be the highest content of alcohols that has been reported for Fischer-Tropsch products.

One of the catalysts utilized in the studies produces a chain-growth probability of 0.73 for carbon numbers from 1 to 9. Like Satterfield and coworkers, the patents reported that two different chain-growth probabilities were obtained.

In example 1, the authors indicate a means of calculating the carbon conversion efficiency for the overall process which is defined as the rate of production of carbon contained in the C_{5+} product in the FTS divided by the carbon atoms in the process feed. The authors state that, "Table VIII lists the product yields and carbon efficiency along with operating parameters for Example 1 and several examples discussed below." However, Table VIII does not contain a column giving efficiencies and the yield given in Table VIII is for C_{7+} rather than C_{5+} as given in the definition. It is not obvious how one can obtain the efficiencies, as defined, from the data in Table VIII. Efficiencies are given in some of the examples together with some indication of the mode of recycle; these are complied in Table XIV.3 by the reviewer.

The carbon dioxide produced in the FTS can be recovered by absorption from the FTS tail gas and can then be recycled to the gasifier, vented to the atmosphere or stored for later sale or use.

When additional diesel fuel is desired, the wax can be heated to 410^{o}C to effect thermal cracking. It was shown that the diesel from wax cracking contained only 0.16% oxygen whereas the diesel produced in the FTS contained 3.05% oxygen.

After removing the carbon dioxide, the tail gases from the FTS can be recycled to the FTS reactor to "...enable further chain growth of olefins and alcohols."

Examples 2 through 11 were ..."modeled using the conditions listed. The modeling is based on the experience with various conditions used in pilot plant studies and represents the expected results using the conditions employed."

In Example 2, the authors write that, "The large carbon dioxide content (approximately 18%) of the gases leaving the separation vessel is undesirable for the synthesis reactor feed. Therefore, the next step in synthesis gas preparation is reduction of the carbon dioxide content to less than about 5% by volume, and in the example to less than 2%."

Examples 3-10 involve various carbon dioxide and/or light gas recycle and some of these results are summarized in Table XIV.3.

In example 11 it is stated that, "...it was found that the tail gases from the Fischer-Tropsch reactor which consist chiefly of hydrogen and carbon dioxide can be converted to liquid hydrocarbons in a second Fischer-Tropsch reactor... A test was conducted in a small slurry reactor using the same iron-based catalyst that was used in the Fischer-Tropsch synthesis. The temperature, pressure and space velocity were also kept the same. The carbon dioxide conversion was 25% for a feed having hydrogen to carbon dioxide ratios of 2:1 and also 1.5:1. Conversion of the hydrogen was 42%, and 88% of the carbon monoxide produced in the water gas shift reaction was converted to hydrocarbons in the Fischer-Tropsch reaction. The chain growth (α) was the same as in the conventional Fischer-Tropsch synthesis."

Apart from the claims, references XIV.1, XIV.6 and XIV.7 are essentially identical. The patent of reference XIV.1 claims the production of an oxygen containing diesel fuel using FTS. The claims in references XIV.6 and XIV.7 cover a variety of carbon dioxide and/or light gaseous product recycle schemes that include both stream(s) and the fraction of each stream to be recycled.

Another grouping of three patents are essentially identical except for the claims [XIV.2-XIV.4]. These three patents are to show, "Several Fischer-Tropsch reaction schemes using a promoted iron catalyst in a slurry reactor produce oxygenated naphtha and diesel fractions on distillation that reduce particulate emissions in diesel engines. High carbon conversion efficiencies and optimum chain growth are characteristics of the process."

These three patents are identical to the above three patents up to the Detailed Description of the Invention and, apart from the one difference described below, this section is the same in the two sets of three patents. In references XIV.2-XIV.4 the paragraph in references XIV.1, XIV.6 and XIV.7:

> "The steam reforming reactor 5 can be of conventional design employing a commercial nickel catalyst such as obtained from Katalco and designated **23-1**. Preferably, the reactor should be operated at from about 1292°F (700°C) to about 1652°F (900°) at system pressure of about 12 psia (82.7 kPa) to about 500 pais (3447 kPa). The flow of input gases through the reactor catalyst bed should be approximately 300 lbs/hr/ft^3 catalyst."

has been replaced by examples of approaches to reduce the amount of carbon monoxide in town gas to a specified level, for example 10% by volume.

It is shown that the water gas shift reaction could be used to reduce the level of CO in the output from the gasifier; however, this approach significantly reduces the heating value of the resulting town gas. It is shown that the removal of the CO_2

produced during the WGS will increase the heat content of the town gas but, in order to have 10% CO in the product, the extent of WGS must be even greater.

The objective of these patents [XIV.2-XIV.4] is to replace the shift reactor with a FTS reactor to remove the excess CO. Thus, a portion of the gas from the gasifier is fed to the FTS reactor while about 20% of the gas bypasses the FTS reactor (Case III in ref. XIV.2-XIV.4). The composition of the blending streams and the town gas are shown in Table XIV.4.

In addition to the town gas, the FTS produces 11.8 barrels of hydrocarbon liquids having five or greater carbon atoms (based on 1.0 MMSCF feed from the gasifier).

Removing the CO_2 will permit the heating value of the town gas of Case III to be increased but this will require a greater fraction of the effluent from the gasifier passing through the FTS reactor (Table XIV.5).

In this instance 12.6 barrels of C_{5+}-hydrocarbons will be obtained.

In another scenario, a WGS reactor is included in the process that can be utilized when the FTS reactor is inoperable or, in another scenario, both the FTS and WGS reactors can be utilized in parallel.

The catalyst activation and the test results of this group of three patents [XIV.2-XIV.4] are identical to those in the first group of three patents [XIV.1,XIV.6,XIV.7]. The examples in references XIV.2-XIV.4 are essentially the same as those in references XIV.1, XIV.6 and XIV.7.

Reference XIV.2 claims a method of thermally cracking a wax produced by a FTS reaction using an iron-based catalyst in a slurry reaction at a temperature of 770°F (410°C) for a sufficient period of time to produce diesel and naphtha fractions.

Reference XIV.3 claims a method for preparing and activating with synthesis gas a material that is catalytically active for Fischer-Tropsch synthesis.

Reference XIV.4 claims a FTS method suitable for producing a diesel product that is cleaner than commercially available that is derived from crude oil and having a cetane number which is higher than 45 and aromatics less than 1% and the same product that contains more than 2 wt.% oxygen.

The final two patents [XIV.5,XIV.8] are essentially identical to each other and, except for a section describing the use in conjunction with power generation and the claims, are identical to references XIV.2-XIV.4. The Fischer-Tropsch processes are used in combination with electric power generation. The example considers a 300 MW off-peak power production rate (during 17 hours of the 24 hour day) in a plant with a thermal efficiency of 33%. The feed gas requirements for the peak and off-peak conditions are 14.87 and 11.15 million standard cubic feet per hour (MMSCFH), respectively. This requires a FTS reactor to handle 3.72 MMSCFH of coal gas during off-peak hours. To prevent slurry bed slumping, the FTS reactor would require an additional 0.45 MMSCFH during peak operation. During peak operation, the FTS conditions would be changed from 250 to 100 psi to maintain an adequate superficial velocity in the FTS reactor. The average production of liquid hydrocarbons would be about 2100 barrels per day.

Reference XIV.5 claims: (1) a FTS process for producing liquid hydrocarbons from a synthesis using an iron catalyst in a slurry reactor with recycle of CO_2 to the gasifier, (2) claim 1 using coal derived synthesis gas and (3) the method of claim 2 wherein the FTS is used in combination with an electric power generation system.

Reference XIV.8 has one claim for a diesel fuel additive for reducing particulate emissions by utilizing the oxygenates in the FTS product so that the diesel contains at least 2 wt.% oxygen.

The discussion in the sections of these patents provides an excellent overview of FTS using an iron catalyst and of process concepts to improve the efficiency of carbon utilization. At times it is difficult for the reader to easily discern whether the data is from modeling or produced by experiment. Rentech has operated a 6-inch 8-foot tall slurry reactor both with and without CO_2 removal in advance of the FTS reactor [XIV.8]. In 1992 it was reported that the longest run was for a two-week period but it is understood that subsequent runs have been made for periods of 60 days or more; however, data for these longer runs do not appear to be available in the public domain.

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XIV.3. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,504,118, April 2, 1996.

XIV.4. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,506,272, April 9, 1996.

XIV.5. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,543,437, August 6, 1996.

XIV.6. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons, U.S. Patent 5,620,670, April 15, 1997.

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XIV.18. C. B. Benham, "A decade of research and development in Fischer-Tropsch applications, Pittsburgh Coal Conf, October 15, 1992.

Table XIV.1

	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel
Cetane Index ASTM 976-80	45 min.	40 min.	62
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*
Temperature °F ASTM D56 Viscosity @ 40°C	550°F-max.	540°F-min. 640°F0Max.	556°F
cSt.	1.4 min.	1.9 min.	1.8
ASTM D445-82	2.5 max.	4.1 max.	
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02
Flash Point °F, min. Corrected to 760 mm Hg ASTM D56-82	100°F	125°F	122°F
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%
API Gravity ASTM D1298	38-41	34.7	48.7
BTU/lb ASTM D240	16,000-17,000	19,810	19,371
Oxygen Content, Wt.%	N/A	N/A	3.05%

* Analyses were below limits of detection.
(1) ASTM D975-81, #1 Diesel
(2) ASTM D975-81, #2 Diesel

Table XIV.2			
Test	Method		Results
Flash Point, ^{o}F	ASTM D56		122
API Gravity @ 60^{o}F	ASTM D1298		48.7
Sulfur Content, Wt.%	Horiba Analyzer		<0.0001
Kinematic Viscosity @ 40^{o}C, cSt.	ASTM D445-82		1.80
Distillation Range	ASTM D86	IBP	314
		90%	566
		FBP	627
Conradson Carbon on 10% Residuum, Wt.%	ASTM D189-80		0.02
Saturates, Wt.%	NMR/90 MHz		30
Alpha-Olefins			45
Internal Olefins			9
Alcohols and Others			16
Oxygen Content, Wt.%	Elemental Analysis		3.05
Average Carbon Chain Length	GC/FID		C_{14}
Cetane Index	ASTM D976		62
Heat of Combustion, BTU/lb	ASTM D240		19,371

Table XIV.3

Efficiencies Taken from Description of Examples
Feed 1,000,000 Std. Cubic Feet/Day

Example	Efficiency	C_{5+} bbl/day	CO_2 Recycle
1	58.1	80.7	
2	50		Yes, reactor and reformer
3	36.8	51.8	No
4	43.6	61.3	Yes, from reformer inlet
5	60.5%	85.2	Yes, reformer and 1/2 FT tail gas
6	71.3%	94.6	Yes, ~ all CO_2 and 1/2 FT tail gas hydrocarbons
7	43.7[a]	60.0	

[a] Same as example 5 except $\alpha = 0.7$.

Table XIV.4
Stream Compositions for Case III

Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.15
CO	26.9	3.69	10.00
CO_2	2.0	17.88	13.56
CH_4	14.1	19.75	18.21
C_2H_6	1.3	2.05	1.84
C_2H_8	0.0	0.19	0.14
C_4H_{10}	0.0	0.12	0.09
LHV (B/ft.3)	388.3	387.1	387.4
Volume (MMSCF)	1.0	0.572	0.786

Table XIV.5
Stream Compositions for Case IV

Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Mixed Gas (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.17	65.34
CO	26.9	3.69	8.59	10.00
CO_2	2.0	17.88	14.52	0.60
CH_4	14.1	19.75	18.57	21.57
C_2H_6	1.3	2.05	1.89	2.20
C_2H_8	0.0	0.19	0.16	0.18
C_4H_{10}	0.0	0.12	0.10	0.11
LHV (B/ft.3)	388.3	387.1	387.7	450.9
Volume (MMSCF)	1.0	0.572	0.773	0.664

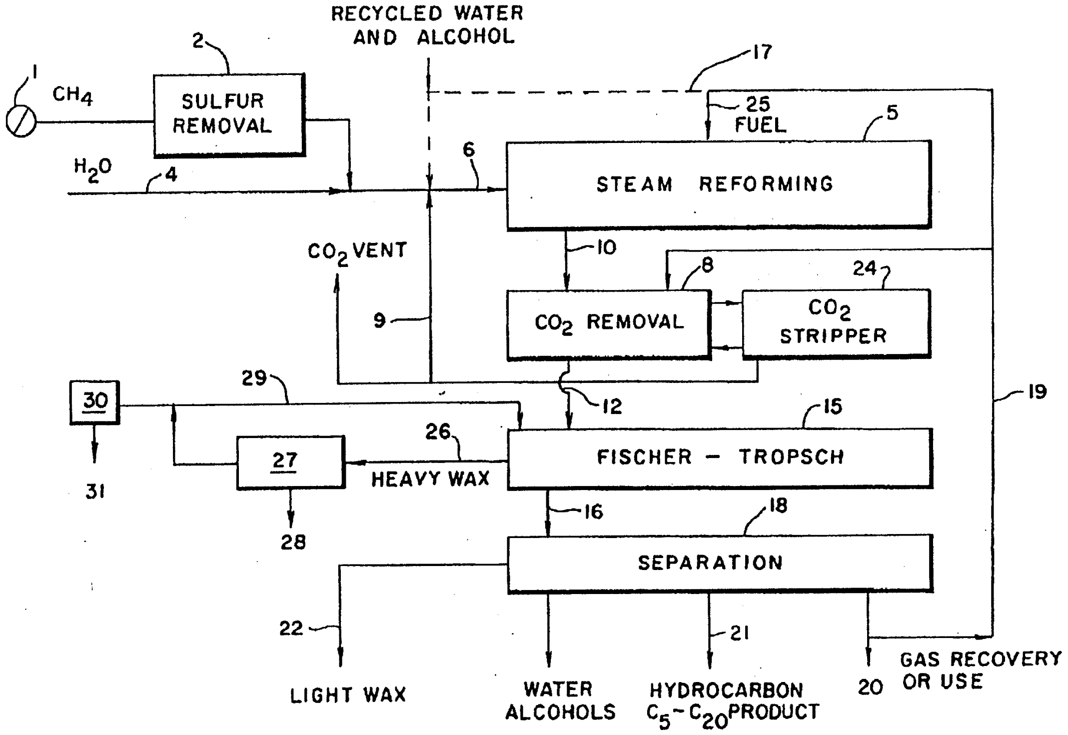

Figure XIV.1. Recycled water and alcohol.

ATTACHMENT IX

Review of Air Products Fischer-Tropsch Synthesis Work

During the 1980s, Air Products & Chemicals worked on several aspects of the Fischer-Tropsch synthesis. These included the development of novel Fischer-Tropsch slurry catalysts and process concepts, the design of a Fischer-Tropsch pilot plant, the hydrodynamics of bubble column reactors, and the development and operation of the LaPorte Fischer-Tropsch facility (IX.1-IX.7). Their patents concerning the preparation of Fischer-Tropsch catalysts contain the following: "The invention was made under DOE Contract No. [one of two contracts] and is subject to government rights arising therefrom."

The focus of the work was on the use of the low H_2/CO synthesis gas ratios expected from coal gasification. However, a limited number of runs with a H_2/CO ratio that would be typical of the gasification of natural gas were made.

The work on the preparation, characterization and performance of cobalt and ruthenium catalysts focused on the use of carbonyl clusters with the expectation that these would lead to highly dispersed supported metal catalysts. As part of this study a baseline catalyst was prepared by the "normal" procedure using a cobalt nitrate precursor and aqueous impregnation techniques.

The workers utilized a number of catalyst supports. These included: γ-Al_2O_3 (Catapal SB, 217 m^2/g, 45 µm), silica (Davison 952, 339 m^2/g, 70 µm), $MgO \cdot 3.6SiO_2$ (Florisil, 298 m^2/g, 75 µm) and titania (Degussa P-25, 50 m^2/g, 2 µm). These supports were used to prepare the catalysts shown in Table IX.1a and IX.1b.

A common impregnation procedure was used to prepare four batches of a catalyst with a formulation of $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ in which the metal precursor to support ratio was held constant (3.55-3.81 wt.% Co with the Co/Zr ratio 0.55). This base case catalyst, including one larger batch, exhibited similar activity and product selectivity, showing that the preparative method was reproducible.

The catalysts covered in the patents (IX.4-IX.6) are prepared using a decomposable salt or organic compound of cobalt, iron or ruthenium. One claim is (IX.5):

"1. Method of making a catalyst comprising the following steps:

(a) treating an inert, inorganic metal oxide catalyst base material with a nonaqueous solution of a decomposable salt or organic compound of a group IVB metal and removing said nonaqueous solution;

(b) impregnating the product of Step (a) with a nonaqueous solution of a decomposable salt or organic compound of a Fischer-Tropsch metal catalyst from the group consisting of cobalt, iron or ruthenium, and removing remaining said nonaqueous solution; and

(c) exposing the product of Step (b) to a reducing atmosphere; all while maintaining said material and said products under conditions sufficient to avoid hydrolysis, oxidation, and calcination thereof."

A number of catalyst formulations were prepared by the patented technique. Fischer-Tropsch synthesis activity and selectivity were obtained in a fixed-bed reactor (screening test) and for those formulations exhibiting a high activity in a 1-liter continuous stirred tank reactor. The conditions used for the screening studies were 240-280°C, CO/H_2 feed = 0.55 - 2.0, 300 psig (2.0 MPa) and a space velocity of 1.0-2.0 NL/g cat/hr.

The $Co_2(CO)_8/Zr(OPr)_4/SiO_2$ (3.5% Co, 6.6% Zr) catalyst was found to be the most active system in the slurry reactor and also gave the best liquid fuel selectivity. The Schulz-Flory pattern was found for the products obtained using this catalyst. The bulk activity ranged from 16 to 54 mole syngas/kg cat/hr. The gasoline range (C_5-C_{11}) products accounted for 20 to 45% of the products and the diesel range (C_{12}-C_{18}) products were 17 to 32%. This catalyst was tested in an extended slurry-phase run that achieved 6 months on stream with a 10% loss in activity.

A comparison was made for 4% cobalt Zr-alumina catalysts in which the dominant difference was the cobalt compound used in the preparation of the catalyst: cobalt carbonyl in an organic solvent and cobalt nitrate in aqueous solution. The specific activity of the nitrate derived catalyst is significantly lower that the one derived from the carbonyl compound when the conversion is effected at 240°C is the CSTR (Table IX.2). However, when the conversions are compared at 260°C, there is less difference between the two conversions; one possibility to account for this is that significantly more sintering of the cobalt occurred for the carbonyl derived catalyst at this higher temperature.

The activity of the $Co_2(CO)_8$-based catalysts decreased with changing supports as follows: $SiO_2 >> TiO_2 > Al_2O_3 > MgO{\bullet}SiO_2$ (figure IX.1). The Co/TiO_2 catalyst was found to exhibit an unusually high selectivity for $C_{3\text{-}5}$ olefins. Zirconium was found to be the better promoter, compared to Ti, for enhancing activity and selectivity, with the optimum Co/Zr ratio being between 0.5 and 1.0.

As the cobalt loading was increased from 4 to 14 wt%, the catalytic activity remained constant and then eventually declined.

The supported Ru catalyst exhibited initially a high activity but the catalyst deactivated rapidly in the slurry reactor. Thus, not much data were obtained with this catalyst.

They found that the following kinetic expression best fitted the data they obtained over a wide range of conversions:

$$-\ (r_{CO+H_2}) = kC_{H_2}/(1 + k\ C_{H_2O}/C_{CO}C_{H_2}). \qquad [1].$$

However, it was not possible to discriminate with great confidence among the kinetic equations tested during the study.

Catalyst Activation

The activation of supported metal carbonyl catalysts is frequently done by thermal decomposition under vacuum or inert gas atmosphere (IX.8). During the early work at Air Products, catalysts were activated in syngas. To accomplish this the catalyst precursor was heated to 180°C in a nitrogen flow at atmospheric pressure. At 180°C, the flow was switched to the synthesis gas ($CO/H_2 = 1$) and then heated to the reaction temperature. At the reaction temperature, the pressure was increased to the one used for the synthesis. Later in their work, they compared the impact of activation in pure H_2 or syngas ($CO/H_2 = 1$). For a 4%Co-zirconia promoted alumina catalyst, they found that the sample activated in hydrogen had a significantly higher activity and higher yield of liquid fuels (figure IX.2a,b; Table IX.3).

Catalyst Promoters

The Air Products work included a comparison of the promotional effects of zirconia and titania for both silica and alumina supports. The titania promoted cobalt catalyst on both alumina and silica supports showed lower catalytic activity than a similar zirconia promoted catalyst. The bulk activity at 240°C for the alumina supported cobalt was 20 % lower with the titania promoter; with the silica supported cobalt this was 40% lower. The titania promoter also produced more methane and light hydrocarbons than the zirconia promoted cobalt catalyst. Similar activity trends were obtained in both the fixed-bed and slurry reactors; however, the differences in the selectivity were less noticeable in the slurry reactor.

Cobalt Metal to Promoter Metal Ratio

In this study the cobalt to promoter ratio for the silica support was conducted with precursors which contained the same level of cobalt but with a variable amount of promoter. Four catalysts were prepared and the compositions are shown below:

Weight % Cobalt	Weight % zirconium	Co/Zr
4.0	4.8	1.2
4.4	2.3	0.53
4.6	0.1	0.15
4.2	0.0	0.0

The effect of the Co/Zr ratio in the gas-phase reactor on the bulk and specific activities for this series are shown in figures IX.3 and IX.4. It appears that the optimum ratio for bulk activity occurs at about Co/Zr = 1; however, for the specific activity it occurs at about Co/Zr = 0.5, the base case catalyst ratio. The usage ratio appears to increase as the zirconium content increases. The base case catalyst provided the highest yield of liquid fuel, C_5-C_{18}.

Three of the catalysts, Zr/Co = 0, 0.53 and 1.9, that were evaluated in the fixed-bed reactor were also evaluated in the CSTR (figure IX.5). Just as in the fixed-bed reactor, the optimum activity was obtained for the base case catalyst with a Zr/Co = 0.53 ratio.

Metal Loading

Metal loadings of 3.5, 11.0 and 14.4 wt.% Co on silica were evaluated. For the base case (3.5 wt% Co) the Zr/Co ratio was 0.53 but this ratio was not used for the catalysts with the higher cobalt loadings. One reason for using the higher Zr/Co ratio for the two higher Co loadings was to be able to make a comparison with the Co/Zr/silica catalyst that is used by Shell Oil for their Shell Middle Distillate Synthesis (SMDS). There was little change in the bulk activity in increasing Co content from 3.5 to 11.0; however, at all temperatures there was a significant decline in activity upon further increasing the Co content to 14.4 wt.% (figure IX.6). Selectivity to liquid fuels declined as the Co loading increased.

Significant increases were observed for the bulk density with increasing Co loadings: 0.394 g/cc for 3.5 % Co, 0.564 g/cc for 11.0% Co, and 0.883 g/cc for 14.4% Co. Thus, as the experiments were conducted in the fixed-bed reactors, the amount of catalyst contained in the 10 cc catalyst volume increased significantly and this may have been a major factor in determining the bulk activity shown in figure IX.6.

In the slurry reactor tests of the 3.5 and 11.0% Co catalysts, the activity at both 240 and 260°C declined as the Co content increased in contrast to the fixed-bed reactor runs (figure IX.7).

Product Selectivity

Satterfield et al. (IX.9) reviewed the literature with respect to product distributions for slurry Fischer-Tropsch reactor operation, particularly with iron catalysts. It was concluded that product hydrocarbon selectivities follow a predicted Anderson-

Schulz-Flory (ASF) distribution characterized by the chain growth probability factor, α, and that previously reported deviations are probably due to experimental artifacts. Fixed-bed temperature gradients, insufficient time to reach steady-state, volatilization of certain fractions, and condensation of high molecular weight material are some of the experimental problems that can give misleading selectivity results. These considerations are for deviations which produce chain-limiting Fischer-Tropsch product distributions; most agree that deviations which produce more high-molecular weight products than predicted by ASF are valid (IX.10). Air Products workers sought to avoid the problems previously encountered by their close attention to experimental details, and by determining product distributions over long-term slurry phase operations with good quantitative mass balances (IX.11).

With the fused iron United Catalysts, Inc. C-73 catalyst, a good fit to the ASF distribution was obtained (figure IX.8). However, for slurry catalyst A2 (later shown to be a cobalt-zirconia-silica catalyst) there was an enhanced product deviation from the ASF distribution for the C_{18}-C_{35} region when the catalyst was operated at 2.21 MPa. The effect of pressure in determining this product enhancement can be seen by comparing curves a and b in figure IX.8.

Another catalyst, B, also shows a deviation from ASF (figure IX.9). There was a significant deviation from the ASF distribution for the C_9-C_{25} products when operating with a feed of $H_2/CO = 0.5$. The yield of 67.3 wt% product obtained in the C_9-C_{25} products represents a 25 wt% increase over what was considered to be the limit of 54.1% imposed by the ASF distribution.

An adequate explanation for these deviations obtained early in the experimental program has not been offered. These and similar catalysts usually provided "standard"

ASF distributions based on the data reported. This implies that some experimental operational problem was responsible for this unusual, and highly desirable, deviation from ASF distribution.

Ruthenium Catalyst

A Ru/Zr/alumina ($Co_2(CO)_8$) was a promising catalyst when tested in the fixed-bed reactor. The fixed-bed activity was 26.7 mol syngas/kg cat/hr (comparable to the Co base case catalyst) and a high specific activity of 0.48 mol/mol Ru/min. Methane production was high at about 20%. Slurry phase testing of this catalyst indicated a significantly lower catalytic activity (8 mol syngas/kg cat/hr).

A Ru/Zr/silica catalyst was also tested and it exhibited a much higher activity (70 mol syngas/kg cat/hr; 0.834 mol CO/mole Ru/min at 240^{o}C; 81 mol syngas/kg cat/hr and 1.05 mol Co/mol Ru/min at 260^{o}C) than the similar catalyst using alumina as a support. The Ru catalyst produced higher molecular weight products than a similar Co catalyst. Methane selectivity was low, never exceeding 5.3%.

The performance of the Ru/Zr/silica catalyst was poor in the CSTR. Initially showing a high activity at 240^{o}C (43 moles syngas/kg cat/hr), it had declined to 4 moles syngas/kg cat/hr after only 280 hours on stream.

These preliminary results led the workers to concentrate their further efforts on their cobalt catalysts.

Improving Water-Gas-Shift (WGS) Activity

Since both the Ru and Co catalysts exhibited very low WGS activity, attempts were made to modify the catalyst to increase the WGS activity. A physical mixture of the base case catalyst and a commercial Cu/Zn/alumina low temperature shift catalyst was employed. The addition of the shift catalyst caused a decrease in the Fischer-

Tropsch synthesis without increasing the WGS activity. A Co/Fe/alumina catalyst was prepared using the carbonyl compound of Co and Fe. There was a 53% increase in the usage ratio indicating increased WGS; however, the bulk activity declined by 40%. A Fe/Co/Zr/silica catalyst showed only a slight increase (14%) in usage ratio and a slight decrease in bulk activity. Thus, the exploratory effort to increase the WGS activity failed.

Extended Runs in CSTRs

A run of nearly 6 months was made with a Co/Zr/silica catalyst (4.43% Co, 7.58% Zr) (IX.12). This catalyst displayed remarkable stability. During the first 1012 hours it was utilized at 240°C, 300 psig, CO/H_2 = 0.5 and space velocity = 1.8 l/g cat/hr, and then from 1012 to 2188 hours at 260°C, 300 psig, CO/H_2 =1 and space velocity = 2.0 L/g cat/hr. The productivity declined from 52.7 to 46.9 mol syngas/kg cat/hr during 1012 hours (figures IX.10 and IX.11) and then declined slowly during operation from 1012 to 2188 hours (figures IX.12 and IX.13). During the second period the product selectivity remained nearly constant (figure IX.14).

After 2188 hours, a series of changes from the base case conditions, 260°C, 300 psig, space velocity 2.0 L/g cat/hr and CO/H_2 = 1.0, were made for the CO/H_2 ratio and the space velocity to generate data for kinetic studies. At intervals, the conditions were returned to the base case to obtain data to correct for the slow catalyst aging. A series of tests were made at two feed set of conditions. In one instance, the impeller speed was altered using constant feed conditions and in the other the space velocity was varied by adding a nitrogen flow, maintaining the same partial pressure of hydrogen and carbon monoxide by increasing the total pressure. Both variations show that mass transfer effects can be neglected.

At 3964 hours, the temperature was increased to 280°C to repeat the series of kinetic measurements. At this temperature the methane production was very high (up to 56.4%) and the wax production very low. At the end of the experiment, the reactor contained only solid, indicating that the operations at the higher temperature had caused the reactor to loose essentially all of the liquid through vapor pressure and/or hydrogenolysis effects.

Cobalt Dispersion

Hydrogen chemisorption was measured to obtain a measure of the metal dispersion of the cobalt and ruthenium catalysts. Air Products reports indicate that they were disappointed with the low dispersions that they obtained; however, the 10-12% dispersion values they obtained for 11 and 14% Co on silica are about as high as reported by later workers. In general, the silica supported Co exhibited a higher dispersion than the alumina supported cobalt at a similar metal loading (Table IX.4). The hydrogen chemisorption was considered to decrease along with the catalytic activity as the cobalt loading was increased for the silica supported cobalt catalysts. The dispersions obtained by the Air Products workers agree with those reported by Reul and Bartholomew (IX.13). Chemisorption was measured at higher temperatures because this led to higher surface areas.

Olefin Reincorporation

In a screening study, ethene was added to the syngas feed for runs with the $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$ catalyst (5.07% Co; 4.39% Zr). Under the reaction conditions employed, the CO conversion should have been 20% or less. When 10 or 20 volume percent ethene was added to the feed, the major result was the production of ethane. The oxygenate production did increase slightly (from 0.2 to 2.4 wt%) but the majority of this fraction was propanol, the product of hydroformylation. The catalyst underwent significant (20% conversion) deactivation during the addition of ethene. The conclusion is that ethene did not undergo significant incorporation; rather it was hydrogenated to ethane.

Kinetic Study

A program was developed to obtain kinetic data from the experimental data (figure IX.15). Experimental data from two runs were made with a catalyst formulation that was essentially the same as the base case catalyst but a more active $Co_2(CO)_8/Zr/SiO_2$ catalyst (4.9% Co; 9.3% Zr). Henry's Law was assumed to apply and to allow for calculation of vapor partial pressures. Henry's Law data was taken from Peter and Weinert (IX.14) and liquid densities were calculated using correlations proposed by Deckwer (IX.15). Mass transfer from bulk liquid to catalyst surface was considered to negligible, based upon the experimental data.

The authors fit the data to five kinetic expressions (to correlate with equations in reference 13, A=2, B=1, C=3, D=4):

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{CO_2}/C_{CO}) \qquad [2]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{H_2O}/C_{CO}) \qquad [3]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + K_1C_{CO_2}/C_{CO} + K_2C_{H_2O}/C_{CO}) \qquad [4]$$

$$-r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{H_2O}/C_{CO}C_{H_2}) \qquad [5]$$

$$-r_{CO+H_2} = kC_{H_2}^{a}C_{CO}^{b}. \qquad [6]$$

For the run with the catalyst similar to the baseline catalyst, the data at high H_2/CO feed ratios and at high space velocities were best described by the first order rate equation:

$$-\ r_{CO+H_2} = kC_{H_2}^{a}C_{CO}^{b}. \tag{7}$$

where a = 1.1 and b = 0. For low H_2/CO data, equation 3 fits the data better:

$$-\ r_{CO+H_2} = k\ C_{H_2}/(1 + KC_{H_2O}/C_{CO}) \tag{8}$$

where k = 0.349 and K = 0.425. The activation energy was in the range of 33-44 kJ/mole.

For the more active catalyst, none of the five equations were able to be used to fully describe the data. They concluded that equation 3 provided the better fit to the data and transformed the equation to a linear form:

$$C_{H_2}/-r_{CO+H_2} = (K/k)\ C_{H_2O}/C_{CO} + (1/k). \tag{9}$$

The data are plotted using equation 7 and is shown in figure IX.16 for 240, 260 and 280°C. From the intercept, the rate constant, k, is derived with values ranging from 0.328 to 0.775 cc/g cat/sec. This allows K to be determined from the slope and values ranging from 0.466 to 0.302 are obtained. An activation energy of 51 kJ/mole was obtained from the Arrhenius plot.

The authors write that, at that time, relatively few kinetic studies of the Fischer-Tropsch reaction using cobalt catalysts have been made (IX.17-IX.22). From the available literature, activation energies for cobalt catalysts are in the range of 67-117 kJ/mole; for iron catalysts they range from 37 to 105 kJ/mole. The activation energies obtained by the Air Products workers for these catalysts are surprisingly low.

The Air Product workers analyzed the kinetic data obtained during run hours 2188 and 3964 in the extended run described above. It was assumed that the deactivation led to a linear decrease in conversion during the kinetic measurements. They concluded that Equation 5, which included water inhibition, fit the data better than the other equations; a plot of the data using the linearized form of Equation 5 is shown in figure IX.17. It had been reported by Huff and Saterfield (IX.23) that this equation describes data with high water concentration quite well. After Equation 5, the data was best fit by equation 6. The rate constant obtained using Equation 5, based upon fresh catalyst activity, are $K = 5.24 \times 10^{9} \exp(-23{,}254/RT)$ cc/g cat/sec and $K = 1.55 \times 10^{-3} \exp(-6{,}250/RT)$ mol/cc. The Arrhenius plot returned an activation energy of 97 kJ/mole, and this value agrees much better with those reported earlier for cobalt catalysts.

Slurry Reactor Hydrodynamics Studies

The final report (IX.24) provides a detailed summary of the literature to that date (about 1983) and experimental data obtained in cold flow simulators of 12.7 and 30.5 cm diameter (1.52 and 4.75 m height, respectively) that was conducted at Air Products. With the simulator, phase holdups, phase dispersion coefficients, and interphase heat and mass transfer coefficients were measured. The measured heat and mass transfer and phase dispersion correlations were found to conform to the literature, while the phase holdup correlations were different from the literature. The product distributions from Air Products' catalyst testing program were combined with the hydrodynamic studies to make predictions of space-time yields of product fuel fractions in large-scale bubble column reactors.

Based upon the study, they concluded:

1. Both hydrodynamic and kinetic effects are important to the proper design of the bubble column reactor.
2. For solid particles below 60 µm, the slurry can be modeled as a pseudo-single phase. Larger size solid particles were distributed in accordance with Cova's sedimentation-diffusion model (IX.25).
3. Of those studied, the most important independent variable affecting the reactor performance was the superficial gas velocity, followed by solid particle loading. The type of liquid had a small effect on the column hydrodynamics. The parameters that had little or no effect in the range studied included the presence of heat transfer internals, solid type, distributor hole size, and superficial slurry velocity.
4. Staging the bubble column system to provide more plug flow behavior of the gas was predicted to result in a 5% increase in conversion rates, assuming the same bubble size, about 0.23 cm, as in the unstaged column. On the other, if the average bubble diameter is decreased to 0.07 cm, the conversion rates are expected to increase by 25%.
5. The gas holdup obtained in the cold flow systems was lower than measured by Deckwer (IX.26) and Mobil (IX.27) but in agreement with results of Satterfield (IX.28) and with the correlations from Air Products' slurry phase methanol project (IX.29).
6. Adding seven, 5.7 cm o.d. x 1.42 m heat transfer internals to the 30.5 cm column had no effect on column hydrodynamics.

7. The heat transfer results agreed with Deckwer's correlation (IX.30) but, unlike Deckwer, the heat transfer rates continued to increase beyond a 10 cm/s superficial gas velocity. Heat transfer tubes would therefore take only a small fraction of the internal volume of a Fischer-Tropsch slurry bubble column reactor.
8. Mass transfer results agreed with Akita and Yoshida (IX.31) and Hikita et al. (IX.30-IX.33).
9. Liquid dispersion results agreed with Kato et al. (IX.34), indicating that above a superficial gas velocity of 3 cm/s, the slurry was well-mixed.

The Air Products workers wrote, "One of the more important aspects of gas flowing through a tubular reactor is its availability at the reaction site. This is ultimately related to the interfacial area between the liquid and gaseous phases. In a two-phase, gas-liquid system, the interfacial area, a, is related to the gas volume fraction, ϵ_G, and mean bubble size, d_{SB}, by

$$a = 6\ \epsilon_G / d_{SB} \qquad [10]$$

Both the mean bubble size, also known as the Sauter mean diameter, and the volume fraction, which is typically referred to as gas holdup or void fraction, are values which are extremely important to optimum reactor design."

The Air Products work followed three steps:

1. Hydrodynamic data were obtained in a 5" ID x 5' (12.7 cm ID x 1.52 m) cold flow simulator.
2. Scale hydrodynamic study to 12" ID x 15.5' (30.5 cm ID x 4.75 m) column.
3. Incorporate kinetic data from catalyst studies with hydrodynamic correlations into a computer model and use this to predict the conversion rates and space-time yields that would be obtained in actual Fischer-Tropsch slurry reactor operation.

Using the model, the heat, mass and momentum transfer parameters which most affect the bubble column design were better quantified.

In the slurry reactor, either mass transfer resistance or kinetic resistance is expected to dominate. Gas holdup, average bubble size and mass transfer coefficient are the important dependent variables that impact mass transfer resistance. Two important factors for kinetic resistance are solids dispersion and liquid dispersion, both affecting catalyst loading, and thereby reactor productivity. Heat transfer rate is also important since this will determine the fraction of the reactor volume required for heat exchangers, and not available for production. The Air Products work attempted to quantify the above mentioned parameters (Table IX.5).

The workers reviewed work prior to 1982 concerning gas-liquid-solid systems. They indicate that Kara (IX.35) found that solid particles promote bubble coalescence and hence the onset of the churn-turbulent regime. However, reports of solids decreasing or increasing gas-holdup can be found in the literature. Kurten and Zehner (IX.36) report Sittig's work on bubble breakup caused by solids. It was shown that bubble breakup occurs when the inertia forces of the solid particle exceed the bubble surface tension forces:

$$(\pi/6)(\rho_S/2)\, d_S^3\, u_{SG}^2 > (\pi/4)\, \sigma\, d_S^2 \qquad [11]$$

which, when rearranged, shows that bubble breakup can occur when the Weber number is greater than 3:

$$We = (\rho_S\, d_S\, u_{SG}) / \sigma \geq 3\ . \qquad [12]$$

This indicates that below the critical Weber number the solid will not cause bubble breakup.

Since for a particle of about 4 or about 100 µm, a bubble rise velocity > 0.1 or 0.65 m/sec, respectively, is needed for the particle to induce bubble breakup, it is not anticipated that Fischer-Tropsch slurry column will experience bubble breakup due to the presence of solid catalyst particles. In fact, it is expected that bubble coalescence will occur, decreasing gas holdups.

Deckwer et al. (IX.15) studied gas holdup in 4.1 and 10 cm ID columns in the bubbly flow regime (1 to 4 cm/sec) using a hydrogenated Fischer-Tropsch liquid and up to 16 wt.% of > 5 micron alumina particles and obtained the empirical correlation:

$$\epsilon_G = 0.053\ j_G^{1.1} \qquad [13]$$

where j_G is the superficial velocity of the gas. It was suspected that foaming occurred in the measurements reported by Deckwer et al. (IX.15). Kuo (IX.27) obtained data for the same system showed that with a sintered plate gas distributor he obtained foaming but that no foaming and a much smaller gas holdup was obtained with a distributer with larger openings. Bukur (IX.37) used the same wax as Deckwer and Kuo and obtained a means of eliminating the formation of a foam region. In the absence of a foam region, Bukur obtained a gas holdup that was comparable to those of Pilhofer and Bach (IX.38) and the results obtained by Air Products.

It was concluded that gas holdup was mostly a function of gas velocity and varies to the first power. Slurry density, or weight loading, has the second largest impact on gas holdup. The larger column (30.5 cm) had a lower gas holdup than the 12.7 cm column at the higher gas velocities. It was considered that this was due to more bubble coalescence in the taller column and that the data obtained in the larger diameter column, being more reliable, would be used in the computer simulation of an operating commercial Fischer-Tropsch reactor.

The gas bubble diameter was obtained over a wide range of conditions. The bubble diameter, d_{SB}, relationship with the gas holdup, the gas liquid interfacial area is related to the Sauter mean bubble diameter and gas holdup by

$$a = 6\ \epsilon_G / d_{SB}\ . \qquad [14]$$

The uncorrected bubble chord lengths were in the range from 0.28 to 0.44 cm. The measured values are slightly larger than the true values because the experimental approaches caused bubble acceleration/elongation during the measurement. The corrected bubble diameters ranged from 0.22 to 0.35 cm and the bubble velocity ranged from 26.3 to 32.7 cm/sec, both range over fairly narrow values. Since the bubble size should be smaller in Fischer-Tropsch liquids than in water, they concluded that the Calderbank (IX.39) correlation suggested a Sauter diameter size of 0.23 cm for a Fischer-Tropsch type system and this produces

$$a = 6\ \epsilon_G / 0.23 = 26.09\ \epsilon_G \qquad [15]$$

which was used in the computer model.

The overall mass transfer coefficient, K_La, is the product of the mass transfer rate per unit area, K_L, and the interfacial area, a. Air Products workers measured K_La because of the variation in the reported values. This variation was primarily due to variation in the reported gas holdup and average bubble size; however, there is also variation in the reported values of K_L. They obtained an empirical correlation for K_La:

$$K_La = (0.30\ \epsilon_G^{1.06}\ d_p^{0.05}) / W^{0.08} \qquad [16]$$

where W = weight fraction of solids. Gas velocity was considered to be the primary factor in estimating K_La.

Liquid dispersion relates to how well mixed the liquid phase is and how much solid can be suspended. The Air Products workers discussed this in terms of two extremes:

1. Ideal mixing, continuous stirred tank reactor (CSTR) behavior where any liquid molecule can move to any other part of the column from one instant to the next, and
2. Plug flow reactor (PFR), where any molecule will move in concert with the other neighboring molecules, entering and leaving the column at the same time.

The axial liquid dispersion coefficient, E_z, provides one was to quantify where a particular reactor lies between these two extremes (CSTR and PFR). E_z will be zero for PFR and infinity for CSTR behavior. In practice, when E_z is greater than 10^{-2} m^2/sec, a well-mixed behavior exists. Knowing E_z, one can plot a sample's concentration as a function of time at a fixed point within the column; such a plot is a residence time distribution (RTD) curve.

A model that is used to describe the sample concentration at any time is Fick's Law:

$$dC/dt = E_Z \, d^2C/dZ^2 \; . \qquad [17]$$

Using the appropriate boundary conditions, an approximate analytical solution which describes the RTD curve at any point within the column was given by Ohki and Inoue (IX.40):

$$dC/dt = E_L \, d^2C / dZ^2. \qquad [18]$$

For the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$dC/dt)_{0,T} = dC/dZ)_{L,T} = 0 \qquad [19]$$

where L = extended bed height and

$$C(Z,O) = \begin{cases} O, & O \leq Z < Z_1 \\ C_O, & Z_1 \leq Z \leq Z_2 \\ O, & Z_2\ Z \end{cases} \quad [20]$$

$$C/C_e = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L)\exp(-n^2\pi^2E_Lt/L^2)] \quad [21]$$

Little difference is obtained if the summation is to infinity, the exact solution, or stops at 100.

The experimental program to address the dispersion issue and to obtain the RTD curve utilized the injection of a sodium chloride solution into water, detecting the movement of the sodium chloride, the tracer, by conductivity measurements at various heights in the column.

The energy dispersion is greatest at the gas distributor inlet and least at the gas disengagement zone at the top of the reactor. However, E_Z was not height dependent was not evident since one dispersion coefficient was sufficient to characterize the entire column. The results of the liquid dispersion runs at Air Products were in agreement with the work of Kato and Nishiwaki (IX.41):

$$Pe = (13\ Fr) / (1 + 6.5\ Fr^{0.8}) \quad [22]$$

where Pe is the Peclet number $((V_G\ d_C) / E_Z)$ and Fr is the Fraud Number $(V_G / g\ d_S)^{1/2}$.

From their experimental work, they obtained data to show that a uniform distribution of 0.5-5 micron sized particles was obtained. With larger particles there was, as expected a distribution of particles along the column height, with more at the bottom than the top. They concluded that nonagglomerating catalyst particles less than 60 microns should be suitable for Fischer-Tropsch bubble column batch operation, as no unsuspended solids were observed.

Heat transfer was studied by placing tubes with heaters in the bubble column. It was noted that the agitation produced by the gas phase within the reactor produces heat transfer coefficients that are higher than those produced by gas or slurry alone. The heat transfer surface needed for internal use is less than required for an external exchanger.

The report ends with an engineering evaluation that utilizes the model proposed by Deckwer et al. (IX.42). The substitution of the Air Products correlations for those in Deckwer's model showed little effect at low gas velocities. At 9 cm/sec the space-time yield was doubled (Tables IX.6 and IX.7). A major reason for this was that the lower gas holdup allowed for more catalyst per unit volume. In the bubble column operation there exists an optimum gas holdup which will maximize column space-time yield. Gas holdups higher than this optimum will be reaction rate-limited while those lower than this will be mass transfer-limited. The optimum gas holdup will be affected by the bubble size (b_{SB}), intrinsic kinetic rate (K_o), catalyst weight loading (W), the rate of mass transfer across the gas-liquid interface (K_L), and the usage ratio (U). The optimum gas holdup is given by the expression:

$$\alpha \text{ opt} = 1 / [1 + (6 K_L(1 + U) / K_oWd_{SB})^{1/2} . \qquad [23]$$

Using this equation allows one to calculate the relative space-time yields for a variety of K_o, W and D_{SB} (Table IX.8).

The Air Products workers compared the space-time yield for a bubble column reactor and for a series of staged reactors. In the first method of calculating the space-time yield, a number of idealized CSTRs are simulated with almost complete recycle of the liquid and catalyst but no recycle of the gas phase. This model would be equivalent to the recirculating cell model used in the literature. In the second method, the extent of backmixing of the gas phase was modeled by applying an axial dispersion model (IX.43).

In this model, a low dispersion coefficient refers to many CSTRs in series, while a high dispersion coefficient refers to very few CSTRs in series. Carberry (IX.44) showed that the two methods are relates so that:

$$N = V_G L/2D \ . \qquad [24]$$

Since the Deckwer computer model incorporates the axial dispersion model for the gas, liquid and catalyst phases, this approach was chosen.

Results of simulating the Rheinpreussen-size column as several stages as having the same total volume as the original single-stage column (figure IX.18) are shown in Table IX.9. Thus, a 5% increase in space-time yield is obtained by using 5 CSTRs but a further increase does not lead to a further increase in yield (figure IX.19).

Design of LaPorte Plant

As part of the work, a design for a pilot plant to be located at La Porte, Texas adjacent to an Air Products plant was completed (IX.45). The bubble Fischer-Tropsch reactor was sized to operate in the churn-turbulent flow regime, in which commercial-scale reactors will operate. The study indicated that this flow regime could be achieved with an effective reactor diameter of five inches. However, it was recognized that the exact diameter of the transition from the quiescent to churn turbulent regime is an unknown function of the slurry viscosity and surface tension. To achieve a 40-50% conversion of the synthesis gas in a single pass at a superficial gas velocity of 0.3 ft/sec would require a 30 foot expanded slurry height.

The reasons for the choice of flow regime were described. Concurrent up-flow bubble columns can operate in any one of three flow regimes (IX.15) and these are illustrated in figure (IX.20) together with an indication of the Air Products cold flow work, the LaPorte design and the Rheinpruessen work. The bubbly flow or quiescent regime occurs at velocities less than typically 0.15 ft/sec. Bubbles are of uniform size and do not interact or coalesce to any substantial degree. At higher velocities, the bubbles do not rise uninfluenced by neighboring bubbles and the churn turbulent regime is entered. Coalescence occurs, yielding larger bubbles and faster rise velocities. Because of coalescence, gas holdup does not increase as quickly with gas flow rate in the churn turbulent regime as in the bubbly flow regime. Where the coalesced bubble would be larger than the diameter of the column, the slug flow regime is reached. Slug flow is undesired because of the low gas/liquid interfacial area and the tendency for the slurry to be lifted out of the reactor along with the gas.

The choice of flow regime was dictated by two economic factors. For a given reactor volume:

1. The highest space time yield or production rate per unit volume is optimal.
2. A tall column is preferred to a short one.

The higher the space-time yield, the smaller the reactor volume required for a given production. The simulations with the Deckwer model and the Air Products hydrodynamic and catalytic data showed that, in every case, the optimum gas velocity for a maximum space-time yield falls within the churn turbulent regime. It was concluded that the value of 9.1 cm/sec (0.3 ft/sec), although slightly below the optimum, would still allow a reasonable conversion for the reactor height chosen.

Air Products workers wrote, "For a commercial plant with multiple trains, it is advantageous to have as few reactor vessels as possible. In the quiescent regime only about 15' of reactor height is required to achieve 90+% conversion of syngas. By increasing the gas velocity into the churn turbulent regime, 90+% conversion of syngas is not achieved until a height of 60'. For equivalent STY's, it is more economical to have N vessels at 60' than to have four times that number of vessels, each with a height of 15'." (IX.45).

The slurry reactor was designed to operate in a fluidized-bed mode. Once charged, the slurry will not be added or removed except for removal of high molecular weight products that form during reactor operation. Gas will flow up the column and exit out the column top.

The design was implemented at the La Porte location and the plant has been modified during the years of operation. To date, four runs, two with an iron catalyst and two with cobalt catalyst, have been conducted.

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IX.45. "Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process, Final Report for Task 4, DOE/PC/30021-T22.

Table IX.1a.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an alumina support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
3.6	6.6					0.25
4.4	1.8					0.31
3.4	6.6				1.6	0.31
2.8	4.9					0.48
1.4				0.51		0.40
1.2			0.3	0.4		
4.7[a]						0.25
3.5		8.6				0.23
2.6				0.85		0.34
2.4			0.02	0.79		0.27
3.9	5.0					0.24
5.1[a]	4.4					0.20
4.2[a]	7.1					0.20
4.0	6.4					0.21
10.8	8.5					0.26
3.5	6.6					0.51
3.7	7.3			0.72		0.26

[a] Cobalt added as cobalt nitrate.

Table IX.1b.

Compositions (wt.% of catalyst) and specific catalytic activity (mol CO/mol metal/min) for catalysts prepared using an silica support during the Last Three-Year DOE Contract (reference IX.1).

Co	Zr	Ti	K	Fe	Mn	Act.
4.4		4.0				0.24
3.7	7.2					0.23
4.6	7.5					0.43
4.0	3.3					0.83
3.5						0.31
	7.3			2.4		n.d.
4.0	4.8					0.44
4.4	2.3					0.32
4.6	2.3					0.32
4.2						0.14
4.1	6.8					0.31
11.0	7.4					0.15
14.4	10					0.07

Table IX.2

Effect of Co source on activity and selectivity of 4% Co on Zr/alumina catalyst tested in the slurry phase using a CSTR at 300 psig, CO/H_2 = 1.0 and 2.0 NL/g cat-hr. (from reference IX.1)

Cobalt Source	Carbonyl	Carbonyl	Nitrate	Nitrate
	240°C	260°C	240°C	260°C
Bulk activity, mol syngas/kg cat/hr	35.3	38.5	15.8	29.9
Specific activity, mol CO/mol Co/min	0.29	0.32	0.09	0.21
Selectivity, Wt.%				
C_1	7.9	10.4	10.9	16.5
C_{2-4}	13.7	15.0	6.5	11.1
C_{5-11}	37.0	44.5	12.9	26.5
C_{12-18}	23.4	25.8	19.8	23.8
C_{19-23}	8.9	2.0	21.9	10.6
C_{24}+	9.1	2.3	28.0	11.5
TOTAL FUELS, C_{5-23}	69.3	72.3	54.6	60.9

Table IX.3 Effect of syngas vs. hydrogenation activation on the activity and hydrocarbon selectivity using a 4% Co on Zr/Al_2O_3 catalyst in a slurry CSTR (from reference IX.1)		
	Syngas	H_2
Space velocity, NL/gcat/hr	1.6	2.0
CO/H_2	1.6	1.5
Pressure, psig	300	300
Temperature, °C	250	258
Hydrocarbon, wt.%		
C_1	11.5	7.2
C_{2-4}	10.4	10.8
C_{5-11}	29.2	34.1
C_{12-18}	15.3	27.9
C_{19-23}	12.5	8.6
C_{24}+	21.1	11.4
C_{5-23}	57.0	70.6

Table IX.4

Metal dispersion for Co and Ru Catalysts (from reference IX.1)

Catalyst	BET Surface Area, m^2/g	Metal Surface Area, m^2/g	Dispersion, %
3.5%Co/Zr/SiO_2	316	1.9 (a)	6
4.0%Co/Zr/Al_2O_3	209	0.3 (b)	1
4.1%Co/Zr/SiO_2	210	1.9 (a)	7
11.0%Co/Zr/SiO_2	302	8.1 (a)	12
10.8%Co/Zr/Al_2O_3	n.d.	5.4 (a)	7
14.4%Co/Zr/SiO_2	145	9.3 (a)	10
4.0%Ru/Zr/SiO_2	325	1.6 (b)	8

(a) Hydrogen chemisorption performed at 100^oC
(b) Hydrogen chemisorption performed at 35^oC.

Table IX.5

Slurry Reactor Design Variables Considered in the Air Products Study (reference IX.21)

DEPENDENT VARIABLES	
Gas Hold-Up	Mass Transfer
Bubble Size	Liquid Dispersion
Solids	Heat Transfer

INDEPENDENT VARIABLES
Slurry Medium: Paraffin, water
Superficial Gas Velocity: 1.52 - 15.2 cm/sec
Superficial Slurry Velocity: 0 - 3.0 cm/sec
Solid: Silica, Iron Oxide
Solid Size: 1 - 5 µm, 45 - 53 µm, 90 - 106 µm
Solid Concentration: 0, 10, 20, 30 Wt.%
Distributor Hole Size: 0.9, 3.2, 12.8 mm
Heat Transfer Internals: None, Plain

Table IX.6

Rheinpreussen Simulation using Deckwer Correlations (from reference IX.1)

REGIME	CHURN TURBULENT		
CATALYST	Base Case	Cat. A	Cat. B
Inlet gas velocity, cm/sec	9.00	9.00	9.00
Gas holdup	0.385	0.512	0.526
Interfacial area, cm^2/cm^3	32.66	43.44	44.66
Temperature, ^oC	260.2	259.7	260.2
Rate Constants			
Preexponential factor (sec wt.% in slurry) x 10^5	1.12	90.3	115
Activation energy, kJ/mol	70	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65
Hydrogen conversion, %	80.4	34.9	49.8
Relative mass transfer resistance	0.106	0.021	0.035
Space-time yield, mol CH_2/hr	2937	1065	1022
Constants in Case Study			
Reactor length, ft (cm): 26.25 (800)			
Reactor diameter, in (cm): 59 (150)			
Contraction factor: -0.5			
Particle diameter, µm: 50			
Reactor pressure, psig (bar): 174 (12)			
Weight fraction catalyst in slurry: 0.20			
Specific heat transfer area, cm^2/cm^3: 0.10			

Table IX.7

Rheinpreussen Simulation using Air Products Correlations (from reference IX.1)

REGIME	CHURN TURBULENT			
CATALYST	Base Case*	Cat. A	Cat. B#	Cat. B with Shift
Inlet gas velocity, cm/sec	9.00	9.00	9.00	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm^2/cm^3	32.66	36.06	41.43	35.39
Temperature, ^oC	260.2	260.4	260.4	261.1
Rate Constants				
Preexponential factor (sec wt.% in slurry) x 10^5	1.12	90.3	115	115
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Relative mass transfer resistance	0.106	0.043	0.069	0.048
Space-time yield, mol CH_2/hr	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm): 26.25 (800)				
Reactor diameter, in (cm): 59 (150)				
Contraction factor: -0.5				
Particle diameter, µm: 50				
Reactor pressure, psig (bar): 174 (12)				
Weight fraction catalyst in slurry: 0.20				
Specific heat transfer area, cm^2/cm^3: 0.10				

*Operating conditions at Rheinpreussen
#Cold flow model gas holdup correlation

Table IX.8

Optimum gas holdup, gas velocity*, and space-time yield (STY) (K_L = 0.0205 cm/s; U = 2) (from reference IX.1)

CASE	K_o, sec^{-1} $wt\%^{-1}$	W, %	d_B, cm	α opt, vol %	V_G cm/sec	STY
1	1.4×10^{-3}	20	0.07	6.8	2.13	1.00
2	1.4×10^{-3}	60	0.07	11.2	12.75	2.72
3	6.1×10^{-3}	60	0.07	20.9	36.43	9.42
4	1.4×10^{-3}	20	0.30	13.1	5.29	0.87
5	1.4×10^{-3}	60	0.30	20.7	36.00	2.17

*Using Air Products cold flow gas holdup correlation

Table IX.9

Rheinpreussen simulation for staged reaction systems (from reference IX.1)

NUMBER OF STAGES	1	20	5	20
DISPERSION COEFF., cm^2/s	72.130	128.8	572.5	143.8
Gas Holdup	0.145	0.148	0.158	0.158
Interfacial area, cm^2/cm^3	4.148	12.717	4.514	4.527
Hydrogen Conv., %	66.1	85.1	69.2	69.2
Rel. Mass Transfer Resistance	0.556	0.310	0.542	0.541
Space-Time Yield, mol CH_2	2,417	3,128	2,529	2,530
Improvement Ratio	1.000	1.294	1.046	1.047

CONSTANTS IN CASE STUDY

Reactor Length, ft (cm): 26.25 (800)

Reactor Diameter, in (cm): 59 (150)

Contraction Factor: -0.5

Particle diameter, m: 50

Reactor Pressure, psig (bar): 174 (12)

Weight Fraction Catalyst in Slurry: 0.20

Specific Heat Transfer Area, cm^2/cm^3: 0.30

Inlet Gas Velocity, cm/sec: 9

Temperature, C: 260.0

Preexponential Factor (see wt% in slurry): 3.45×10^7

Activation Energy, kJ/mol: 94l7

Inlet Ratio, mol CO/mol H_2: 1.98

Usage Ratio, mol CO/mol H_2: 1.98

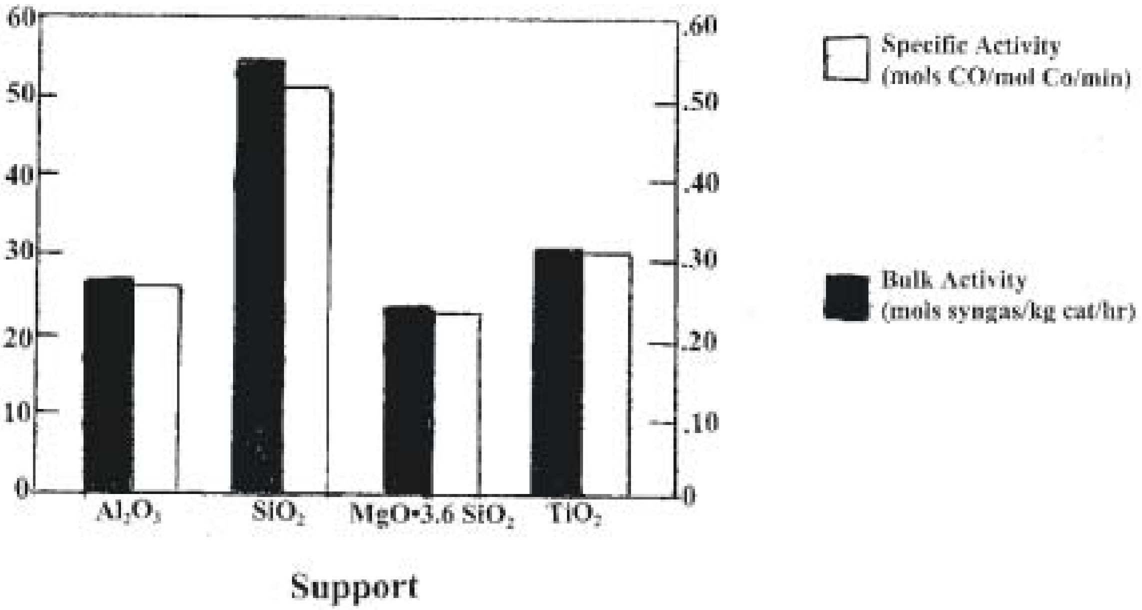


Figure IX.1. Activity of $CO_2(CO)_8$-based catalysts, fixed bed reactor (240°C, CO/H_2 = 1.0, GHSV = 1000 hr^{-1}, 300 psig).

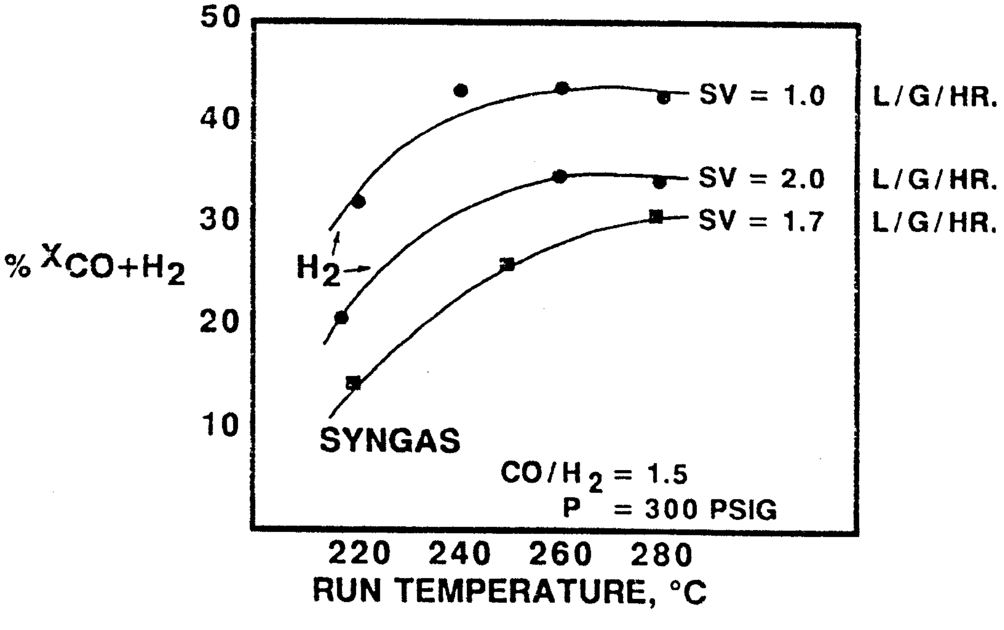


Figure IX.2a. Effect of syngas versus hydrogen activation on conversion.

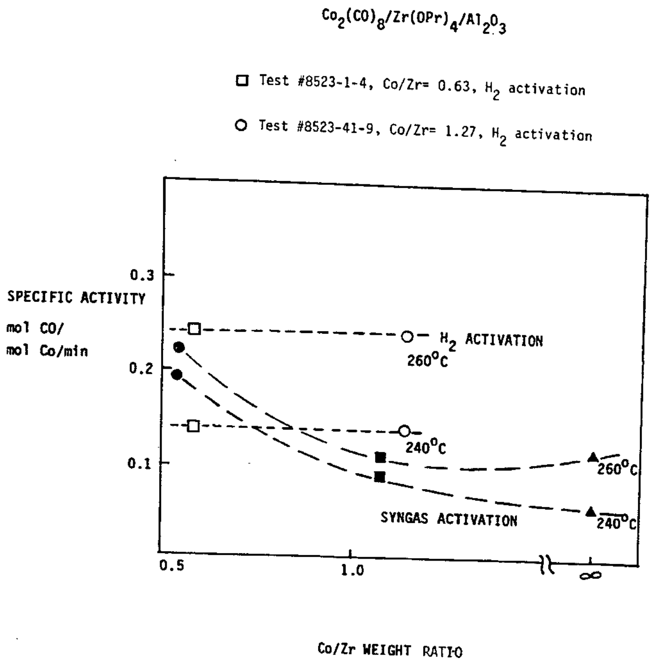


Figure IX. 2b. CO/Zr ratio effect on activity.

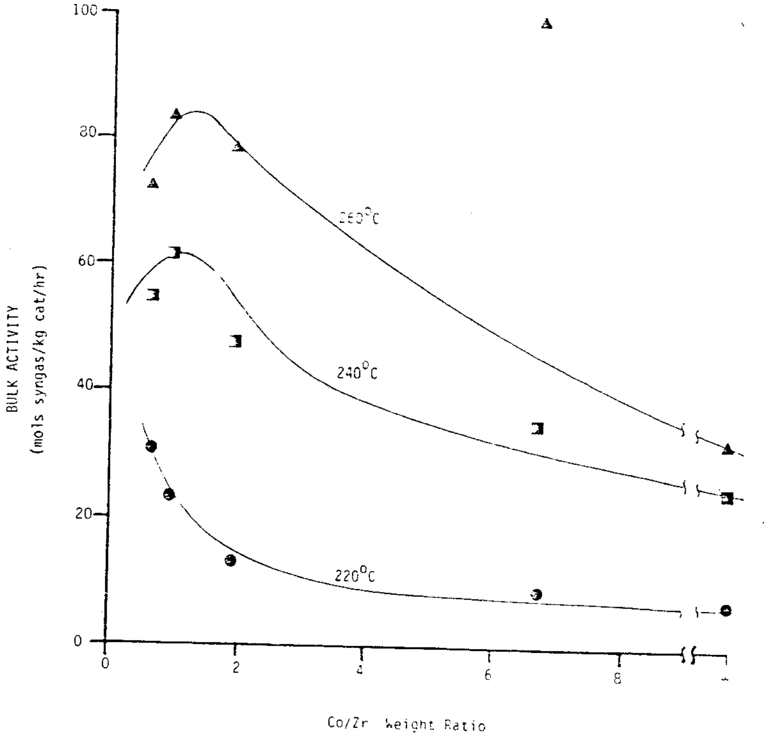


Figure IX.3. Effect of Co/Zr ratio on bulk activity (gas phase, CO/H_2 = 1, SV = 1000 hr^{-1}, 300 psig).

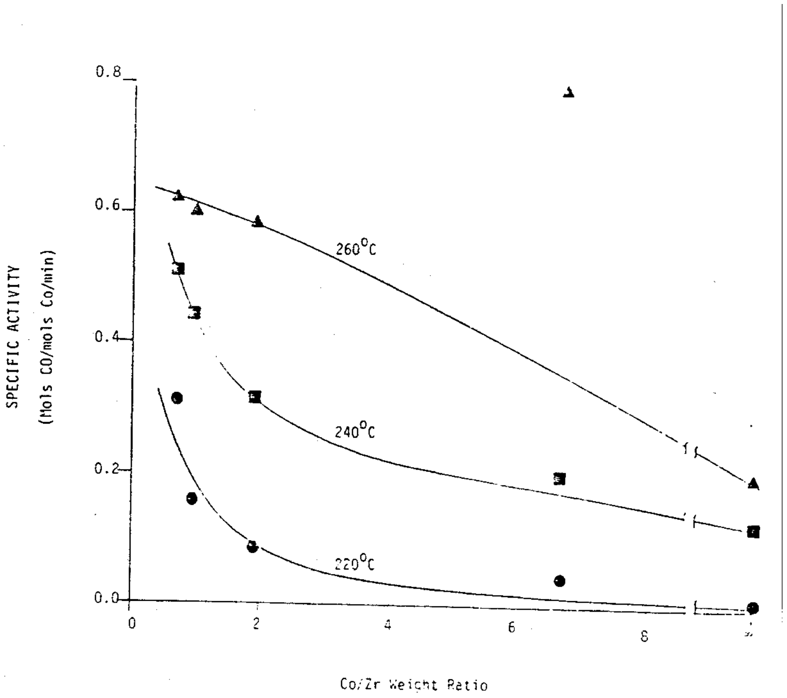


Figure IX.4. Effect of Co/Zr ratio on specific activity (gas phase, $CO/H_2 = 1$, SV = 1000 hr^{-1}, 300 psig).

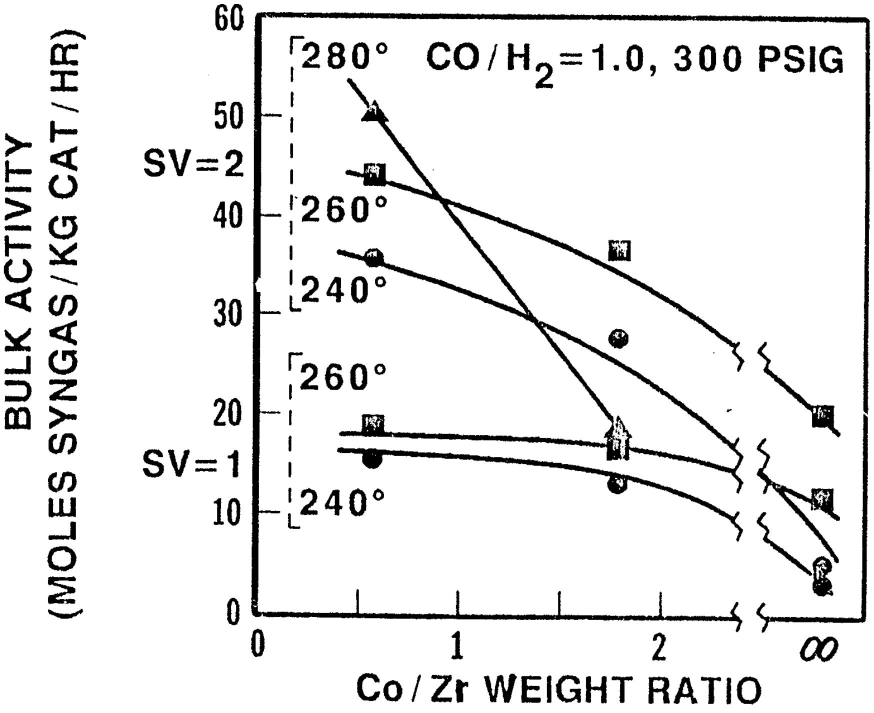


Figure IX.5. Effect of Co/Zr weight ratio on slurry-phase activity of Co/Zr/silica catalysts.

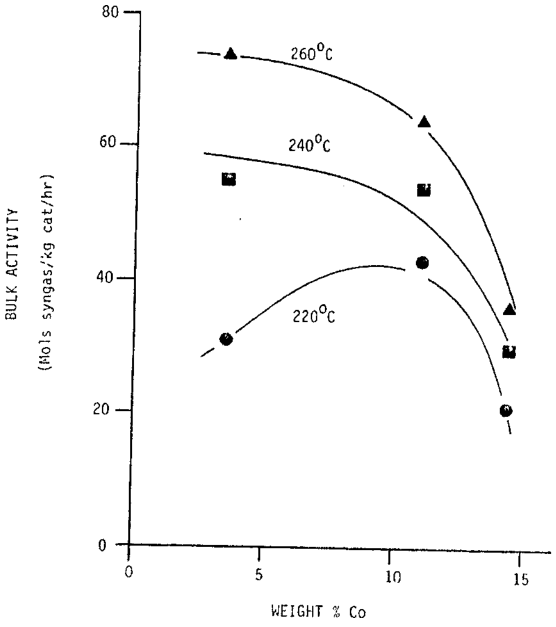


Figure IX.6. Effect of cobalt loading on bulk activity of $Co/Zr/SiO_2$ Catalyst (fixed bed reactor , $CO/H_2 = 1$, 1000 hr^{-1}, 300 psig).

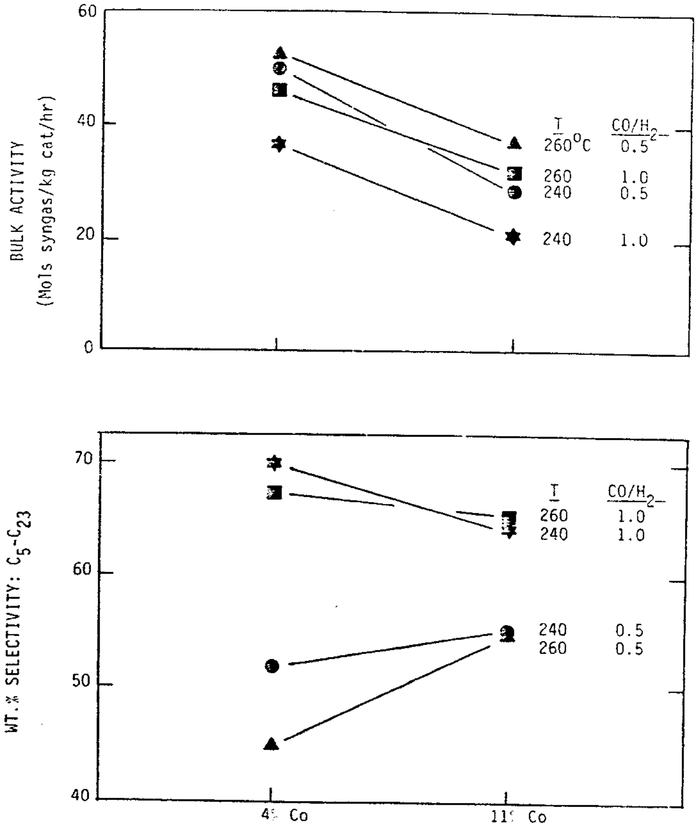


Figure IX.7. Effect of Co loading on $Co/Zr/SiO_2$ performance.

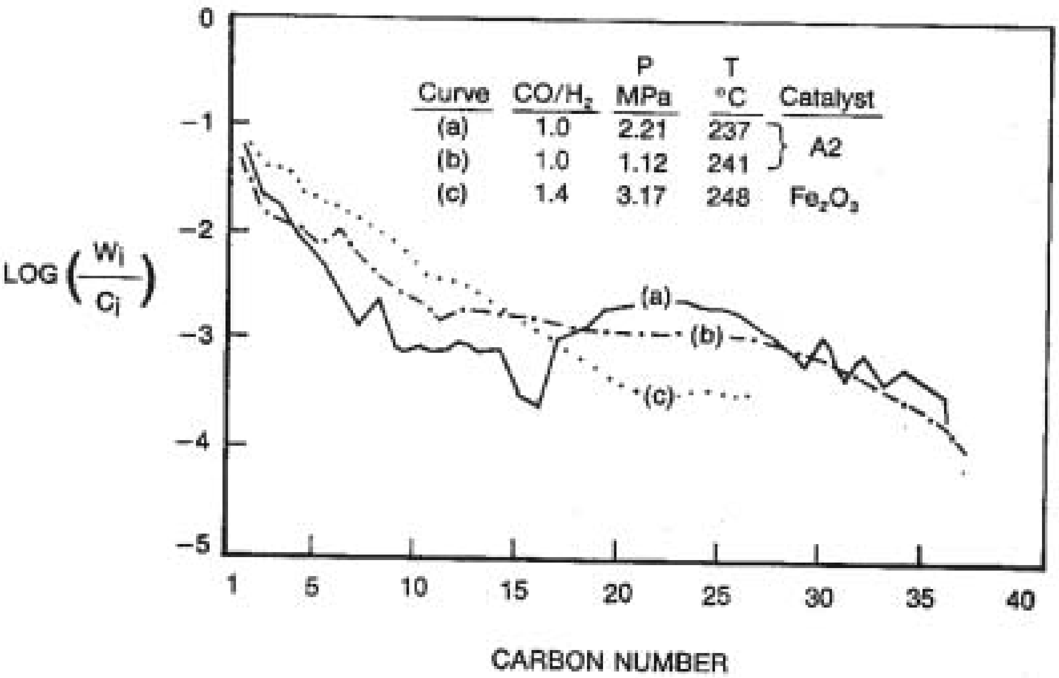


Figure IX.8. Hydrocarbon Schulz-Flory distribution of slurry catalyst A2.

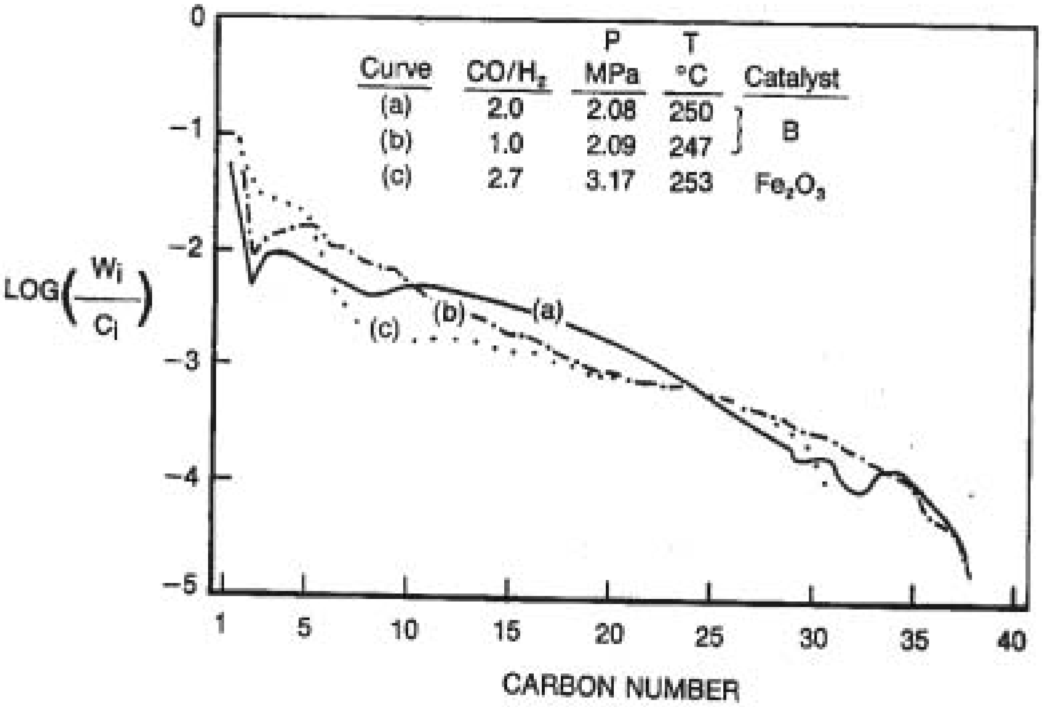


Figure IX.9. Hydrocarbon Schulz-Flory distribution of slurry catalyst B.

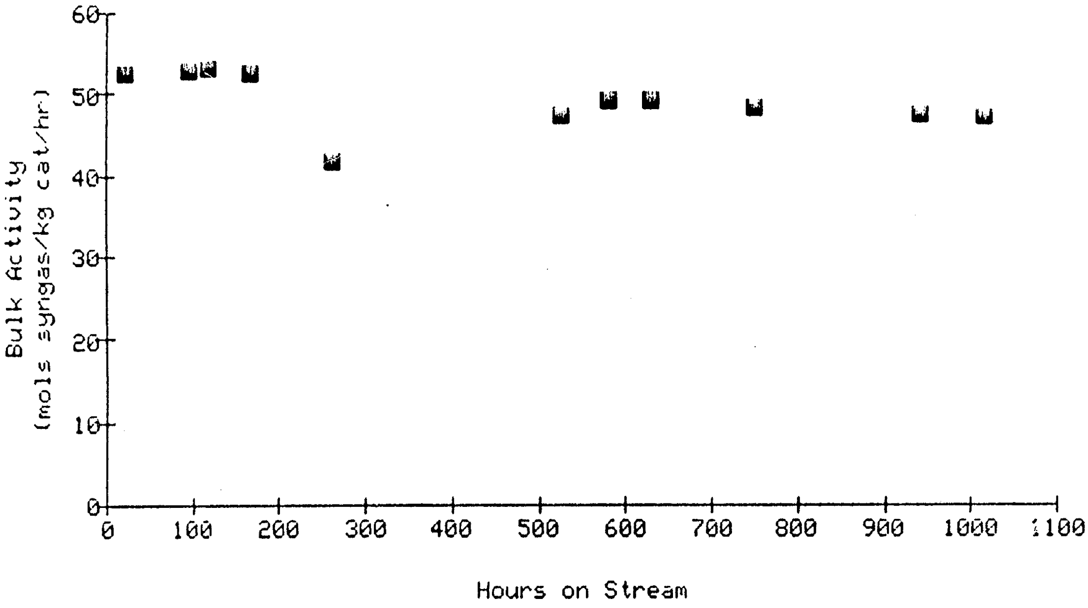


Figure IX.10. Bulk activity maintenance - extended slurry test 8862-1-31 Co/Zr/SiO$_2$, 240°C, CO/H$_2$ = 0.5, 1.8 L/g/hr, 300 psig.

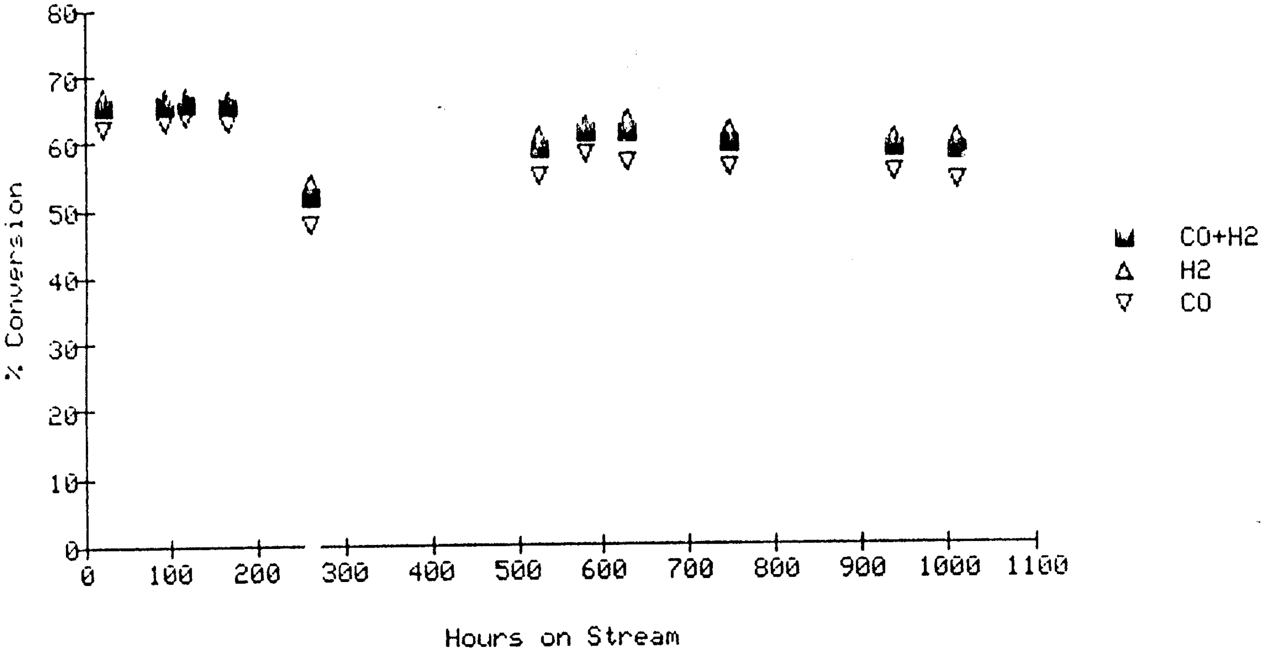


Figure IX.11. Conversion maintenance - extended slurry test 8862-1-31 Co/Zr/SiO$_2$, 240°C, CO/H$_2$ = 0.5, 1.8 L/g/hr, 300 psig.

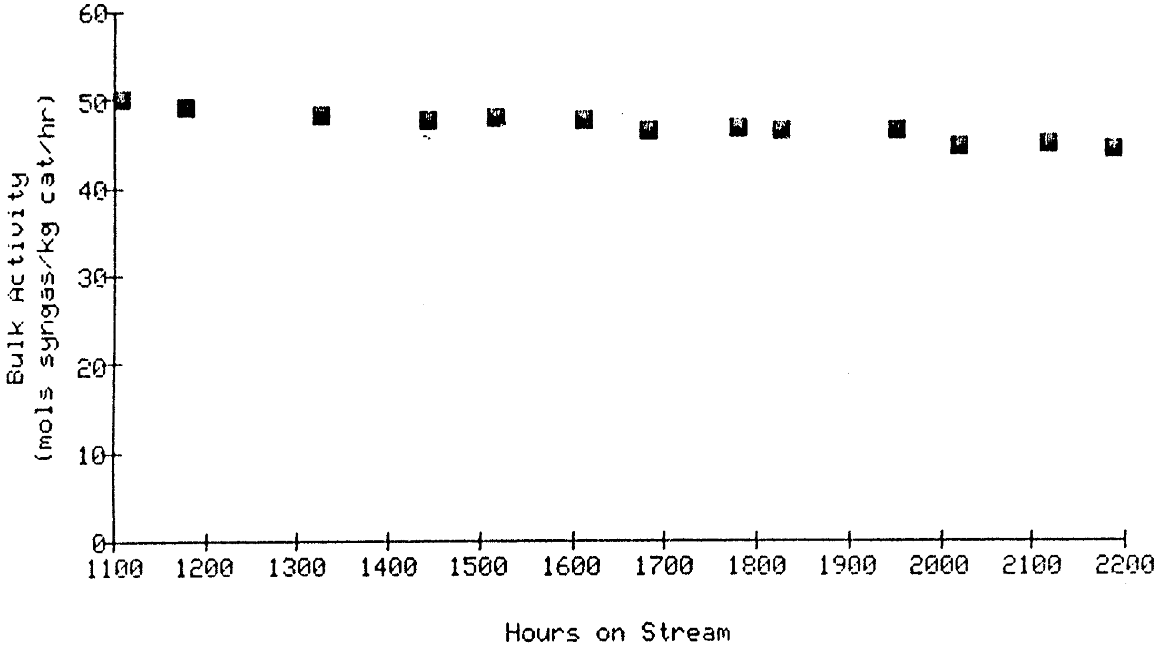


Figure IX.12. Bulk activity maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

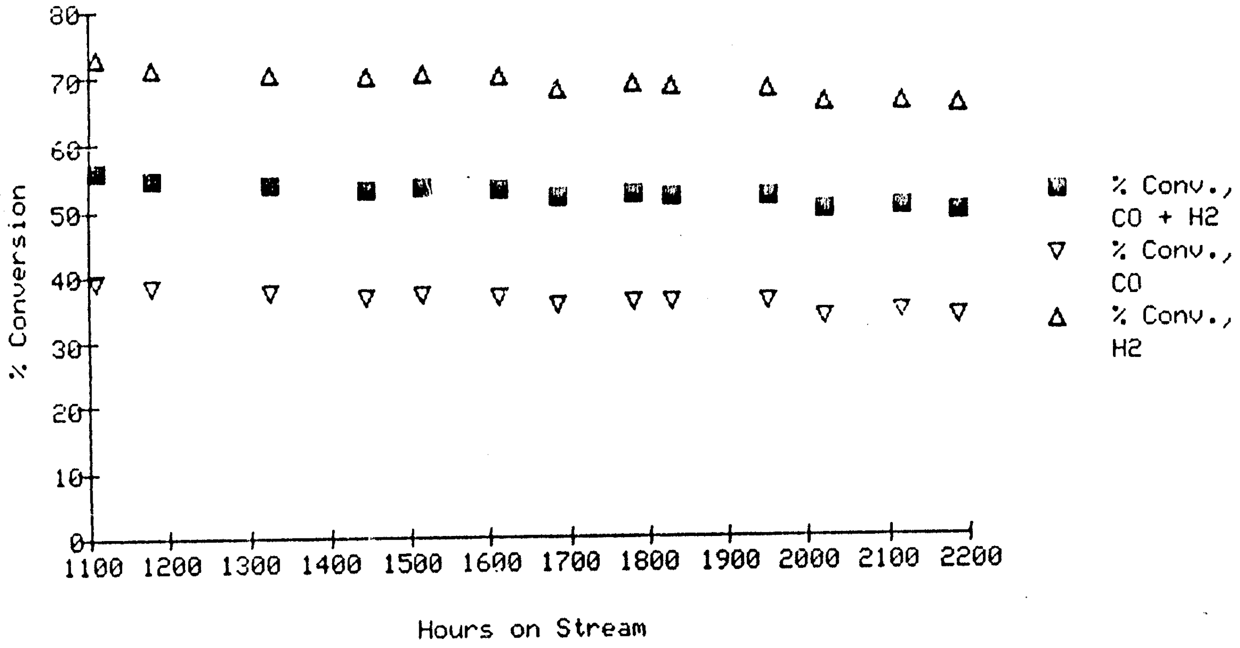


Figure IX.13. Conversion maintenance - extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

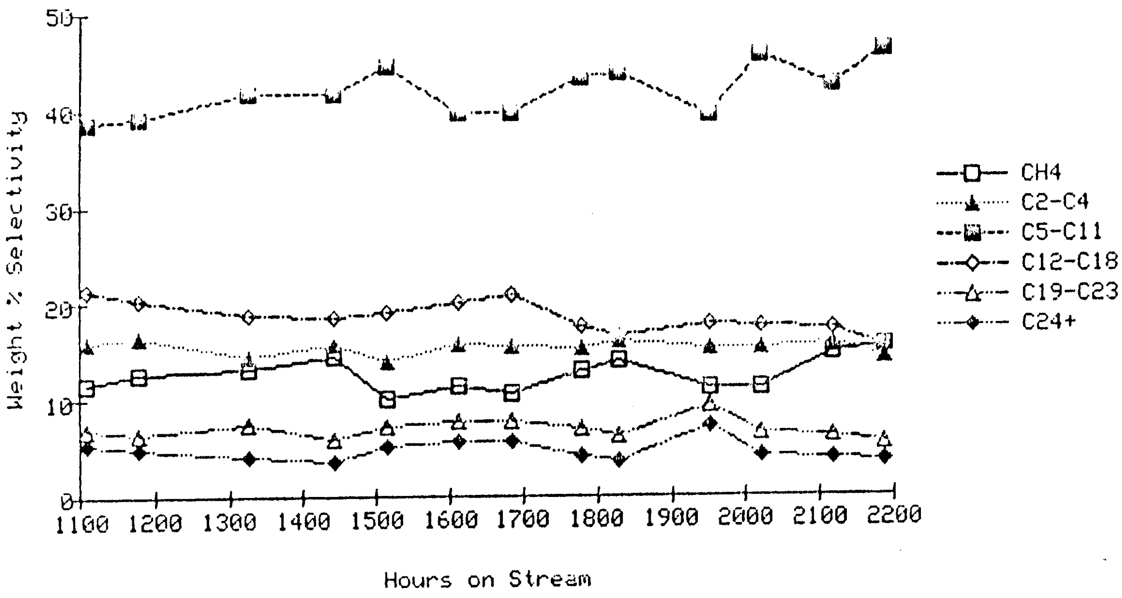


Figure IX.14. Hydrocarbon selectivity — extended slurry test 8862-1-31 (Co/Zr/SiO_2, 260°C, CO/H_2 = 1.0, 2.0 NL/g/hr, 300 psig).

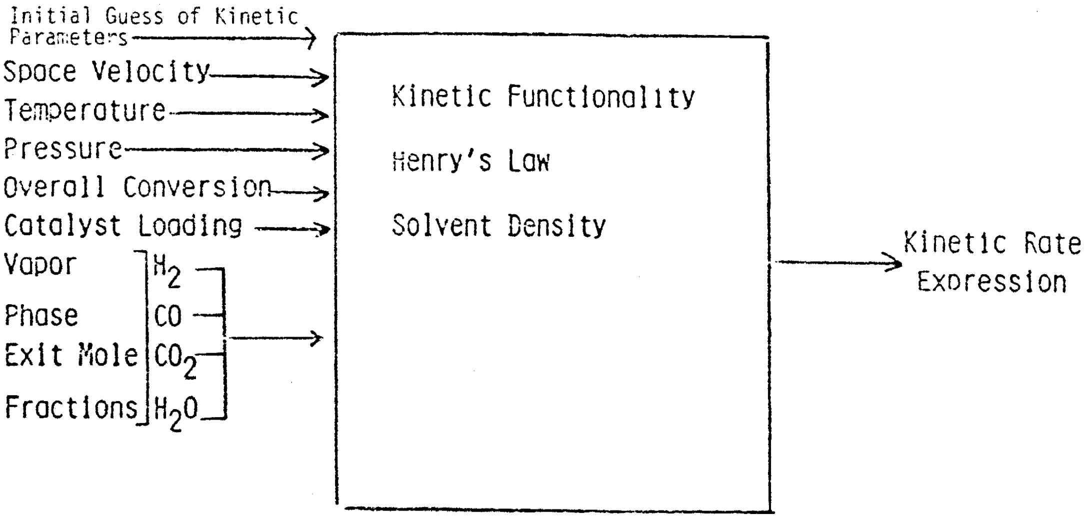
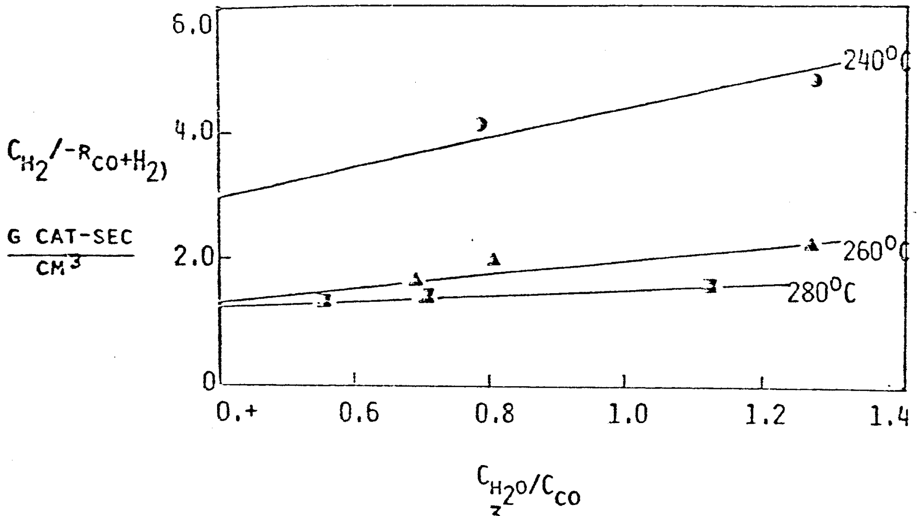


Figure IX.15. Kinetic data analysis program ($\rho = 0.758-0.555 \bullet (T_k-373)$ (ref. 12); $He_{H_2} = 34.162 \bullet \exp(739.485/T_k) \bullet 14.23$ psia/mol/kg oil (ref. 11); $He_{CO} = 44.583/T_k) \bullet \exp(433.391/T_k) \bullet 14.23$; $He_{CO_2} = 119.925 \bullet \exp(-438.926/T_k) \bullet 14.23$; $He_{H_2O} = 275.113 \bullet \exp(-1122.92/T_k) \bullet 14.23$.



	K, CM^3/G CAT.SEC.	K
240	0.328	0.466
260	0.709	0.439
280	0.775	0.302

Figure IX.16. Fitting $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ data.

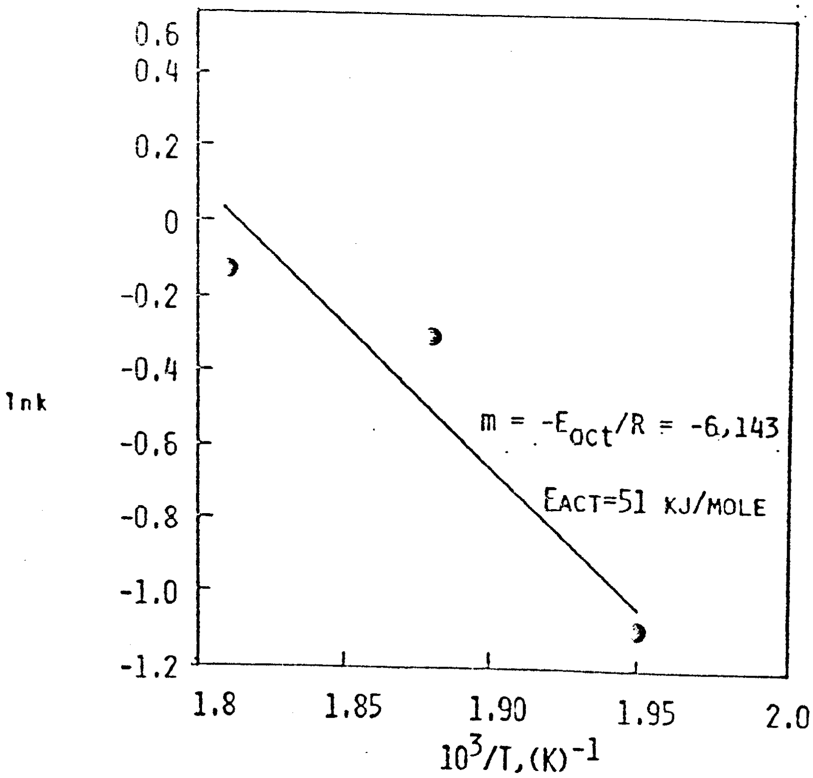


Figure IX.17. $Co_2(CO)_8/Zr(OP_R)_4/SiO_2$ activation energy.

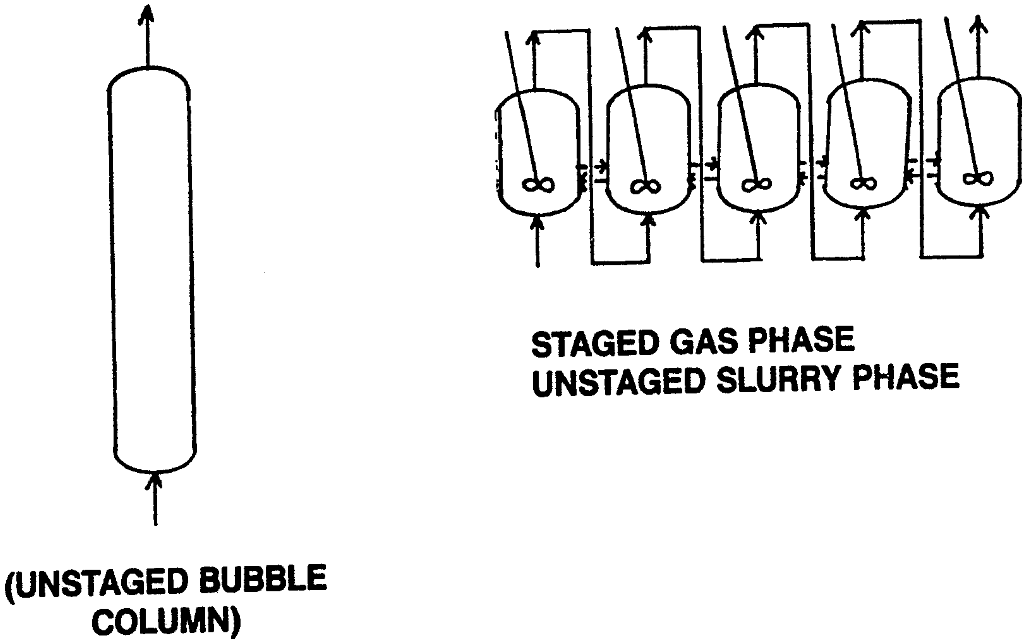


Figure IX.18. Staged reaction systems.

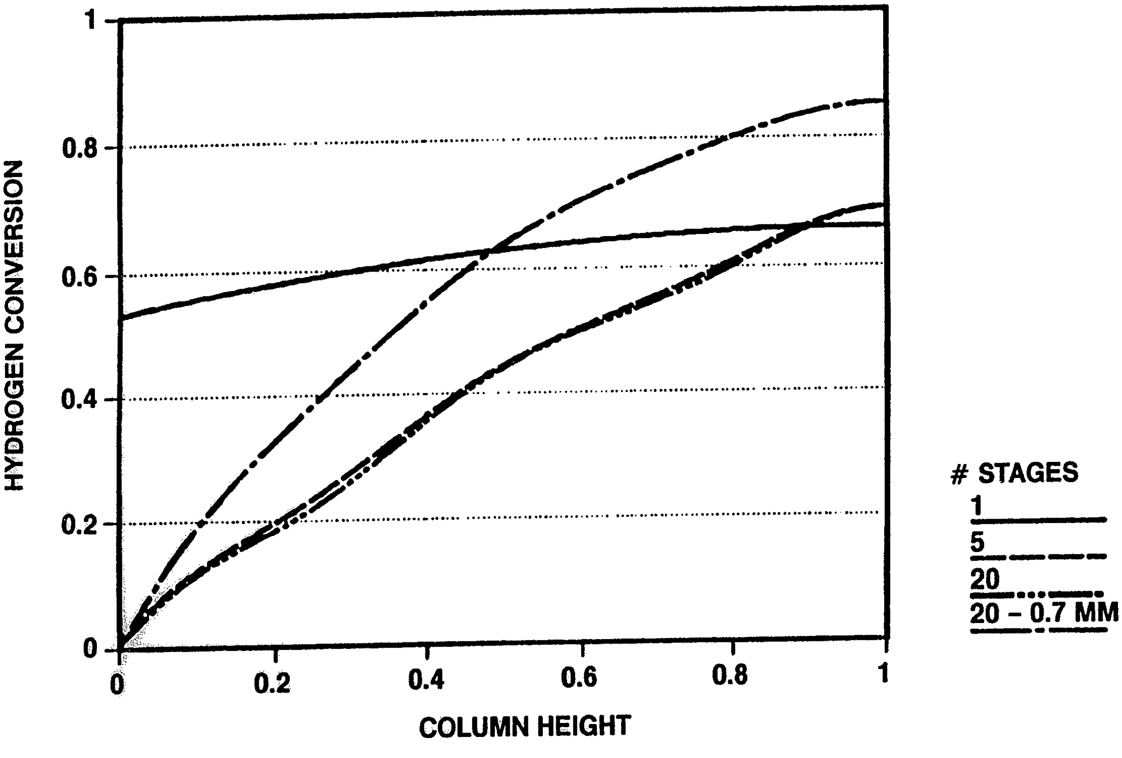


Figure IX.19. Hydrogen conversion vs. column height.

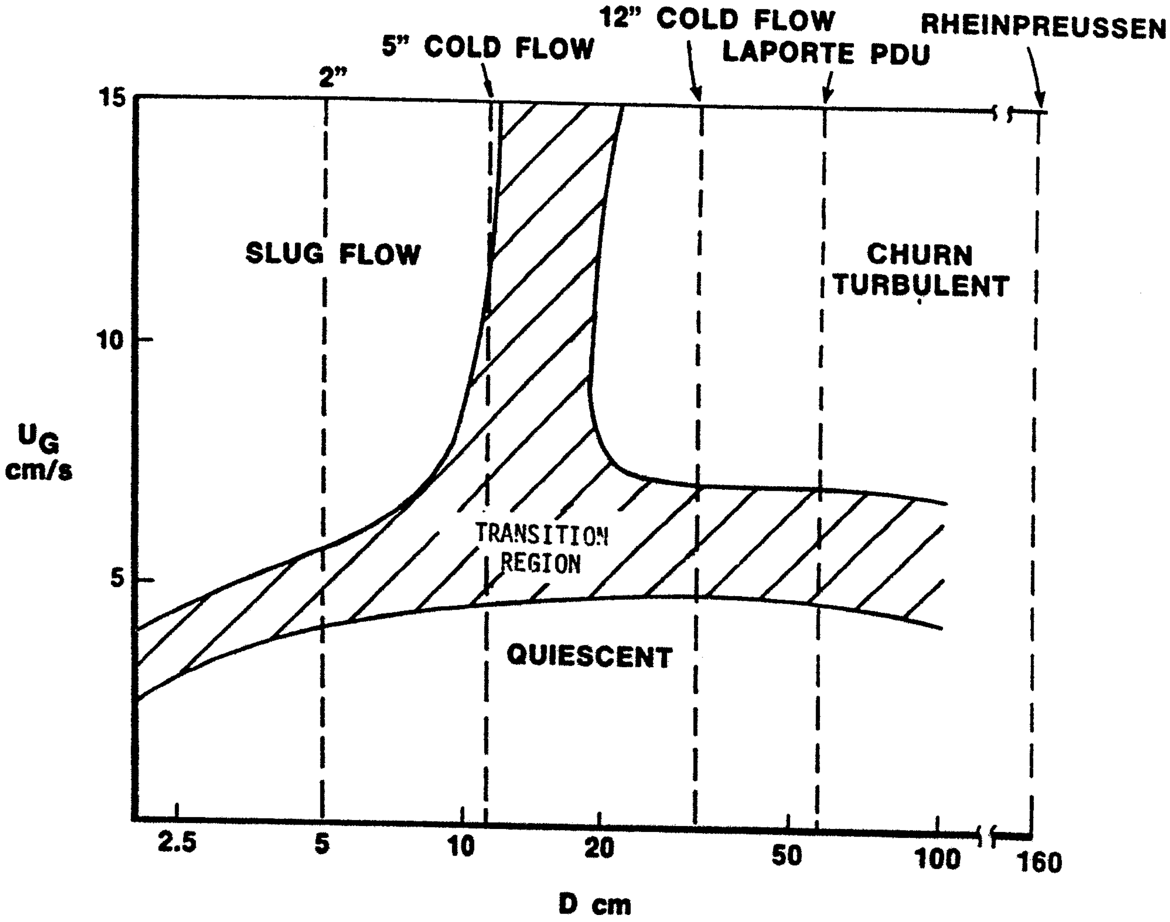


Figure IX.20. Bubble column flow regimes.

ATTACHMENT X

Review of Exxon Patents

Edwin N. Givens

and

Burtron H. Davis

ATTACHMENT X

Review of Exxon Patents

INTRODUCTION

It is quite apparent from searching the patent literature that Exxon has been actively involved in conducting research on conversion of synthesis gas to fuels and chemical products for many years. They have used CO as a chemical reactant for producing olefins and alcohols in addition to preparing liquid fuels. Since the mid 1970s the number of patents that have been assigned to Exxon and the types of examples contained in those patents reflect an increasing interest in converting synthesis gas to hydrocarbons. The earlier patents that were obtained during this period contain numerous examples of synthesis gas conversion at ambient pressures that gave very small CO conversions, typically less than 10%. More recently, the data reflect a more sophisticated evaluation of catalysts and the beginning of a string of patents that relate to improvements in equipment and operation. The latter are a result of the operation of a sizable pilot facility at their Baton Rouge Laboratory. These patents have addressed many of the finer points of reactor design.

The search was focused on synthesis gas conversion, i.e. the Fischer-Tropsch reaction, and limited to U. S. patents that were assigned to Exxon that were abstracted by Derwent through mid-1995. There are apparently numerous other patents that were issued to Exxon that relate to CO conversion which are not included, such as those related to conversion of CO to hydrocarbons or alcohols. Exxon's approach to developing a patent portfolio in this technology area is unlike most of their competitors, in that they have obtained an extensive number of composition of matter patents. Supplementing these patents are a large number of process related patents that apply to either methods for preparing these materials or the use of these compositions in the conversion of synthesis gas. In some of the composition of matter patents that are of interest for synthesis gas conversion, the claimed materials are used for hydrocarbon conversion without mention of their use as catalysts for the FT reaction. Based upon the addresses of the inventors in these various patents, it is clear that significant work on the FT reaction has been going on at Exxon's New Jersey and Baton Rouge laboratories. Although there is overlap in the type of work that was being done in these laboratories, it appears from the timing of the patents that the approaches that were being taken were quite independent. Those differences were apparent from the discussion in the patents regarding various elements of catalyst composition and the claims that are made regarding those compositions.

The Exxon patent portfolio includes a large number of patents on iron and iron-containing catalysts. The majority of these cases relate to compositions that have spinel structures that are isostructural with Fe_3O_4 but contain one or two additional metal atoms, with iron usually being the dominant metal. In these patents, the spinel structures are expressed interchangeably either as $M_xN_{3-x}O_4$ or as $M_{3-x}N_xO_4$, where M is almost exclusively Fe. For consistency, the first format is used exclusively throughout this discussion. Other iron-related catalysts are also covered including catalysts in which the iron, as the oxide, is used as a substrate, and others in which the iron is deposited on other substrates.

There is extensive coverage for catalysts in which titania and titania containing materials are used as metal supports. These include combinations of titania with vanadium, tantalum and niobium oxides (Group Vb) which are used either as intimate mixtures or as coatings on the surface of titania. All of these supports apparently give rise to unique metal-support interactions that had not hitherto been reported. Other coverage was obtained for titanias that are coated with silica. Some of these patents specify titanias having rutile as the dominant crystalline phase which is favored at high temperatures. One case claims an anatase based catalyst that was stabilized though addition of silicon, zirconium and tantalum. In many of these cases, the catalyst is formed by impregnating the oxides with metals from Group VIII, of which cobalt or ruthenium are the most common. In other cases, addition of rhenium, thorium, cerium, copper, hafnium, zirconium, and uranium is claimed. Although many of the catalysts that are covered in these patents fall into one of the above categories, they have also obtained coverage in several related areas. Catalysts comprising ruthenium or combinations of several Group VIII metals on manganese oxide are covered as are cobalt-manganese spinels. Coverage of catalysts comprising Group VIII metals supported on various oxide supports was obtained which specifically apply to FT type processes.

In almost all of these cases the use of an alkali promoter is also covered, either in the main claim or a dependent claim. Almost without exception, potassium is specified as the alkali metal of choice, although in a few rubidium has been specifically mentioned. Most of the patents specify that the catalysts can be used in either a fixed-bed or a slurry type process, although in some cases they can be applied to both. Generally, powder catalysts are specified for slurry operations while sintered spinel type catalysts apply to fixed-bed type operations. There are, however, cases which claim that the catalysts are useful for either slurry or fixed-bed type operations.

The third area of significant coverage includes various process improvement patents that relate to process equipment or operation, most of which have been obtained in recent years. These include 2-stage processes, modified feeds, modified reactor designs, methods of reactor operation and methods of catalyst pretreatment. Many of these patents contain data that were taken from highly sophisticated pilot plant operations, some of which were quite large in size.

Iron

A number of patents were issued to Exxon related to the use of iron in FT synthesis. Most apply to catalysts in which the iron is in combination with other metals. However, two patents were issued that apply to the use of iron alone. These were catalysts that were prepared using a laser technique in which volatile iron compounds were thermally decomposed to form iron carbides having particle diameters of less than 0.1 μm. Most of the iron containing catalysts that are covered in these patents relate to spinels in which Fe is combined with different metals in the spinel structure, including cobalt, manganese, zinc, and titanium. Various promoters are also added, including cerium, copper and potassium. Two patents covered catalysts in which thallium was deposited on an iron support, while others covered catalysts prepared by depositing Fe salts onto supports. One covers an Fe/TiO_2 catalyst that was prepared by converting an impregnated Fe salt to the carbided form. Another covered catalyst prepared by decomposing Fe and Co carbonyl compounds in the presence of CO which deposited them onto finely divided supports which were then reduced in H_2.

Particulate Iron Catalysts

A patent issued to Rice et al. (X.99) claims compositions comprising finely divided particles of iron and carbon in absence of Si produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron reactants, and pressure sufficient to give non-pyrophoric particles having diameters from 1-100 nm. The iron reactants are selected from iron carbonyls, iron acetylacetonate and ferrocene. A related patent issued to Rice et al. (X.100) claims the same compositions which are subsequently impregnated with $\geq$2% of a promoter selected from a group of salts and oxides of alkali and alkaline earth metals. These patents specify these compositions can be used in either slurry or fixed bed FT reactions. Data were presented in the examples for a fixed-bed catalyst in which the claimed composition was deposited on a refractory MgO support. Laser generated Fe carbide, either with or without K, was found to be considerably more active than Fe carbides generated from either Fe_3O_4 or from mixtures of $Fe(CO)_5$ and C_2H_4 in the presence of $SiH_2(CH_3)_2$ (see Table X.1). The Fe_3O_4 and silane generated carbides have lower CO conversions and higher methane yields while the catalysts of these inventions produce more olefins in the C_2-C_4 fraction.

A catalyst was illustrated which was prepared by reacting Fe_3O_4 until all of the iron was converted to a carbide phase which was predominantly Fe_5C_2 and Fe_3C. The iron carbide phase was dispersed in a matrix of 40 to 70 wt.% of amorphous carbon. The comparison of the activated Fe_3O_4 catalyst and the laser generated catalyst is for activity for CO conversion on a volume of gas/volume of catalyst basis. The laser generated sample contained 5-15 wt.% of amorphous carbon phase. If we take into account (1) the difference in density of amorphous carbon and iron carbide (factor of 2) and (2) the difference in the amount of amorphous carbon (factor of about 5-8), we calculate that the material produced by the laser technique will contain 10 to 20 times as much iron as the material prepared from Fe_3O_4. Thus, while the material prepared using the laser technique is about two times as active as the material derived from Fe_3O_4 when the comparison is based on volume of catalyst, it is estimated by us to be 5 to 10 times less active on the basis of the iron content. Furthermore, it has been shown that, under reaction conditions utilized for slurry phase synthesis, a significant fraction of the iron carbide is gradually converted to Fe_3O_4 (X.101) during synthesis. Thus, the relative advantage of the catalyst generated by the laser technique depends upon how it is compared to the precipitated catalyst.

Spinels Containing Fe

The first patents assigned to Exxon that apply to the use of spinel or spinel-derived compositions for converting synthesis gas appeared in 1985. These materials were generally prepared by one of two methods and they had distinctly different morphological features. In one case, high surface area materials were prepared by co-precipitation of salts coupled with moderate heating. These materials have been used directly as slurry catalysts. The second method of preparation involves sintering of metal/metal oxide mixtures at much higher temperatures to give low-surface-area, fused materials, which after grinding and sizing are used directly in fixed bed applications. Hydrogen reduction of either of these products at temperatures of 400^{o}C leads to alloys, which when treated with CO, give high surface area carbides containing considerable carbon inclusion. The reduced and carbided spinels are then used as catalysts in either slurry or fixed-bed applications.

A number of different combination of metal spinels have been patented in this series, all of which, except one, contain iron. In all the Fe cases, the claims cover spinel compositions that allow the use of high concentrations of Fe. From an economical standpoint, this is favorable since the cost of co-metals is generally greater than for Fe. The different Fe-containing combinations that are covered, most of which are promoted with potassium, are:

- Fe-Co, either with or without added Cu,
- Fe-Mn containing Cu,
- Fe-Zn containing Ce or Cu,
- Fe-Zn-Ti and/or Mn with Ce and
- Co-Mn with Cu.

The only non-Fe containing spinel that was covered was a Co-Mn spinel that is promoted with Cu. This catalyst is discussed with the manganese supported catalysts.

Fe-Co Spinels. Both high and low surface area spinels are covered. High surface area spinel compositions and reduced and carbided iron-cobalt alloy compositions derived from the spinels that are isostructural with Fe_3C and chi-Fe_5C_2 are covered in a patent issued to Soled and Fiato (X.102). Because of their fine particle size, the preferred use of these materials is in a slurry process which is covered in a patent issued to Soled and Fiato (X.103). High surface area copper promoted Fe-Co spinel compositions are covered in a patent issued to Soled and Fiato (X.104) while their use as a catalyst in a slurry process is covered in Soled and Fiato (X.105). Low-surface area Fe-Co spinel compositions are claimed by Fiato et al. (X.106) and their use as catalysts in a fixed-bed process is claimed by Fiato et al. (X.107). The use of the carbided and reduced form of these low-surface area Fe-Co spinels in a slurry phase process is claimed by Fiato and Soled (X.108). No patents were found that contain claims related to low-surface area Cu-promoted Fe-Co spinels.

Fe-Mn Spinels. High surface area K and Cu promoted Fe-Mn spinels are covered in a patent issued to Fiato and Soled (X.109). The use of this spinel as catalyst in a slurry process is covered in Fiato and Soled (X.110) and in a fixed-bed process in Iglesia et al. (X.111). The corresponding low surface area spinels derived from sintering mixed oxides was covered in a prior patent issued to McGrath and Rubin (X.112) and assigned to Kellogg. An alternative method for forming Fe-Mn alloys directly at low temperature without going through the spinel is covered by Soled et al. (X.113).

Fe-Zn Spinels. Two patents comprising compositions of Fe and Zn using different promoters were issued. In one patent compositions comprising sintered combinations of metal oxides of Fe and Zn promoted with Ce and K are covered in Gates and Fiato (X.114). In the other, compositions containing Fe and Zn promoted with Cu and K are covered in Soled et al. (X.115).

Fe-Zn Spinels with Ti and/or Mn. Compositions comprising sintered combinations of metal oxides of Fe, Zn, Ti, and/or Mn promoted with K and Ce are claimed in Fiato et al. (X.116).

Fe-Co Spinels

Seven patents assigned to Exxon relate to Fe-Co spinels, five of which were issued either from applications filed on December 14, 1983, or were continuations-in-part of applications filed on that day. Cross reference was also made to applications which apparently never issued as patents. The series of seven patents that did issue fit into three different groups with at least two patents being in each group. One of the groups relates to Cu promoted Fe-Co spinels while the other two groups relate to Fe-Co spinels that are prepared by two different methods. In one group the spinels are prepared by sintering mixtures of metal-metal oxides while in the other, spinels are prepared by precipitating metal oxides from the respective metal salt solutions. In each of these three groups, two of the patent specifications are identical differing only in their claims. In the one group that includes a third patent, the specification differs only slightly from the other two. For each of the three groups, one patent is a composition of matter case for a specific Fe-Co containing spinel and the other(s) claims either a fixed-bed or slurry process that employees the claimed catalyst composition.

The empirical formula of the spinels claimed in these cases can be written as $Fe_xCo_{3-x}O_4$ where compositions having x-values $\geq$2.4 or 2.7 are claimed. Prior art existed for structures having x values of 2, i.e. Fe_2CoO_4 (X.117). Among the various spinel compositions that were patented, there appears to be a pattern of obtaining coverage for both slurry and fixed-bed type FT processes. In the case of the Fe-Co spinels, specific claims are made to fixed-bed processes using catalysts derived from spinels prepared by sintering metal-metal oxide mixtures. These are classified as having low surface areas (less than 5 m^2/g). For slurry processes, patents were issued that claim use of catalysts derived from both low surface area spinels as well as those prepared by precipitating metal oxides from the respective metal salt solutions. This latter group is classified as high surface area spinels having surface areas greater than 5 m^2/g. In these Fe-Co spinel cases, patents were not found that claim the use of high surface area spinels in a fixed-bed process, although such claims were obtained for Fe-Mn spinels, which are discussed below.

High surface area spinel compositions are covered in a patent issued to Soled and Fiato (X.4) that claims Group 1A or IIA promoted high surface area spinels having compositions $Fe_xCo_{3-x}O_4$ with x-values $\geq$2.4 and BET surface areas >5 m^2/g. A second composition in this same patent, given in claim 20, comprises reduced and carbided iron-cobalt alloy that is isostructural with Fe_3C and has a BET surface area >5 m^2/g. A third independent claim covers compositions that are isostructural with chi-Fe_5C_2 having surface areas >5 m^2/g that are produced by carbiding iron-cobalt alloy which is isostructural with alpha Fe and has a BET surface area >5 m^2/g, which is produced by reducing the high surface area spinel composition. Therefore, compositions are claimed that include the spinel, the reduced alloy and the resulting carbided alloy. The specification is even broader in that it anticipates the application of the spinel, the alloy and the reduced-carbided spinel in either a fixed-bed or slurry-type process. The corresponding process related patent issued to Soled and Fiato (X.5) claims a slurry process that uses the catalyst that is claimed by Soled and Fiato (X.4). The two specifications are identical except for the claims. Although there is a slight difference in the spinel compositions that are claimed in these two cases, in that Soled and Fiato (X.4) claim spinels having Fe/Co ratios $\geq$4/1 while Soled and Fiato (X.5) claims Fe/Co ratios $\geq$7/1, this would not likely have any real impact on the application of the invention.

Low surface area Fe-Co spinel compositions are covered in a patent issued to Fiato et al. (X.8) that claims hydrocarbon synthesis catalyst compositions comprising an unsupported, Group Ia or IIa metal salt promoted low-surface area iron-cobalt spinel, an initial empirical formula $Fe_xCo_{3-x}O_4$, where x is $\geq$2.625, a powder X-ray diffraction pattern isostructural with Fe_3O_4 and having an initial BET surface area <5 m^2/g. Various dependent claims are included such as the use of diluents like silicas, aluminas, titanias, oxides of La, Ce, Cr, and Mn and mixtures including zeolites, glasses, etc. K_2CO_3 is claimed as a promoter and potassium promoted compositions are claimed that are substantially carbided by contact with CO/H_2 at elevated temperatures. Two process patents were issued that are related to use of low-surface area spinel compositions in synthesis gas conversion reactions. One patent, issued to Fiato et al. (X.9), claims a process for synthesizing hydrocarbons containing C_2-C_6 olefins by contacting a fixed-bed of catalyst, having the initial spinel composition specified in Fiato et al. (X.8), with synthesis gas. The specifications of Fiato et al. (X.8) and Fiato et al. (X.9) are identical, except for different claims. The second process patent issued to Fiato and Soled (X.10) claims a slurry process utilizing the carbided and reduced unsupported spinel of Fiato et al. (X.8), which reflects the need to *ex situ* pretreat the spinel before placing it in the slurry reactor.

Catalyst preparation

The following method was used to illustrate the preparation of several of the high surface area spinels. A solution containing Fe and Co nitrate salts and an ammonium α-hydroxy carboxylic (glycolic) acid was evaporated and the recovered solid was heated at 350°C for 2 hours and then impregnated with K_2CO_3 and dried. The material, prior to impregnation with potassium, had a very small particle size, an x-ray diffraction pattern isostructural with Fe_3O_4, and surface area >100 m^2/g. The specification refers to prior art for the preparing of Fe_2CoO_4[19] that involved evaporating aqueous solutions of metal glycolates, lactates, and tartarates to dryness. The prior art apparently limited claims to Fe/Co ratios > 4.

The invention was illustrated for various low-surface area spinels prepared by sintering mixtures of metal oxides and metals in combinations having the stoichiometric composition necessary to provide the correct empirical formula. Sintering is done first in an inert or vacuum atmosphere at temperatures preferably from about 800 to 900°C for about 8 to 24 hours. The material is then exposed to air and heated an additional 24 hours until the x-ray diffraction pattern of the material is isostructural with Fe_3O_4. Sintered pellets are crushed, sieved and then impregnated with aqueous potassium carbonate to a 1% K loading providing a material having a surface area of 0.25-0.30 m^2/g.

Reduced and carbided slurry catalysts are prepared starting with both high and low-surface area spinels. The preparation starting with low-surface area spinel is described in Fiato and Soled (X.10) and the preparation from high-surface area spinel is described in Soled and Fiato (X.4). In both cases, the respective spinel powders were reduced at 400^oC in H_2 for 4 hours to produce an alloy, which was passivated with dilute oxygen. These materials had surface areas of 3 and 8 m^2/g and x-ray diffraction patterns isostructural with alpha iron. The active catalyst was produced by carbiding the alloys in dilute synthesis gas and passivating with dilute oxygen to give products having x-ray diffraction patterns isostructural with chi Fe_5C_2 and BET nitrogen surface areas of 118 and 173 m^2/g. The resulting catalysts contained 60-70% carbon and had the composition $Fe_{2.85}Co_{0.15}O_4$/1 wt.% K.

The form of the active catalyst generated by these two different preparative methods was not differentiated from each other. Both, after reducing and carbiding, give materials that are isostructural with chi-Fe_5C_2 or Fe_3C, apparently contain sizable amounts of carbon, and have surface areas >100 m^2/g.

Slurry Catalysts. A number of examples were provided in the five cases which illustrate the use of catalysts derived from spinels for converting synthesis gas. Catalysts to be used in slurry reactors were pretreated in various ways before being placed in the slurry reactor and exposing them to synthesis gas at reaction condition. The methods of pretreatment included:

- Adding the spinel to the slurry reactor and reducing in H_2 before exposure to synthesis gas;
- Reducing and carbiding the spinel *ex situ* before introducing into the reactor;

! Reducing the spinel in H_2 to form the alloy before introducing into the reactor.

Conversion and product distribution data were provided for each of the respective catalysts and compared with data obtained on a high surface area Fe_3O_4/1%K catalyst that was prepared in the same manner as the high surface area spinel.

There was a big difference in the activities of the *in situ* treated spinel slurry catalysts. The high surface area Fe-Co spinel oxide that was reduced in situ with flowing H_2 (1 atm) for 1 hour at 200°C gave 60% CO conversion, whereas both the high surface area Fe spinel and the low-surface area Fe-Co spinel that were pretreated in the same way were inoperable. They gave CO conversions of only 8 and <4%, respectively (see Table X.2). *Ex situ* treatment had little effect on CO conversion of the high surface area spinel derived catalyst which gave essentially the same CO conversion as the *in situ* treated spinel, namely 64 and 60%, respectively. By contrast, *ex situ* treatment of both the low-surface area Fe-Co spinel and Fe spinel catalysts improved their activity, giving 42 and 65% CO conversion, respectively. Apparently insufficient carbided catalyst was formed in the *in situ* pretreatment of the low-surface area spinel, whereas the *ex situ* treatment was sufficiently severe to convert the low-surface area spinel to the carbided form. In the comparisons that were provided, the Fe-Co spinels produced more C_5+ hydrocarbons and less C_2-C_4 olefins than the Fe spinel catalysts. Although data with a 2/1 H_2/CO synthesis gas mixture in Table X.2 on *ex situ* treated catalysts indicate a difference between the CO conversion of the reduced-carbided low- and high-surface-area Fe-Co spinel derived catalysts, i.e. 42 and 64% conversion, respectively, other data with a 1/1 H_2/CO synthesis gas mixture showed no difference in activity (see Table X.3). The latter data indicate that the *ex situ* reduced and carbided high- and low-surface-area Fe-Co spinel derived catalysts, as well as the activity of the *ex situ* reduced and carbided high-surface-area Fe spinel catalysts, have essentially the same activity. The activity of the *ex situ* low-surface-area Fe-Co spinel and the lack of activity for the *in situ* treated low-surface-area spinel appears to be one reason why Fiato and Soled (X.10) claim a slurry process utilizing only the carbided and reduced low-surface area spinel.

Alloys active for CO conversion are formed by reducing the high-surface-area Fe-Co spinel *ex situ* with H_2 at 350°C for 12 hrs followed by further reduction with H_2 at 400°C for 24 hrs. CO conversions with either 1/1 and 2/1 H_2/CO synthesis gas mixtures were higher than the correspondingly reduced Fe-only spinel, as shown in Table X.4. Although the correspondingly reduced high surface area Fe-only spinel was not quite as active as the Fe-Co alloy, its selectivity for CO_2 production was much smaller. The hydrocarbon selectivity of the Fe-Co spinel was greater and its methane and C_5+ selectivities were less than for the Fe-only spinel. In this series of patents, no claims were made nor information provided on alloys produced from reduced low-surface area Fe-Co spinels.

Fixed-Bed Catalysts. Only catalysts prepared from low surface area Fe-Co spinels were used as fixed-bed catalysts. Although high-surface area spinel derived catalysts were anticipated for use in fixed-bed reactors, no claims nor examples were found that relate to such usage. An example was provided in which low-surface area $Fe_{2.85}Co_{0.15}O_4$ spinel was reduced at 500°C with a mixture of 90% H_2 in N_2 at 100 psig for 5-7 hrs before exposing to synthesis gas. It was more active for CO conversion than a comparably prepared and treated Fe_3O_4/1%K spinel, as shown in Table X.5. At a run temperature that was 35°C lower than the control sample, the Fe-Co conversion of

CO was higher than for the Fe-only catalyst at the same space velocity. Both CO_2, hydrocarbon yields and olefin content in the C_2-C_4 fraction were higher for the Fe-Co catalyst while the C_5+ and C_6+ products were greater for the control.

In all the Fe-Co spinel patents, there was only one example of a spinel having an Fe-Co concentration that did not fall within the claimed limits. That spinel, having an x value of 2.20, falls below the 2.4 value specified in the claims. The CO conversions and hydrocarbon yields were essentially the same for this catalyst as for those that fell within the claimed limits, i.e. x values either $\geq$2.4 or >2.625, both of which were used in different patents (see Table X.6). Regardless, all of these catalysts had Fe/Co ratios that were greater than 2 (x value 2.0), which was consistent with the prior art value discussed above.

In almost all of the patents regarding the FT reaction that are assigned to Exxon, only a few discuss the exotherm that is observed in any of the experimental reactors. In one of the patents, assigned to Fiato et al. (X.8) claiming Fe-Co spinel derived materials as catalysts for fixed-bed FT reactors, the exotherms observed in those reactors are discussed. Actual maximum bed temperatures are given for runs in which furnace temperatures were from 225 to 290°C. In these runs made with a cobalt spinel having an x value of 2.625 ($Fe_{2.625}Co_{0.375}O_4$/1 wt.% K), exotherms of 8 to 44°C were observed at 240°C and 290°C, respectively (see Table X.7). Over this range the corresponding CO conversion increased from 31% to 97%. The CO conversion follows the same trend as does the difference between the furnace and bed temperatures. At the higher temperature, the hydrocarbon selectivity deteriorated resulting in increased conversion to methane, whereas at the lower temperature the olefin selectivity was higher, i.e. 55.3% versus 37.1%, and the C_6+ yield was also higher. The effect of furnace temperature at 235 and 270°C for a $Fe_{2.85}Co_{0.15}O_4$/1 wt.% K spinel, where x = 2.85, is also shown in Table X.7. In this case the actual bed temperatures were not reported but can be assumed to be about the same as for runs made at the same temperature. The CO conversion and CO_2 and hydrocarbon yields for the x = 2.85 spinel were essentially the same as for the x = 2.625 spinel. At high conversion, hydrocarbon selectivity of the x = 2.85 spinel was better giving less methane, more C_6+, and more C_2-C_5 olefin yields. This provides further evidence that lower cobalt concentration provides better yields.

Copper promoted Fe-Co spinels. Two patents claim Cu promoted Fe-Co spinels as slurry phase catalysts. A patent issued to Soled and Fiato (X.6) claims compositions comprising a reduced-carbided Cu-promoted Fe-Co alloy, produced by contacting a Cu-promoted Fe-Co alloy with a carbiding atmosphere, which was prepared by reduction of a Group Ia or Group IIa metal salt promoted Fe-Co spinel possessing a BET surface area greater than 5 m^2/gm. The spinels correspond to high surface area spinels prepared by precipitating the Fe and Co nitrate salts, as presented in Soled and Fiato (X.4). A corresponding patent issued to Soled and Fiato (X.7) which, except for the claims, is identical to Soled and Fiato (X.6) claims a slurry process using a catalyst comprising an unsupported Cu-promoted Fe-Co spinel having an initial BET surface area >5 m^2/g and a Fe/Co ratio $\geq$4/1.

Copper promoted spinels are prepared by impregnating Fe-Co spinel with an aqueous solution of cupric nitrate, drying, and then impregnating with an aqueous solution of K_2CO_3 followed by a final drying to give a composition of $Fe_{2.85}Co_{0.15}O_4$/(1 wt.% K, 1 wt% Cu). *Ex situ* carbided catalysts were prepared by reducing the spinel in a 40% H_2, 20% CO and 40% He containing stream at 400°C for 24 hrs. After cooling to room temperature, the oxygen (1%) passivated sample gave an X-ray diffraction pattern isostructural with Fe_5C_2, had a BET surface area of 150 m^2/g, and contained 40-50% carbon. Corresponding Co-free and carbided spinels were also prepared by the same method.

Examples were included which illustrate the use of these spinels as catalysts in a slurry reactor both in *in situ* unreduced as well as *ex situ* carbided forms. CO conversion for the *in situ* reduced catalysts followed the sequence Cu/K-promoted Fe-Co spinel > K-promoted Fe-Co spinel > Cu-free Fe spinel (see Table X.8). However, data were not provided that showed relative selectivities for hydrocarbon versus CO_2 formation. The CO conversion activities of the *ex situ* carbided-reduced Fe and Fe-Co spinels were quite similar as were the methane and C_2-C_4 olefin selectivities. The olefin concentrations (52-59%) in the C_{10} fractions from these catalysts were quite high.

Iron - Manganese Spinels

A composition of matter and three process related patents assigned to Exxon cover iron-manganese spinels. Two cases that were originally filed on December 20, 1983 were abandoned and refiled in December 1985. Both applications resulted in patents that issued in 1986. Apparently at some time during the application process, claims for a fixed-bed process were split from the slurry bed process application and refiled as a separate application. The latter fixed-bed application was subsequently abandoned, refiled and again abandoned before being refiled in 1990, which apparently resulted in a patent covering a fixed-bed process. Unlike the Fe-Co spinel cases, only high-surface-area Fe-Mn spinels were covered, since prior art appears to preclude coverage for Fe-Mn spinels prepared by sintering mixtures of iron oxide and manganese oxide.

The first patent in this series, issued to Fiato and Soled (X.11), claims compositions comprising an unsupported Group Ia or Group IIa metal and copper promoted Fe-Mn spinel having a BET surface area >30 m^2/g, an Fe/Mn ratio >2, and an empirical formula of $Fe_xMn_{3-x}O_4$, where x is >2. The second patent issued to Fiato and Soled (X.12) is identical to Fiato and Soled (X.11), except for the claims, and claims a slurry FT process using a catalyst comprising the composition of Fiato and Soled (X.11). The third patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the composition of Fiato and Soled (X.11) in a pelletized form.

In the examples, a high-surface area Cu-K promoted $Fe_{2.25}Mn_{0.75}O_4$ spinel was prepared by combining Fe and Mn nitrate, in a molar ratio of 3/1, with a solution of ammonium glycolate having a pH of 6.5 in a ratio to give a total metal ion to glycolate ion ratio of 1/1. Water was removed at room temperature and the solid was air calcined at 175^oC for 2 hours to produce the spinel having a surface area >50 m^2/g. Promoter was added by impregnating the spinel with 2 atomic % K and 1 atomic % Cu. Interestingly, a paper that appeared in 1985 by Maiti et al., (X.118) at about the same time that the final application was filed, also reported preparing Fe-Mn spinels by base precipitation of Fe and Mn nitrate salt solutions. The reduced and carbided form of the resulting solids, none of which contained promoters, was active for FT synthesis gas conversion. Even though the Maiti paper disclosed materials related to the claimed compositions, it apparently did not preclude the issuing of a patent for these compositions.

Under slurry conditions, the high surface area K-Cu dual-promoted Fe-Mn spinel gave higher CO conversions than either the comparable K or Cu promoted spinels, as shown in X.Table 9. At half the catalyst loading, CO conversion for the Cu promoted catalyst was higher at 69% than the 34% and 36% conversion for the K-promoted catalyst. The methane selectivity was also favorable in that it was lower for the dual promoted catalyst. The effect of Fe-Mn ratio is shown in Table X.10. CO conversions for Cu-K promoted spinels having Mn concentrations with x values >2, as claimed in this patent, were higher than for two spinels having x values of 0.25 and 1.5, which were below the Mn concentrations in the compositions claimed in this patent.

Unlike patent coverage for the Fe-Co spinels, which claimed both high and low-surface area compositions, none of the patents assigned to Exxon claimed compositions or processes comprising low-surface area Fe-Mn spinels as catalysts or precursors to catalysts for synthesis gas reactions. Such catalysts are apparently covered by a previous patent issued to McGrath and Rubin (X.14), and assigned to Kellogg, which claims a process for converting synthesis gas using a catalyst comprising elementary Fe with manganese oxide and alkali compound as promoters. Fiato and Soled (X.11) showed that a reduced low-surface area Fe-Mn composition reported by McGrath and Rubin (X.14) was inactive for CO conversion in the slurry process. This composition had an empirical formula of $Fe_{2.86}Mn_{0.14}O_4$/0.7 atomic % K and was prepared by sintering a paste of $Mn(NO_3)_2$ and Fe_3O_4 containing K_2CO_3 at 1400°C for 6 hrs and reducing with H_2 at 371°C for 48 hrs. For comparison, two low-surface area (<5 m^2/g) K and K-Cu promoted Fe-Mn spinels were evaluated. They were prepared by fusing a mixture of Fe_2O_3, Fe and Mn_3O_4 at 800-1000°C for 48-72 hours and impregnating with K or with K and Cu to give spinels having a composition of $Fe_{2.25}Mn_{0.75}O_4$ and containing 2 atom % K or 2 atom % K/1 atom % Cu. Both of these materials were inactive for CO conversion in the slurry process (see Table X.9). However, based upon the fact that reduced and carbided low-surface area Fe-Co spinels are quite active for CO conversion in the slurry process (see Table X.3), similarly pretreated Fe-Mn spinels may also be active; however, such information was not provided.

The use of glycolate in the production of the $Fe_xMn_{3-x}O_4$ spinel is covered in an independent claim that specifies the use of α-hydroxy aliphatic carboxylic acid. The spinel prepared in the examples using glycolate, as the carboxylic acid, was more active than spinel prepared by precipitating a solution of the salts using ammonium hydroxide. The latter spinel was prepared by calcining at 500°C. The CO conversion for the glycolate spinel was 68.9% versus 20.5% for the ammonium hydroxide prepared spinel.

Another related patent issued to Soled et al. (X.15) claims a process for producing powdered metal-based iron alloys which are structurally the same as prepared by reducing $Fe_{2.25}Mn_{0.75}O_4$. This method comprises heating a mixture of powdered mixed metal oxide with a stoichiometric amount of calcium metal in an inert atmosphere at 850°C for 72 hours, leaching out the Ca and calcium products with an aqueous acid and recovering the metal-based alloy. The other method used by Fiato and Soled (X.11) involves sintering the metal oxides at 1000°C to form the alloy.

The patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the Cu-K-promoted Fe-Mn spinel composition in a pelletized form. Comparison between a fixed bed and slurry operation for this catalyst indicates the slurry catalyst gives higher conversion, similar CO_2 selectivity, and lower methane and higher C_5+ olefin yields (see Table X.11).

Fe - Zn Spinels

A patent issued to Gates and Fiato (X.16) claims a sintered combination of metal oxides having the following components (preferred metals) from Group VIII (Fe), Group

IIB (Zn), Group IA (K), and the Lanthanum Group (Ce). Although there are no limits on the claimed composition, the only catalyst prepared in the examples had an empirical formula of $Fe_{2.81}Zn_{0.19}O_4{\cdot}Ce_{0.08}K_{0.08}$ (atom ratio of 1.0/0.065/0.03/0.03). This corresponds to an Fe_2O_3 concentration of 87 wt.%, which, surprisingly, falls outside the 5-80 wt.% range specified in the independent claim 7. The spinel catalyst was prepared by sintering a mixture of Fe_2O_3, ZnO, and CeO_2 at ~1050°C in air for 24 hours. It had a BET surface area <2 m^2/g and XRD indicated it was a highly crystalline mixture of mixed spinels and iron oxides in a CeO_2 phase. The composition is very similar to the Fe/Zn/Ti-Mn spinels that are discussed below. The spinels were reduced in H_2 at 500°C for 7 hours, after which they were pacified by exposure to oxygen at 25°C. The reduced form still contained unreduced metal oxides as shown by X-ray diffraction analysis. The passivated reduced catalysts, after preheating in H_2 in a fixed bed reactor at 500°C, gave the same level of CO conversion as a Zn and Ce-free 1% K/Fe_2O_3 that was prepared in the same way. The Zn-Ce containing catalyst gave lower methane and higher C_7+ liquid selectivity in addition to producing a higher yield of CO_2, as shown in Table X.12.

Another patent issued to Soled et al. (X.17) claims compositions comprising Fe, Zn, and Cu and one member chosen from the group of K, Rb, or Cs wherein the Fe/Zn atomic ratio is ≥5 and the alkali metal/Cu atomic ratio is ≥2. The claim specifies spinel compositions having empirical formulas of $Fe_xZn_{1-x}O_4$ with x values ≥2.5. Although compositions having single phase spinel structures are preferred, the compositions claimed in the patent are not limited to a method of preparation, specific structures or any morphological feature. A corresponding patent, having an identical specification, issued to Soled et al. (X.119) claims a FT process utilizing these catalyst compositions.

Only methods that generate high surface area materials were used in the examples to demonstrate the preparation of three different spinel compositions, i.e. $Fe_{2.8}Zn_{0.2}O_4$, $Fe_{2.45}Zn_{0.55}O_4$ and $Fe_{2.3}Zn_{0.7}O_4$. Only the first catalyst, which was prepared by two different methods, fell within the range specified in the claims. All three catalysts were prepared by mixing a solution of iron nitrate and zinc nitrate with an ammonium glycolate solution having a pH of 6.5, forming a precipitate, and drying and heating in air at 350^{o}C/1 hr. The resulting spinels were impregnated with K_2CO_3 and $Cu(NO_3)_2$ and dried in a similar fashion. The second $Fe_{2.8}Zn_{0.2}O_4$ spinel was prepared by adding ammonium hydroxide to a solution of iron nitrate and zinc nitrate to a final pH of 9. The washing, drying and impregnation steps were the same.

Although the catalysts were claimed to be useful in either fixed-bed or slurry FT reactors, the examples included only slurry reactor applications. The effect of promoter on synthesis gas conversion of Cu, K and Cu-K promoted $Fe_{2.8}Zn_{0.2}O_4$ showed that the K/Cu promoted catalyst gave higher CO conversion and methane selectivity, as shown in Table X.13. Surprisingly, the highest CO conversion was observed for a spinel having a Fe/Zn ratio less than 5 which falls outside the claimed composition range. It is not clear why this composition was not included in the claimed range of compositions.

Comparative performance tests of the zinc ferrite based catalysts were conducted with 2g samples of catalyst and 72g of octacosane in a 300 cc Parr CSTR. The synthesis gas (H_2:CO = 2:1) feed rate was 180 cc/min at 75 psig and 270^{o}C. Activation was accomplished by heating up to and at 270^{o}C in synthesis gas. Nitrogen (20 cc/min) was added as an internal standard. The superficial space-velocity (V/V/hr) based on an initial catalyst density of 1.8 g/cc was approximately 15,000 V/V/hr. CO conversions in excess of 60% were maintained during initial 80 hr test. Methane selectivity of 4.5% (CO_2 free) was obtained. C_{5+} selectivities were >75% on a CO_2 free basis. On this basis, the space velocity (including 20% inert gas) was about 6 NL/hr-g catalyst (Table X.14); this compares favorably with the activity of cobalt catalysts discussed later. The Exxon workers report that the pressure useful in the process will range between 150 and 450 psig and preferably 250 and 400 psig. They state that higher pressures can be used but these can lead to high levels of condensed water which can retard activity. This statement implies that the catalyst either has low water-gas shift activity or is being operated under conditions where the fraction of CO converted to hydrocarbons, and not CO_2, is very high.

Fe-Zn-Ti and Fe-Zn-Mn Spinels

A patent issued to Fiato et al. (X.18) claims compositions comprising sintered combinations of metal oxides taken from Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn), Group Ia (K), and the Lanthanum Group (Ce) such that the sintered combinations comprise a series of spinels of Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn) and a Group Ia metal oxide in a lanthanum group oxide matrix. The preferred metals are shown in parenthesis. There were specific limits on concentration of the metal oxides in the mixture which are quite similar to the sintered combination in Gates and Fiato (X.16) which included Fe, Zn, Ce and K. In that case, the only limits on concentrations of the metals were in a subordinate claim. The sintered catalysts are red-brown or red-purple, have BET surface areas ≤ 2 m^2/g and are highly crystalline. The crystalline phase comprise hematite, magnetite, ilmenite, a series of mixed spinels and CeO_2. A corresponding identical patent issued to Fiato et al. (X.120) claims a FT process utilizing this catalyst.

The catalysts are prepared, as in Gates and Fiato (X.16) by sintering a mixture of oxides having the correct atomic ratio and reducing in H_2 at 500°C for 6 hrs. The K, Ce, and K/Ce catalysts in a fixed-bed reactor configuration had CO conversion activities that varied with the promoter following the order K/Ce > Ce > K, as shown in Table X.15. At a reasonable CO conversion level the C_2-C_3 olefin selectivity was high and the methane selectivity was lower for the K/Ce spinel. Data were also given at higher reactor temperature, i.e. 305°C, as well as at lower space velocity, which resulted in excess of 80% CO conversion with high olefin concentrations in the C_2-C_4 fraction plus a sizable yield of C_5+ product.

K, Ce and K/Ce catalysts having compositions in which Ti was replaced with Mn were also included. The atomic ratio of the metallic components in the catalyst containing both K and Ce was 1.0 Fe/1.0 Mn/0.07 Zn/0.05 K/0.04 Ce. On a weight basis, this composition (43.6% Fe_2O_3/48.2% MnO_2/3.1% ZnO/1.2% K/3.8% Ce) is excluded from being a covered composition since it fell outside the specified composition in the main claim. Specifically, the MnO_2 composition of 48.2 wt.% of the total oxides is excluded, unless there is an error in the composition as stated in Example 6, since the claims specify a range for MnO_2 of 10 to 40 wt.% of the combination. The performance of the K, Ce and K/Ce promoted Fe/Mn/Zn spinels in a fixed-bed reactor configuration are shown in Table X.16. The K/Ce dual promoted spinel provides high activity, low methane selectivity and high C_2-C_3 olefin selectivity.

Thallium Impregnated Iron Supports

Two patents were issued regarding thallium and iron catalysts. One is a composition of matter case issued to Wright (X.121) and the second, a process patent issued to Wright et al. (X.122). Both cases involved several filings and abandonments;

there is also a difference in the inventors for the two cases. Overall, the texts in these two are very similar, though not identical. The main claims cover all Fe-Tl compositions wherein the thallium compound, being supported or unsupported, is substantially deposited on the surface of the iron compound, with the iron compound in the trivalent state. Included in a dependent claim is incorporation of promoters including Co, Zn, Cr, Mn, Ba and Group I metals.

The main claim appears confusing since it states that the thallium may be both supported and unsupported but is also substantially supported on the surface of the iron. The examples contain numerous examples in which the thallium was impregnated onto the surface of the iron, however one catalyst was prepared by impregnating a melt of ferric nitrate and thallium nitrate onto a magnesium-alumina spinel. This presumably is a supported example. Also, there is nothing in the claims regarding pretreatment of the catalyst to reduce the Tl and Fe to the metallic or carbided forms, although a number of different methods for preparing the catalysts are included in the examples.

Several techniques for preparing Fe/Tl catalysts were presented in the examples. Several Fe-Tl catalysts were produced having Fe/Tl ratios from 10/1 to 2.5/1 by precipitating solutions of ferric nitrate with ammonium carbonate and impregnating the washed and dried solids (110^oC for 12 hrs in air) by an incipient wetness method with solutions of thallium nitrate or thallium chloride. Examples were also given for preparation of other Fe/Tl catalysts supported on alumina, cesium-doped and magnesia-doped aluminas, and commercially available iron oxide. Examples explaining the preparation of several fluoride impregnated catalysts were also provided. Test results were provided on only a limited number of these preparations.

All of the Fe-Tl catalysts that were prepared in the examples were run under FT conditions that gave CO conversions up to 97%. The product contained large concentrations of liquid hydrocarbons in the C_5-C_{11} range that was rich in olefins and contained a lesser amount of aromatics. Data for a 10 Fe/1 Tl catalyst prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate and reducing at 270^{o}C/18 hrs are shown in Table X.17. Over a range of temperatures from 270 to 350^{o}C, the maximum C_6+ yield at CO conversions >90% was ~20% with methane yields ranging between 6 and 15%. CO conversion is very dependent on space velocity, however, methane, C_5-C_{11} liquid, C_1-C_4 gas, alpha-olefin and aromatic selectivities are only weakly dependent on space velocity. It was suggested that the aromatics yield is probably related to conversion of olefins. None of the examples provided any data on CO_2 yields.

The performance of two Fe-Tl catalysts in the FT reaction was compared with an Fe/K and a commercial ammonia synthesis catalyst. Two Fe-Tl catalysts, having Fe/Tl ratios of 10/1 and 5/1, were prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate. The method for preparing the Fe/K catalyst that contained 4% K is not clear and no further description of the commercial ammonia synthesis catalyst was given. Selected results from runs presented in Example 9 in the patent are shown in Table X.18. In the patent, in several instances, differing sets of results are given for the same run condition without any explanation. For example, included in Table X.18 are two sets of data that were both taken at 350^{o}C and 300 GHSV for the 10 Fe/1 Tl catalyst. Due to the lack of clarity in the presentation of the data, it is difficult to draw any conclusions regarding the CO conversion activities of these various catalysts. However, the product selectivities in these runs are quite similar. The discussion in Example 9 of the patent states that CO conversions were initially in the 80-98% range. Whereas the Fe/0.4K catalyst appeared to lose activity after about 18 hours on stream, conversion for the Fe/Tl catalyst decreased to only 40-60% after several days on stream. The selectivity for the 10 Fe/1 Tl catalyst appears to be maximum at 270°C at a CO conversion of 46.8%.

Iron - Cobalt Impregnated Slurry Catalysts

A patent issued to Fiato et al. (X.123) claims a process for preparing a slurry FT catalyst system in which an Fe-Co catalyst is formed (in situ) in the absence of air. A corresponding identical patent, except for references and claims, issued to Fiato et al. (X.124), claims a FT process utilizing this catalyst system. The catalyst is prepared by adding Fe and Co carbonyl compounds, or Fe and Co compounds which are capable of forming carbonyl complexes, in a CO atmosphere, along with a powdered support, to a hydrocarbon liquid. The iron and cobalt compounds are present in a ratio of from 35:1 to 1:10. This combination is decomposed in the presence of CO such that the cobalt complex is decomposed to the metal at a lower temperature followed by decomposition of the Fe complex at a higher temperature. The slurry is heated in H_2 to reduce the metals and their decomposition products. Representative complexes are $Fe_3(CO)_{12}$, bis(dicarbonylcyclopentadienyliron), $[CpFe(CO)_2]_2$, and $Co_2(CO)_8$. Potassium carbonate, that promotes olefin formation in the reaction and decreases the formation of methane, may be added to the mixture in the first step.

In the examples in the patent, $[CpFe(CO)_2]_2$ and $Co_2(CO)_8$ were added to the reactor either alone or in the presence of a support. In each case shown in Table X.19, the absolute amount of Fe and Co in the reactor was the same except for the run in which Fe_2O_3/1% K was added as the support. In runs with a 1:1 H_2/CO synthesis gas mixture, CO conversions were 20-30% with the C_2-C_4 fraction being predominantly olefinic. After 96 hours on stream, conversion had increased from ~21 to 27%. In a comparative run, an *ex situ* catalyst, $Fe_{2.85}Co_{0.15}O_4$/1%K, gave <5% CO conversion. For this run, the preparation of the catalyst nor its concentration in the reactor were not given.

TITANIA AND TRANSITION METAL OXIDE SUPPORTS

An extensive number of patents were obtained related to the use of titania containing catalysts in various applications, including the FT reaction. Early patents in this area disclosed the unique features of titania containing supports but did not refer to any FT type of application. However, these cases were fundamental to many of the subsequent patents that were issued for FT application. A patent issued to Tauster et al. (X.125) disclosed compositions comprising Group VIII metals supported on bulk oxides of titanium, vanadium, niobium, tantalum, zirconium titanate and barium titanate which were reduced in H_2 before use. A corresponding approach of coating a support with titania and adding a Group VIII metal is disclosed in a related patent issued shortly thereafter to Wheelock (X.126). Numerous patents have subsequently been issued using these approaches.

Tauster et al. (X.27) claimed that H_2 reduced Group VIII metals supported on Group IVb and Group Vb oxides are distinctly different from the same metals deposited on common carriers such as alumina, silica, carbon, magnesia, and silica alumina. These metals deposited on common carriers are found to retain their capacity for H_2 chemisorption, whereas the same metals when supported on various Group IVb and Group Vb oxides exhibit a marked suppression of this capacity. This change is attributed to the chemical nature of a strong metal-support interaction (SMSI) that consists essentially of covalent bond formation between metal atoms of the supported phase and metal cations of the oxide support at the surface.

Such an interaction between the supported metal and the support is highly unusual. Typically, the role of the support is simply a geometrical one which exerts the major influence in the preparation of a well dispersed supported-metal catalyst. Thus chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided that they are employed in their high surface area form, e.g. >100 m^2/g. In these situations no strong chemical interaction between the support and the metallic phase is required to bring about good dispersion. If surface interaction occurred, the results observed for temperature-programmed-desorption of H_2 from Pt/alumina and Pt/silica catalysts, which are very similar, would be expected to be quite different.

The patent argues that although covalently-bonded species are observed in the hexagonal barium titanates and Lewis acid-base intermetallic compounds, which are representative of cation to cation and metal-atom to metal-atom types of bonding, respectively, the metal-atom to cation bonding in the SMSI are unique to the structures of this invention. In a Lewis acid-base intermetallic type of bonding structure, the titanium would be present as zero-valent. By photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), zero valent titanium was not found in a composition of this invention, i.e. a 2% Rh/TiO_2 catalyst that had been reduced in H_2 at 550^oC.

In the broadest sense, the catalyst composition consists of a catalytic metal component selected from the group consisting of Group VIII metals, and mixtures thereof, supported on a transition metal oxide selected from the group Ti, V, Nb, Ta, alkaline earth titanates, and mixtures thereof. These SMSI oxides can be used either in the pure state or, alternatively, in combination with additional oxides such as alumina, silica, magnesia, zirconia, hafnia, thoria, ceria, etc. They may be prepared by coprecipitation from solutions containing precursor salts of the respective oxides or by deposition of the precursor salt of the SMSI oxide on a carrier. The latter compositions, comprising titania deposited on the surface of an inorganic oxide support to which Group VIII metals are added, were disclosed by Wheelock (X.28) who anticipated a stabilizing interaction between Group VIII metals and Group IVb metal oxides.

The key characteristic of the SMSI oxides is that after the critical temperature for reduction is reached, the supported metal is no longer able to absorb H_2 and CO at room temperature. However, the supported metal particles are still in a high state of dispersion and retain their ability to chemisorb oxygen resulting in high ratios of adsorbed oxygen to metal atoms. Since the SMSI effect is a chemical interaction between the supported metal and the carrier, it is necessary for the metal to be well dispersed in order to provide sufficient interfacial contact between metal and support. Thus large metal crystallites are incapable of significantly affecting the properties of the surface metal atoms in contact with the gas phase. Therefore, the particle size of the supported metal should be preferably 50 Å or less. There also is a difference in the temperature of H_2-activation needed to confer SMSI properties on the Group VIII metal, which varies primarily with the particular SMSI support. A SMSI state is achieved when a composition, e.g. Group VIII metal supported on the oxide of Ti, V, Nb, Ta, a mixture thereof, or a Zr or Ba titanate, is subjected, as a final preparative step, to reduction in a reducing atmosphere at a temperature sufficient to cause the composition to exhibit the suppression of H_2 and CO chemisorption.

<u>Properties of Titania Supports</u>. Tauster et al. (X.27) did not address the question of surface area and how it relates to the development of the SMSI state, although they used the argument that chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided they are employed in their high surface area form, e.g. >100 m^2/g. Based upon data contained in a subsequent patent issued to Arcuri et al. (X.127) the titania supported catalysts prepared by Tauster et al. (X.27) probably had only moderate surface areas. Arcuri et al. (X.29) showed that the rutile to anatase ratio increased with higher air calcination temperatures which caused a corresponding decrease in surface area (see Table X.20). They also found reduction of a calcined sample with H_2 at 450^{o}C did not prevent further decrease in surface area upon further calcination in air at 500^{o}C. These data suggest that the surface areas of the titania used by Tauster et al. (X.27) was initially about 60 m^2/g and because of the thermal transformation of anatase to the rutile form, the final surface areas were probably somewhat less than the starting material and somewhat enriched in the rutile form. In a still later patent issued to Mauldin and Riley (X.128), additional data were reported showing increases in rutile concentration with calcination temperature (see Table X.21).

Vannice and Garten (X.129) described the titania that was probably used in many of these patents as being prepared by flame hydrolysis of $TiCl_4$ and having a surface area of ~60 m^2/g after thermal treatment at temperatures ≤500^{o}C. A number of the cases referred to a material of this type that was designated as Degussa P-25 and was described as having a BET surface area of 50 m^2/g and contained 65% anatase and 35% rutile titania in Wachs and Yang (X.130). Although a number of these patents contained claims that specified limits on the concentrations of the crystalline forms in the titania phase, several actually contained these limits in either the main claim or another independent claim. This, of course, provides an unalterable requirement for the catalyst of the invention and was peculiar to a series of five patents, four of which claim titanias having high rutile contents while the fifth claims a stabilized titania having a high anatase content. Interestingly, the four high rutile cases, that originated from work presumably done at the Baton Rouge laboratories, were filed on the same day, June 29, 1984, and no subsequent patents had such a restriction in their main claim, although several continued to claim such materials in dependent claims. The level of rutile specified in the claims is >40%.

An alternative to using bulk titania is supports in which titania would be coated onto common, inorganic oxides. Such compositions were covered in a patent issued to Wheelock (X.28) which disclosed compositions comprising Group VIII noble metals and titania deposited onto inorganic oxides. Interestingly, that patent actually specified in its main claim that the titania existed on the surface as clusters. Whether such speculation regarding the morphological form of the catalyst, which was based upon ion scattering experiments, limits the compositions claimed by the invention is not clear. Assuming that it does not, Exxon then has rights to all compositions comprising Group VIII noble metals on titania coated inorganic oxides, of which platinum was specifically mentioned.

Ruthenium on Titania and Transition Metal Oxide Supports

The earliest Ru on titania Exxon patent that was found related to application in NO_x reduction. A composition of matter patent issued to DeLuca et al. (X.131) claimed a composition comprising ruthenium in combination with zirconium titanate or zirconium titanate in admixture with titanium dioxide, but not with TiO_2 alone. Ruthenium on titania compositions had been disclosed in previous patents, one of which was issued to

Kobylinski and Taylor (X.132), and assigned to Gulf, which claimed a process for reducing the content of nitrogen oxides in the exhaust gases from internal combustion engines. Such patents probably precluded claiming such compositions.

A problem with Ru/TiO_2 catalysts is the loss of Ru oxide upon treatment at temperatures around 840^{o}C. DeLuca et al. (X.33) claimed decreased volatility of Ru oxide from compositions comprising Ru on zirconium titanate, either with or without additional titania being present. Tauster et al. (X.27) claimed the use of these materials in hydrocarbon conversion reactions but not in a FT type application. Various combinations of these supports, either alone or in combination with supported metals, are claimed in subsequent composition of matter patents or as catalysts in various FT process application patents. Several patents were issued regarding ruthenium on titania type supports. The claims in all these cases included not only titania but numerous combinations with silica, alumina, carbon, Group Vb metal oxides, and various alkali, alkaline earth and rare earth oxides. Exxon came close to claiming the composition Ru on TiO_2 in a patent issued to Arcuri et al. (X.29) which claimed catalyst compositions comprising ruthenium with rhenium on titania. A companion process patent that utilized this catalyst, which was essentially identical except for the claims, was issued to Arcuri (X.133). The titania support in these compositions were specified as having rutile concentrations >40%. The examples in these patents showed in extended runs with synthesis gas that Ru/TiO_2 that contained rhenium had a longer half-life at a level of 97% CO conversion than rhenium-free catalyst (see Table X.22). The interactive effects of these two metals on catalysts containing 0.5-1.0% Re with ruthenium concentrations from 0.1-1.0% indicate that the highest CO conversions were obtained for catalysts containing 0.5% Re and 1.0% Ru (Table X.23). The effect of the ratio of rutile to anatase in the catalyst is shown in Table X.24 in which the catalyst containing 67% rutile in the titania had the slowest deactivation rate when operating at the 90% CO conversion level. Also, methane selectivities were much lower for the catalysts containing higher levels of rutile.

Several of the ruthenium-titania patents that were issued relate to processes that use Ru on titania. Vannice and Garten (X.31) claimed the use of a reduced Ru on titania, which they prepared by impregnating $RuCl_3$ onto titania and reducing in H_2 for 1 hr at 450°C. The Ru/TiO_2 catalyst gave higher olefin yields than a related Ru on η-Al_2O_3 (see Table X.25), albeit at a CO conversion level of 10% or less in both cases. Mauldin (X.134) claims a process for converting methanol in the presence of H_2 using a catalyst comprising ruthenium composited with titania. At a 4/1 methanol to H_2 ratio, conversion to hydrocarbon product was 76% after 35 hrs on stream (see Table X.26). Either in the absence of H_2 or the presence of added CO, conversions dropped significantly. CO was presumed to adsorb preferentially on the catalyst preventing reaction of the methanol.

Vannice and Tauster (X.135) claimed a FT process using a catalyst comprising Ru deposited on V, Nb and Ta oxides either alone or in combination with silica, alumina, or carbon type supports. Titania was not included in the claims. Preparation of the catalysts was by methods as presented in Tauster et al. (X.27) which was incorporated by reference. Higher olefin yields were obtained with the catalysts of the invention under conditions that the CO conversions were less than 18% (see Table X.27).

Madon (X.136) also claimed a FT process using a catalyst comprising Ru deposited on the same supports claimed by Tauster et al. (X.27), i.e., Ti, V, Nb and Ta oxides. In an improvement over Vannice and Tauster (X.37), this case claimed a process which employed a reduced catalyst which was contacted with a mixture of H_2 and CO for at least 10 hours, after which continued contact with H_2/CO gave a C_5-C_{40} hydrocarbon product having a paraffin to olefin ratio in the C_5-C_{20} fraction of $\geq$1.5. With a 0.76% Ru on TiO_2 catalyst, in excess of 80% CO from a 1.39 H_2/CO synthesis gas mixture was converted to liquid products under conditions shown in Table X.28. All of these catalysts were shown to be more active than Ru supported on conventional SiO_2 or Al_2O_3 (see Table X.29).

A patent issued to Wachs and Yang (X.137) claims a catalyst comprising Ru supported on a surface modified titania support wherein the support comprises an oxide of a metal selected from the group Nb, V, and Ta supported on the titania. In a corresponding patent, Wachs and Yang (X.32) claim a method for preparing this catalyst composition by depositing noncrystalline metal oxides of V, Nb, and/or Ta on a titania support having a 50 m^2/g surface area. In a related patent, Wachs and Chersich (X.138) claim a simple Ta_2O_3/TiO_2 composition prepared in this manner. No related patents claiming V and Nb oxide modified titania surface compositions were found. In Wachs and Yang (X.39) the modified support was impregnated with a solution of the Ru precursor which was reduced to the metal form. In the examples, all of the catalysts contained 1% Ru loadings. The activity of the catalysts containing various concentrations of the oxide promoters were compared with an impregnated physical mixture of TiO_2 and Ta_2O_5 in a fixed bed reactor (see Table X.30). Although the patent states that the data clearly show the difference between the catalysts of this invention and prior art Ru/TiO_2 catalysts, it is a challenge to recognize any differences.

A patent issued to Fiato and Miseo (X.139) claims slurry catalyst compositions consisting of titania, the decomposition product of $Ru_3(CO)_{12}$ formed in the presence of

H_2, and an inert alkane hydrocarbon. Fiato and Miseo (X.140) claim a process for preparing the *in situ* Ru/TiO_2 slurry catalyst. Preparation includes adding TiO_2, a Ru carbonyl complex, and an inert alkane hydrocarbon to a slurry reactor and increasing the temperature of the reactor to 230-270°C and pressure from 4 to 20 atm for 2-6 hr while adding a gas mixture of N_2:H_2 to cause the decomposition of the Ru carbonyl complex to form a slurry catalyst composition. In the example, a TiO_2 that had been pretreated with H_2 for several hours was added to the reactor with the Ru carbonyl complex and then subjected to the carbonyl decomposition step. The catalyst was highly active and selective for production of liquid hydrocarbons giving 40 to 60% CO conversion at 240°C with an alpha of 0.80. When TiO_2 was not present in the reactor, the Ru carbonyl complex was incompletely reduced and gave only 15% CO conversion (see Table X.31). The performance of the slurry catalyst was compared with a particulate Ru/TiO_2 and a Ru supported on ceria and alumina. The Ru - TiO_2 slurry catalyst had the highest CO conversion (55%) with a selectivity very similar to the particulate Ru/TiO_2 catalyst.

A patent issued to Mauldin (X.141) claims a process wherein the Ru on titania catalyst is pretreated with steam or steam and H_2 at 200 to 550°C to mildly agglomerate the ruthenium. By this procedure, Ru particles are generated having the same size as obtained after start-up with synthesis gas. The same effect occurs upon treating in air at 500°C where the crystallite size of the Ru grows from 12 to 30 Å. In the examples, a Ru/TiO_2 was prepared by impregnating a titania having a rutile content of 73% with ruthenium nitrate in acetone solution. One portion of this material was calcined in air at 500°C for 4 hours. Another was contacted with mixtures of steam with H_2 or N_2 at elevated temperature, as shown in Table X.32. The oxygen chemisorption decreased while the Ru crystallite size increased. The performance of the Ru/TiO_2 that had been treated in air at 500°C for 3 hrs was compared with an untreated sample. Results after several times on stream, as shown in Table X.33, indicate that the selectivity to methane was higher and to C_2+ hydrocarbons was generally lower than for the untreated catalyst. The catalyst treatments that were presented in the patent, including air or steam with H_2 or a carrier gas, provide an advantage over a non-treated catalyst, as determined by Ru crystallite size, oxygen chemisorption or synthesis gas conversion and selectivity.

A patent issued to Pruett and Bradley (X.142) claims compositions comprising bimetallic cluster compounds containing Ru with Tl, In or Ga. A cluster having the formula $[(C_2H_5)_4N][(Ru_6C(CO)_{16})_2Tl]$ deposited onto an alumina surface was reduced in H_2 at 200°C and used for conversion of 1.5/1 H_2/CO mixture at 7 MPa and 275°C. The product contained a mixture of linear hydrocarbons and alcohols.

Rhodium on Titania

A patent issued to Vannice and Garten (X.143) claims a process in which synthesis gas is passed over a catalyst comprising Rh on a titanium-containing oxide support. The activity of this catalyst, reduced at 450°C and 100 kPa, though quite low, was higher than for a Rh on alumina catalyst (Table X.34). The product was largely methane.

Cobalt on Titania and Transition Metal Oxide Supports

There has been a considerable amount of activity by Exxon regarding cobalt on titania catalysts with a number of patents being issued that parallel the ruthenium cases discussed above. Included in the series were three filed on June 29, 1984 from the Baton Rouge laboratory that relate to titanias having rutile concentrations $\geq$40%. Very broad coverage was obtained in a patent issued to Payne and Mauldin (X.144) which claims catalyst compositions comprising cobalt on high-rutile titania which are useful for both synthesis gas and methanol conversion. A subsequent patent issued to Behrmann et al. (X.145) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of titania to an average depth of 0.02 to 0.20 mm with a cobalt loading, on a total bulk basis, from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. A related patent issued to Iglesia et al. (X.146) claims a method for preparing supported cobalt catalyst on which the Co is deposited to a depth of less than about 200 µm on the rim of the catalyst particles. Other patents issued to Payne and Mauldin (X.147) and Behrmann et al. (X.148) claim processes that utilize these catalysts for conversion of synthesis gas. The addition of rhenium as a promoter to this family of catalysts, i.e. rhenium with cobalt on titania, was also covered. Catalysts in which the Co and Re were concentrated at the surface of the spherical particle was claimed by Behrmann et al. (X.47). Rhenium is claimed to improve activity for CO conversion for cobalt as it does for ruthenium. Bulk Co/TiO_2 catalysts, either with or without thoria, were claimed in a patent issued to Mauldin (X.149) with addition of thoria being claimed to be especially beneficial for conversion of methanol. Since the main claim in this case specified an inorganic oxide support, with titania being mentioned in a dependent claim, compositions that were covered were actually broader than titania itself, although titania supports were the only ones used in the examples.

Of the nine examples on Co/TiO_2 in the Payne and Mauldin (X.46) case, the first six relate to conversion of methanol and the last three to conversion of synthesis gas. The latter examples with synthesis gas are repeated in Payne and Mauldin (X.49) while the first six, which are related to methanol conversion, were probably included in Application Number 626,026, which was filed on the same day, as noted in Payne and Mauldin (X.49), but apparently never resulted in an issued patent. A process patent issued to Mauldin (X.150) used the Mauldin (X.51) catalyst comprising rhenium and cobalt on titania.

The examples of bulk titania catalysts in Payne and Mauldin (X.46) were prepared from calcined Degussa TiO_2, which was impregnated with Co nitrate and/or perrhenic acid. The addition of perrhenic acid to the substrate is a puzzle, since none of the catalysts contain Re, nor do any of the claims refer to catalysts containing Re. At any rate, the impregnated materials were then calcined in air at 250 or 500°C and reduced in H_2 at 450°C. Thoria containing catalysts were prepared by impregnating the support with a thorium compound or salt in a similar manner to give thorium concentration up to 10%. Actually, the specific thorium compounds or salts that were used to impregnate the substrate were not mentioned anywhere in the specification. Another set of cobalt-titania catalysts were also prepared having both high and low rutile concentrations. The low rutile concentration catalyst was prepared by impregnating cobalt carbonyl onto uncalcined Degussa P-25 titania that had a rutile concentration of 28% while the high-rutile catalyst was prepared from Degussa P-25 that had been calcined at 600°C. The impregnated cobalt carbonyl was decomposed either by heating at 257°C in vacuo for 1 hr, or by calcining at elevated temperatures. Catalysts were tested in a fixed bed reactor either with synthesis gas or with methanol after reducing in H_2.

A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of spherical titania with an average thickness of 0.02 to 0.20 mm. A corresponding patent issued to Behrmann et al. (X.50) claims use of these compositions in a FT process. The cobalt loading in these catalysts, on a total bulk basis, was from 0.04 to 0.15 g/cc, which is ~4-17 wt.%, depending on the packing density of the titania. Special techniques for depositing the cobalt along with Re as a promoter were used wherein the metals were concentrated at the surface of the spherical titania particles having diameters of approximately 1 mm. The activity of rhenium promoted Co/TiO_2 catalysts, in which the metals are deposited on the surface of spherical titania substrate, is related to the thickness of the metal layer. With these catalysts that were prepared from spherical titania, the methane concentrations in the hydrocarbon product, relative to the converted CO, was lower than for Co-Re/TiO_2 in which the metals were uniformly distributed onto powdered substrate (see Figure X.1). The metals were deposited onto the surface of the spheres by either spraying a metal-containing solution onto the titania spheres and quickly removing the solvent or treating spheres that had been saturated with one solvent with a metal-containing immiscible solvent which would not penetrate into the particle.

Another method to prepare rim-type supported cobalt catalysts is covered in a patent issued to Iglesia et al. (X.48) who claim that contacting a support particle with a molten cobalt salt results in deposit of the cobalt to a depth of less than about 200 µm on the rim of the support. After reduction in H_2, these catalysts are more active than incipient wetness impregnated catalysts where the Co is evenly distributed throughout the particle, as shown in Table X.35, where a lower GHSV is necessary to achieve the same level of CO conversion. Each of the rim-impregnated silica based catalysts have a higher volume of CO conversion per volume of catalyst per hour. Crushing the 2.2

mm spheres provided a slight increase in CO conversion which denotes some additional diffusional effect in the rim catalysts even though the Co is located primarily at the surface of the particle. There is also an advantage of having higher Co concentrations on higher surface area supports, as shown in Table X.35.

The advantage of incorporating a binder into titania was covered in patents issued to Mauldin and Riley (X.30) which claim support compositions comprising titania in which up to 20% alumina or zirconia is incorporated. A corresponding essentially identical patent issued to Mauldin and Riley (X.151) claims a FT process utilizing these catalysts. Their data show that incorporating a small amount of alumina increases the volume of CO converted per gram of cobalt/hr, as shown in Figure X.2. This increased activity is attributed to an increase in cobalt dispersion due to the increase in pore volume of the binder. Hydrocarbon synthesis activity suffers at higher alumina concentrations, however, because the Co oxide is only partially reduced on the alumina, as compared to titania where complete reduction occurs. This is reflected in the higher turnover numbers for the titania and the steady decline as incorporation of alumina increases (see Figure X.3). Thus, incorporation of small amounts of alumina results in an increase in activity. Higher dilutions, however, result in a decline in activity. An example is also presented that shows that catalysts prepared by spraying Co salts onto titania substrate containing 3.5% alumina binder using the method of Behrmann et al. (X.47) were more active than spherical titania without the binder.

A method for impregnating cobalt onto supports was covered in a patent issued to Mauldin and Riley (X.152) which claims a process for preparing a FT catalyst in which a catalytically effective amount of Co is impregnated and dispersed as a film or layer on the peripheral outer surface of a particulate porous inorganic oxide support, wherein the catalysts are prepared by spraying a bed of the fluidized particulate support particles with a liquid containing a dispersed or dissolved Co metal compound. The operation is performed at specified operating conditions of 0.6 g liquid/ft^3 fluidizing gas. Titania was one of the supports specified in a dependent claim. In the examples, solutions of cobalt nitrate and perrhenic acid were sprayed onto particulate material and reduced at 450°C for 1 hr. Conversion of a 2/1 H_2/CO feed at 200°C, 280 psig and 1000 GHSV after 20 hrs on stream was 79% with product selectivities for CH_4 of 6.0%, CO_2 of 6.0% and C_2+ of 93.6%.

Synthesis Gas Reactions. Co/TiO_2 catalyst has a higher activity toward synthesis gas conversion, as shown in Table X.36, than conventional cobalt on silica or alumina or Co-Mg-thoria on kieselguhr, which was prepared following a published procedure (X.153). The 0.91 Schulz-Flory alpha value for the titania catalyst was higher than for conventional catalysts and was reflected in a C_{10}+ hydrocarbon yield that was 〉75%. Higher CO conversions in these Co/TiO_2 catalyst appear related to higher rutile concentrations and higher O_2 chemisorption values of the starting catalysts as shown in Table X.37. The pseudo first-order CO conversion rate constants calculated by Equation 1 correlate directly with the oxygen chemisorption values for these four catalysts, as shown in Figure X.4.

$$k = \frac{GHSV}{P} \ln \frac{1}{(1-x)} \tag{52}$$

where:

x = fraction CO conversion,

P = reactor pressure in atm, and

GHSV = space velocity at ambient temperature and pressure in hr^{-1}.

Similar results were obtained with catalysts prepared by impregnating cobalt carbonyl onto 28% and 100% rutile titanias where the carbonyl was decomposed by heating in vacuum. Synthesis gas conversion over these catalysts shows that the high rutile catalyst gave much higher CO conversion (see Table X.38). Cobalt catalysts prepared either from the nitrate or the carbonyl gave essentially the same results.

Incorporation of 0.5 to 3% Re in the Co/TiO_2 catalyst further improved both oxygen chemisorption and CO conversion, as shown in Table X.37. The improvement resulting from addition of Re is probably through improving the reduction of the Co in the pretreatment step (X.154). Results from a 200 hr extended run, presented in (Figure X. show that CO conversion dropped from about ~98% to ~80%. Comparison with a Ru/TiO_2 catalyst with the Co-Re catalyst under the same conditions (Figure X.6) indicate the Co-Re catalyst was significantly more active than the Ru catalyst while both had similar selectivities for methane and CO_2 (Figure X.7).

<u>Methanol Reaction</u>. Examples of methanol conversions were given for a number of cobalt catalysts including Co/TiO_2, Co-Re/TiO_2, Co/ThO_2/TiO_2, and Co-Re/ThO_2/TiO_2. The effect of rutile concentration on methanol conversion was observed for catalysts containing 12% cobalt on titania. The 100% rutile catalyst completely converted the methanol while the 55% rutile titania support gave only 66% conversion (see Table X.39). The selectivities were also quite different with the catalyst having the lower rutile content being more selective for producing C_2+ hydrocarbon product and less CO_2.

Experimental data showing the effect of adding thoria on the conversion of methanol is provided in Payne and Mauldin (X.46). In these cases the rutile contents of the catalysts were not specified (see Table X.40). Assuming that the titania components in these catalysts had the same rutile concentration, the data show that addition of thoria to the catalyst increases methanol conversion, decreases methane yield, and gives nearly the same Schulz-Flory alpha values. Comparisons with other state-of-the-art catalysts showed that conventional FT 100 Co/5 ThO_2/8 MgO/200 Kieselguhr catalyst gave higher methanol conversion but poorer C_2+ hydrocarbon selectivity under the run conditions. Compared to Co on silica or alumina, both Co-titania catalysts, with or without thoria, gave better C_2+ selectivity at comparable or higher methanol conversion levels. The liquid product was highly paraffinic as reflected in the 78.2% straight chain paraffinic content of the C_8 fraction from the thoria containing catalyst. Even over the Co/alumina catalyst, where methanol conversion was 64%, the yield of dimethyl ether was only 2.4%, indicating the non-acidic nature of the alumina support. At the low methanol conversion levels, dimethyl ether formation was quite small.

The presence of rhenium with cobalt in 56% rutile titania catalysts, either with and without added thoria, increased MeOH conversion (see Table X.41). Addition of 0.5 wt.% Re to Co/ThO_2/TiO_2 increased methanol conversion quite sharply from 49% to 100%. Conversion to CO_2 increased sharply while C_2+ yields decreased from 74% to 56%. The effect of Re/TiO_2 on methanol conversion was not provided.

Hydrogen partial pressure has a strong effect on methanol conversion and product selectivity. Payne and Mauldin (X.46) showed that increasing the H_2 partial pressure at constant methanol space velocity increased conversion from 38% to 83% (see Table X.42), decreased the yields of CO+CO_2, and sharply increased methane selectivity. The C_2+ yield appears to go through a maximum at a H_2 partial pressure of 17 psi. At low methanol pressures over a 12% Co/2% ThO_2/TiO_2 catalyst, the products are almost exclusively CO and H_2, except for a very small amount of methane.

A patent issued to Mauldin et al. (X.155) claims cobalt-titania catalyst to which is added small amounts of hafnium, zirconium, cerium or uranium to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatment. The concentration of promoter to cobalt was specified as a weight ratio greater than 0.01 to 1 and typically between 0.04-0.25 to 1. Although there were no limits placed on the catalyst composition, the catalysts presented in the examples were prepared by impregnating high rutile titania either sequentially with Zr, Hf, Ce or U compounds followed by Co nitrate or simultaneously with the promoter metals and cobalt nitrate. In the preparation of these catalysts when the metals were added sequentially, the catalysts were calcined between metal additions. The final catalysts were then calcined at 400, 500 or 600°C to simulate catalyst regeneration and tested for synthesis gas reactions. CO conversions for the promoted catalysts were higher than for the non-promoted catalysts at all air treat temperatures >150°C, as shown in Figure X.8. The 500°C catalyst regeneration data plotted in Figure X.9 show that addition of approximately 0.5 wt.% promoter provides optimal thermal stabilization giving CO conversions of 70-80%. The examples also showed that addition of 0.06 wt.% Hf and 0.3 wt.% Zr, both of which fell within the limits of the claimed compositions, was not adequate to stabilize the Co/titania, although higher concentrations did stabilize the catalysts.

Synthesis gas conversion data were provided for a 2/1 H_2/CO mixture that was passed over a Co-Hf-TiO_2 catalyst at 1000 GHSV and 204°C at 280 psig to give 89% CO conversion with a 91% C_5+ hydrocarbon product selectivity. No other synthesis gas data were provided. Comparative runs with methanol, however, are reported for each of the metal promoters (see Table X.43). All of the promoted catalysts gave higher MeOH conversion than the unpromoted catalysts with about the same selectivities for higher hydrocarbon product.

Silica Promoted Co/TiO_2

A patent issued to Iglesia et al. (X.156) claims compositions of cobalt on an inorganic refractory support comprised of a major portion of titania to which up to 15 wt.% silica has been added. This catalyst is utilized in another process related patent issued to Iglesia et al. (X.157). These two cases are identical except for the claims. The patent specifies that the Co may be incorporated onto the inorganic refractory titania support either before or after adding the silica or silica precursor. Incorporation of rhenium in the catalyst is covered in a subordinate claim. Although the main claim does not specify Re in the catalyst, the examples include only Re-containing catalysts.

In the examples, a series of catalysts, as described in Table X.44 were prepared starting with a CoRe/TiO_2 (Catalyst A) that was prepared by depositing Co and Re components from an acetone solution onto a 97% rutile titania and calcining at 250°C for 3 hrs. Two silica containing catalysts (Catalysts B and C) were prepared by impregnating Catalyst A with tetraethoxysilane (TEOS), treating with a stream of H_2O (40 Torr) in He while heating at 400°C for 13 hrs after which it was reduced at 250-400°C for 2-14 hrs. A catalyst that was free of silica but exposed to the same H_2O treatment (Catalyst D) was prepared by treating Catalyst A with H_2O (40 Torr)/He while heating at 400°C/13 hrs, after which it was reduced at 250-400°C for 2 to 14 hrs. The activities of the catalysts were determined at run times up to almost 200 hrs under conditions to give ~60% CO conversion. There was little difference in hydrocarbon selectivity observed by incorporating silica into the samples. Although the CO_2 yield was in every case quite small, it dropped to an almost imperceptible level with silica.

The increased stability of the silica containing catalysts was observed in reduced carbon buildup at low temperatures on the surface of the catalyst in the presence of CO. The "effect of SiO_2 during carburization suggests that it may prevent short term deactivation during the first few hours in H_2/CO environments; the effect is to increase the apparent site activity by maintaining surface cobalt atoms available during hydrocarbon synthesis."

Anatase Titania Supported Cobalt Catalysts

A patent issued to Soled et al. (X.158) claims both a composition of matter and a method for preparing a catalyst containing anatase titania. What appears to be the omnibus claim is claim 13 which claims a catalyst composition comprising Co composited with a ternary metal oxide support of titania having the general formula $Co/Ti_{1-x}M_xO_2$ where x is 0.01-0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum and wherein the titania is an anatase polymorph stable under oxidative regeneration at temperatures of 400-750 °C. Claim 1, on the other hand, claims a method for preparing this catalyst which comprises contacting a titanium alkoxide or titanium chloride, such as $TiCl_4$, with a metal alkoxide or metal chloride, respectively, to form a solution; adding water to the mixture of alkoxides or an aqueous base to the mixture of chlorides to form a co-precipitate; separating the co-precipitate; calcining the dried co-precipitate to form a ternary metal oxide; depositing a cobalt metal compound solution onto the surface of the ternary metal oxide to form a composite; and activating the composite to form a catalyst. Activating the composite includes drying and calcining followed by reduction of the Co. Depending on the precedence of claims 1 and 13, the coverage may be broad as defined in claim 13 or it may be very narrow being confined to the composition prepared by the method disclosed in claim #1.

Neither the claims nor the specification in this case discuss the coexistence of mixtures of rutile and anatase forms in the titania. Likewise, the concentration of the anatase phase in the titania prepared by the method of this invention was also not revealed. If the composition of the claimed catalyst is limited to the material prepared according to the method in claim 1, then the question of anatase concentration is mute. However, if the patent covers all $Co/Ti_{1-x}M_xO_2$ compositions per claim 13 where M is silicon, zirconium, and tantalum and where titania is in an anatase form, the limits on anatase concentration covers only titania compositions that contain, at most, very small amounts of rutile. Regardless, this case is likely an improvement over Iglesia et al. (X.58) which claims cobalt on silica-modified titania wherein no limitation on the form of the titania is made. It also must be an improvement over Mauldin et al. (X.57) which claims catalysts comprising zirconium added to titania to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatments. In the main claim, there are no limitations on the form of the titania. These three cases, however, provide Exxon with coverage for cobalt impregnated anatase to complement their many cases on rutile-rich titanias.

Apparently the reason why the anatase phase is stabilized at high temperatures is related to substitution of Si, Ta, and Zr cations into the anatase structure of the catalyst which apparently retards the formation of $CoTiO_3$ preventing the entrapment of the cobalt and preserving its specific surface area. Once cobalt titanates form, a higher temperature is required to reduce them to the metal. Through addition of Si, Ta, and Zr, the amount of the $CoTiO_3$ is decreased. For a Si incorporated polymorph, the concentration of the $CoTiO_3$ is decreased, as determined by XRD, and its concentration is a function of calcination temperature, as shown in Figure X.10. Silica incorporation has no affect on the thermal properties of the catalyst but increases by approximately 100 centigrade degrees the temperature for onset of carburization in a synthesis gas stream, as shown in Figure X.11.

Catalysts incorporating each of the promoters were prepared and their stability to calcination was reported in the examples. Anatase titania was prepared by first hydrolyzing $Ti(t\text{-}buO)_4$ and calcining at 430°C. Co as Co nitrate was then impregnated onto the substrate and calcined at 430-700°C. Calcining at 430°C gives anatase having a surface area of 120 m^2/g while calcining at 700°C transforms the anatase to rutile having a surface area of 2 m^2/g. Silicon promoted titanate was prepared by adding the silicon alkoxide, tetramethylorthosilicate (TMOS), to $Ti(t\text{-}BuO)_4$ following the above procedure. Surface areas containing various levels of silicon substitution were obtained upon calcination at 700°C:

Si, %	m^2/g
1%	52
3%	76
5%	119
14%	133

Zirconium promoted titanate was prepared by adding zirconium n-propoxide to $Ti(t\text{-}BuO)_4$ following the above procedure. A catalyst containing 3% Zr had a surface area of 36 m^2/g while a 14% Zr catalyst had a surface area of 56 m^2/g, both of which stabilized the anatase. A tantalum promoted titanate was prepared by adding tantalum ethoxide to $Ti(t\text{-}BuO)_4$ following the above procedure. A catalyst containing 14% tantalum had a surface area of 71 m^2/g. No FT data were provided in the patent.

Cobalt-Ruthenium on Titania

A patent issued to Iglesia et al. (X.159) claims a catalyst prepared by a process comprising impregnating titania with solutions of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the metals with an oxygen containing stream to form the oxides and reducing the oxides. A corresponding patent issued to Iglesia et al. (X.160) claims a process that utilizes this catalyst. The intimate contact of the Co and Ru in the catalyst lowers the temperature at which the cobalt is reduced to the metallic form. This results in a decrease in the amount of carbon deposited upon heating in synthesis gas at temperatures up to 500°C. Intimate contact is obtained by reducing the metals on the surface, calcining in air to reform the oxides and then reducing to the metal form. Unlike many of the other composition of matter patents, a corresponding process patent was not found.

TGA and DTA data provided in the patent showed that the carbon deposited more slowly on calcined Co-Ru/TiO_2 when subjected to a 1:1 H_2/CO synthesis gas mixture than on either Co/TiO_2 or uncalcined Co-Ru/TiO_2. The patent states that the advantage of the Co-Ru combination relative to other catalysts is that "a combination of increased cobalt oxide reducibility and inhibited catalyst poisoning by carbon are believed to account for the increased number of active sites observed on calcined CoRu/TiO_2 catalysts."

Energy dispersive X-ray (EDX) analysis of uncalcined versus calcined CoRu/TiO_2 catalysts that had been aged in process runs for 700 hrs showed that both aged catalysts were identical. Apparently Ru in fresh uncalcined CoRu/TiO_2 catalyst cannot be detected since its concentration over the surface is below detection limits. However, in calcined CoRu/TiO_2 catalyst that has been reduced, Ru can be detected in the cobalt particles where it concentrates sufficiently to be detected by EDX. Apparently, Ru also concentrates in aged uncalcined CoRu/TiO_2 catalysts since the EDX analysis was the same as the calcined sample.

In the examples, three titania catalysts were prepared starting with a sample containing 70% rutile. The first catalyst, Co/TiO_2, was impregnated with cobalt, calcined at 400°C for 4 hrs in air and reduced in H_2 at 400°C for 16 hrs (Catalyst A). Ruthenium was then impregnated onto this catalyst and reduced to give reduced-Co-Ru/TiO_2 (Catalyst B). A portion of this material was calcined in air at 300°C/4 hrs and reduced in H_2 to give the calcined-reduced Co-Ru/TiO_2 composition of this invention (Catalyst C). A Co/SiO_2 catalyst was prepared for comparison by impregnating silica with a cobalt salt (Catalyst D). In synthesis gas runs in which the space velocity was adjusted to attain comparable conversion levels (see Table X.45), the cobalt time yields of the calcined-reduced Co/Ru/TiO_2 catalyst was higher than for the other three catalysts. This appears to be similar to Gulf patents where reduced-oxidized-reduced catalysts had a higher activity than the reduced catalyst (X.161). The methane and C_5+ selectivities of reduced-Co/Ru/TiO_2 and the oxidized-reduced Co/Ru/TiO_2 were very nearly the same, but slightly better than Co/TiO_2 or Co/SiO_2 catalysts.

Data were provided that showed that hydrogen regeneration of oxidized-reduced Co/Ru/TiO_2, catalysts that had been aged from 10-30 days, was more complete than for the untreated Co/Ru/TiO_2 catalyst (see Table X.46). CO conversions and methane and C_5+ selectivities were higher for both the fresh and regenerated oxidized-reduced Co/Ru/TiO_2 catalyst than for the untreated reduced Co/Ru/TiO_2 catalyst and the ruthenium free Co/TiO_2 catalyst.

Iron on Titania

A series of three patents were issued to Fiato and Kugler which are identical except for the claims. Fiato and Kugler (X.162) claim a composition consisting of a mixture of iron carbide and ilmenite, either with or without an alkali metal promoter, having an Fe_2O_3 concentration of 2-25 mg/cm^2, wherein the catalyst is formed by depositing an iron salt onto titania, calcining, treating with H_2 free of CO at 300-500°C until the composite is reduced and then contacting with CO at a temperature that is 100-200°C lower than the H_2 reduction temperature. In this preparation, the iron precursor deposited on the titania is calcined to form the iron oxide which is reduced in H_2 to form Fe metal which then reacts with CO to form carbide. X-ray diffraction showed that the calcined material contained anatase and rutile forms of TiO_2, $FeTiO_3$ (ilmenite), and metallic Fe. Xray diffraction of the sample after CO treatment showed that the TiO_2 and ilmenite were unchanged, metallic Fe disappeared, and Fe_5C_2 was formed.

In one of the other cases, Fiato and Kugler (X.163) claim a process for producing hydrocarbons from synthesis gas using this catalyst composition. In the other, Fiato and Kugler (X.164) claim a process for improving the activity of this catalyst in a FT reaction by cycling the temperature in the reaction zone, by increasing the temperature by 50-150°C above the FT reaction temperature in the absence of H_2 for from 1-6 hours and then returning to reaction temperature and reestablishing the H_2 content of the feed stream. None of the examples actually illustrated the effectiveness of this procedure.

The activity of a series of catalysts indicated that the Fe concentration in these catalysts must be $\geq$2 mg Fe_2O_3/m^2 of titania (see Figure X.12). The activity of an Fe supported titania catalyst of this invention that had been both reduced and subsequently carbided, with an Fe concentration of 0.002 g Fe/m^2 TiO_2, was higher than a corresponding material that had not been carbided, i.e. 27 versus 60% CO conversion, respectively. The hydrocarbon selectivities for the carbided catalyst was lower for methane and higher for C_5+.

A patent issued to Wachs et al. (X.165) claims catalysts comprising an iron carbide on a modified titania support comprising at least 25% of an oxide of Nb, V, and Ta in a noncrystalline form and containing at least 2 mg Fe, as Fe_2O_3, per m^2 support surface. A corresponding process patent, which was essentially identical, issued to Wachs et al. (X.166) claims a process for producing hydrocarbons using this catalyst. These cases relate to an application by Wachs and Chersich (X.40), that was filed on the same day, that claims compositions of tantalum oxide on titania support that were used as catalyst supports. The background on this case was that the Fe/Group Vb oxide/TiO_2 combination was anticipated in the specification by Tauster et al. (X.27) but not actually claimed as compositions of that invention. The Wachs et al. patent (X.67) differs in that the titania surface was modified by addition of limited amounts of Nb, V, and Ta to modify the TiO_2.

The catalysts used in the example were prepared by slurrying Degussa P-25 titania with an ethanol solution containing either $Nb(C_2H_5O)_5$ or $VO(C_2H_5O)_3$. The solvent was removed, the V or Nb ethoxides were oxided, and the resulting powders calcined in pure O_2 at 575°C for 2 hours. The resulting supports contained 10% Nb_2O_5 or V_2O_5 on TiO_2. The Fe precursor was impregnated onto the support, reduced in H_2 at 500°C for 5 hrs, and carbided by exposure to synthesis gas. Results from runs with synthesis gas (see Table X.47) show that at similar CO conversions levels, i.e. 47-49% or 60-70%, the vanadia and niobia catalysts gave lower methane and higher olefin selectivities than a Fe/TiO_2 catalyst. At the same run temperature, i.e. 270°C, the methane yields were lower for the catalysts of the invention.

Nickel on Titania

Two patents related to nickel-titania catalysts were issued; in one, Ni as a promoter of titania based catalysts was claimed while in the second, titania promoted bulk Ni catalysts were claimed. The first patent issued to Vannice and Garten (X.167) claims a FT process that uses a catalyst comprising nickel on a titanium-containing oxide support with a Ni concentration up to 75% by weight. The second patent issued to Kugler and Garten (X.168) claims a FT process using a catalyst comprising bulk nickel promoted with up to 10% titania. These two patents pretty well cover the use of all possible combinations of Ni and titania catalysts in the FT reaction.

In the first patent, Vannice and Garten (X.69) claim that nickel on titania exhibits higher activity, improved selectivity to higher hydrocarbons, improved life and tolerance to sulfur, and resistance to Ni carbonyl formation. The catalysts were prepared by impregnating nickel salts onto the titania support and reducing in H_2 at temperatures >400°C. Synthesis gas conversion at 1 atm over these Ni/TiO_2 catalysts was higher than with bulk nickel or Ni on silica, alumina, and graphite. C_2+ paraffin selectivity versus CO conversion is shown in Figure X.13. In these runs, the Ni/TiO_2 catalysts had higher CO conversions per gram Ni, and lower methane and higher C_2+ hydrocarbon selectivities. Still, the methanation reaction was quite high for the Ni/TiO_2 catalyst. An experiment was described in which the volatility of the Ni was shown to be lower over the TiO_2 catalyst than a Ni/SiO_2 catalyst (see Figure X.14).

In the second patent, Kugler and Garten (X.70) claim the addition of titania to bulk nickel shifts hydrocarbon selectivity from methane to C_2-C_6 hydrocarbons, along with trace quantities of C_7 product. The influence of increasing titania concentration up to 8.4%, as shown in Table X.48, was to increase the CO conversion while the selectivity to higher hydrocarbons increased. Since the relative rates for CO conversion and CH_4 formation both increased, the changed product distribution reflected the much higher increase in the rate of CO conversion versus the smaller increase in methanation rate. The selectivity of the 8.4% TiO_2 on Ni catalyst is very similar to the selectivity of 10% Ni on TiO_2.

A physical mixture of 1/1 Ni powder and TiO_2 behaved very similarly to Ni powder indicating that for such a physical mixture a synergistic interaction did not occur upon activation in H_2. The effect that was observed with the catalysts prepared by addition of solutions of the Ti oxide precursor to bulk Ni indicates a chemical interaction between the titania and the Ni, since a change in activity and selectivity occurs. Evidence for a chemical interaction was observed in ESCA that showed that Ti exists on the catalyst surface before reduction as Ti^{+4}. After reduction in H_2 at 250°C, some of the Ti is in a lower oxidation state but not reduced to the metallic form. The titanium promoter changes the surface area and chemisorption properties of the bulk nickel. Small quantities of Ti additive increases the surface area while creating an oxide layer, as observed by ESCA. Concomitantly, H_2 chemisorption was reduced due to physical blockage of the sites. The highest CO conversion level was observed at the lowest H_2 chemisorption level for the Ti promoted samples.

MANGANESE OXIDE SUPPORTS

Exxon has been assigned 2 patents which claim compositions, or use thereof, comprising the five Group VIII metal oxides of iron, cobalt, nickel, iridium and ruthenium on manganese oxide supports which are reduced at a temperature sufficient to suppress hydrogen chemisorption. These cases parallel Tauster et al. (X.27) who claim catalyst compositions comprising Group VIII metals on Group IVb and Group Vb metal oxides that are reduced at a temperature to suppress hydrogen chemisorption. Since manganese falls in Group VIIb, it falls outside of Tauster et al. (X.27). There are other manganese patents assigned to Exxon which involve the use of manganese in spinels which are discussed elsewhere in this review.

Ruthenium

A patent issued to Kugler et al. (X.169) claims a FT process that provides improved yields of C_2-C_4 olefins that uses a catalyst comprising ruthenium on a manganese containing support which has been reduced at a temperature sufficient to suppress hydrogen chemisorption. Manganese can be used in its pure form or combined with alumina, carbon, silica, or oxides of Groups IVb and Vb. A 1% Ru/MnO catalyst was prepared by impregnating MnO with $RuCl_3$ and reducing with H_2 at 450°C. Synthesis gas mixtures, having H_2/CO ratios from 1.6 to 3, were passed over the catalyst at 300°C and at 1 atm pressure to give CO conversions less than 10%. Under those conditions Ru/MnO catalyst gave higher yields of C_2-C_3 olefins and lower yields of CH_4 relative to a Ru/Al_2O_3 catalyst.

Iron, Cobalt, Nickel, Iridium

A composition of matter patent issued to Tauster and Fung (X.170) claims compositions comprising iron, nickel, cobalt and iridium supported on a manganese containing oxide support, the improvement comprising contacting said composition with a reducing atmosphere at temperatures $\geq$300°C, except for iridium which requires a temperature $\geq$250°C, to produce a catalyst composition which exhibits suppressed hydrogen chemisorption. Under these conditions, the reduced materials would, therefore, be in the SMSI state as defined by Tauster et al. (X.27). Two different 2% Ir/MnO catalysts were prepared by impregnating the metal onto two different MnO substrates. The two MnO substrates prepared by reducing battery grade MnO_2 in H_2 at 540 and 740°C had surface areas of 21.7 and 7.8 m^2/g, respectively. Less than 0.01 atoms of hydrogen were adsorbed per atom of Ir for each of these catalysts that had been reduced in H_2 at 500°C versus values of 0.46-1.08 for samples reduced at 200°C. A sample (prepared at 740°C) reduced at 350°C adsorbed less H_2 (0.041 atoms per atom Ir) indicating it was in the SMSI state.

Cobalt - Manganese Spinel

A patent issued to Soled et al. (X.171) claims compositions comprising a copper promoted Co-Mn spinel having a formula $Co_{3-x}Mn_xO_4$ where x is 0.5-1.2. Subordinate claims specify a Cu concentration from 0.1 to 5 g-atom percent based on the total amount of Co and Mn in the catalyst and a surface area >5 m^2/g. A corresponding patent, having an identical specification, which was issued to Soled et al. (X.172), claims a Fischer-Tropsch process using this composition. The spinel was prepared using the alpha-hydroxy aliphatic carboxylic acid method that has been used for all these high surface area spinels. A Co_2MnO_4 spinel, having a surface area of 30-60 m^2/g that is isostructural with Fe_3O_4, was prepared from a solution of $Co(NO_3)_2$ and $Mn(NO_3)_2$ in the presence of citric acid and ethylene glycol, which was evaporated and calcined in air at 350°C for 30 min. The resulting spinel was impregnated to give a 1 wt.% Cu concentration. The activity of the Cu-promoted spinel in a slurry reactor with synthesis gas was compared with the spinel without added Cu under conditions shown in Table X.49. The catalyst was first reduced in situ with synthesis gas. The Cu-promoted Co_2MnO_4 spinel had higher activity and gave higher olefin selectivity than unpromoted Co_2MnO_4 spinel or a Co_3O_4/1% Cu catalyst.

GROUP VIII METAL SUPPORTED CATALYSTS

Several patents were issued in which inorganic metal oxides were used as supports for Group VIII metals. A patent issued McVicker and Vannice (X.173) claims catalysts prepared by depositing K or Rb Group VIII metal carbonyl cluster complexes on a high surface area support material, drying in the absence of oxygen and reducing at elevated temperatures. A companion case, issued to McVicker and Vannice (X.174), which is identical both in title and text, excluding claims, covers a process application for these catalysts. The catalysts were prepared by depositing bimetallic carbonyl compounds onto high surface area supports from solutions in organic solvents. At least some, if not all, of the materials were highly sensitive to air. A whole laundry list of potential bimetallic carbonyls were presented, of which 6 were actually used in catalyst preparations. Of the Group VIII carbonyls, only Pd and Os were not specifically included in dependent claims. Re, Ru and Ir, which were actually used in preparing catalysts, were specifically covered in dependent claims. Supports that were specifically claimed were alumina, silica, silica-alumina, titania, zirconia, hafnia, tantala, niobia, vanadia, and magnesia.

Several catalysts were tested by passing a 3/1 H_2/CO synthesis gas mixture over the catalysts at 250 to 284^{o}C and 1 atmosphere. Under these conditions, very low CO conversions were observed. More long chain olefins were formed over the cluster catalysts of this invention than with conventional catalysts prepared by impregnating alumina (eta) with aqueous solutions of Fe nitrate and KNO_3.

Palladium on Alumina

A patent assigned to Vannice and Garten (X.175) claims a process for producing methane by passing synthesis gas over palladium supported on an acidic metal oxide selected from alumina and HY zeolite with the palladium metal particle being maintained at <100Å. CO conversions of 3.5% were obtained when a 3/1 H_2/CO mixture at 1 atm was passed over these catalysts. Methane was essentially the only hydrocarbon product. The methane yield per Pd surface was higher for the catalysts of this invention than for Ni on a 5% Ni/Al_2O_3 catalyst, although the CO conversion over the nickel catalyst was 55% under these conditions.

Platinum on Alumina

A patent issued to Vannice and Garten (X.176) claims a process for producing dimethyl ether by passing CO and H_2 over platinum supported on alumina. Over a 1.16% Pt/Al_2O_3 catalyst at 274°C for a 1/1 H_2/CO gas mixture at 10 atm pressure, 2.5% CO was converted to hydrocarbons with a hydrocarbon selectivity of 70% methane, 8% ethane, and 23% dimethyl ether.

Nickel on Silica or Alumina

A patent issued to Yates and Murrell (X.177) claim Ni catalysts having Ni surface areas of 200-400 m^2/g prepared by slurrying a Ni metal precursor in a nonaqueous solvent with a high surface area refractory oxide, removing the solvent and reducing with H_2 to form Ni metal. A use for these catalysts is in hydrocarbon synthesis as in the FT reaction. Ethane hydrogenolysis and benzene hydrogenation are included in the examples. However, no examples are provided that cover conversion of synthesis gas. The specification states that several co-metals, of which potassium is one, should be avoided since they act as catalyst poisons.

MOLYBDENUM CATALYSTS

A patent issued to McCandlish and Kugler (X.178) claims a FT process using a catalyst comprised of molybdenum oxycarbonitride. The catalyst, in which the oxygen, carbon and nitrogen are distributed throughout the bulk structure, is prepared by thermally decomposing an ethylenediammonium molybdate at 650^{o}C in an inert atmosphere. The catalyst was pyrophoric and could be passivated with oxygen for handling in air. The active form was easily regenerated in H_2 at 450^{o}C. CO conversions up to 20% were obtained over this catalyst at 254 to 315^{o}C with a 1/1 H_2/CO synthesis gas mixture at 1 atm and 2400 GHSV. Methane was the dominant product under these conditions.

ALCOHOL SYNTHESIS

A patent issued to Apesteguia et al. (X.179) claims catalyst compositions consisting of a solid solution or coprecipitated mixture of a first oxide and a second oxide, wherein the first oxide is selected from yttria and rare earth oxides and a second oxide is a Group Ia oxide and Group Ib metal. These catalysts are useful for conversion of synthesis gas to alcohols, especially isobutanol and methanol. Several representative catalysts were prepared: Cu impregnated onto cerium oxide; coprecipitated Cu, MgO and ceria; K impregnated onto coprecipitated Cu, MgO and ceria; Cu supported on MgO and yttria. These catalysts provided very large yields of alcohols, primarily methanol along with lesser amounts of isobutanol (see Table X.50). Methane and CO_2 yields were also quite sizable.

PROCESS IMPROVEMENTS

Although the overwhelming number of FT related patents that have been assigned to Exxon are related to catalyst compositions or their use, several patents related to improvements in the design or operation of the FT process have been issued. Many of the more recently issued patents have concentrated on process improvements. The FT-type process improvements that are covered are:

- use of 2-stage process configuration to improve hydrocarbon selectivity,
- improved product selectivity through olefin addition to the feed,
- improved CO conversion and C_5+ selectivity through water addition to the feed,
- modified gas inlet system to improve axial distribution of particulate catalyst in a slurry reactor,
- use of downcomers to redistribute catalyst in a slurry reactor,
- use of pentane as heat transfer fluid,
- bundled tubular reactor with shell-side cooling,
- fixed-bed start-up protocol to prevent temperature runaway,
- method for defining operating conditions for a slurry reactor,
- method for activating ex situ reduced cobalt slurry catalyst,
- method for rejuvenating and redistributing catalyst in a slurry reactor,
- method for removing fines from particulate catalysts.

2-Stage Processes

Two different 2-stage process configurations are covered. In one, a patent issued to Kim and Fiato (X.180) claims a process in which synthesis gas contacts in a reaction zone in a first bed a first catalyst having a high olefin selectivity and contacting the resulting olefins in a second bed with a catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons. The claim specifies that the first bed catalyst is selected from a group consisting of Fe/Zn/Ce/K, Fe/Mn/K and Fe/Co/K and the second bed catalyst is selected from the group consisting of Ru/TiO_2, Ru/SiO_2, and Ru/Al_2O_3. The process operates at 150-220 psig with the temperature of the first catalyst being about 260-280°C and the second catalyst being about 190-210°C. The range of the preferred H_2/CO ratio, as stated in the specification, was 1.5 to 2.5. An example is provided that shows that over a Fe/Zn/Ce/K catalyst at a CO conversion of 59%, the selectivity to CO_2 was 26% with the remaining product being hydrocarbons (see Table X.51). Hydrocarbon formation is split between the 1st and 2nd catalyst beds in a ratio of 45/55. Based upon approximately equal yields from the two beds and equal yields from each of the two catalysts operating alone, a linear combination predicts a decrease in methane selectivity and an increase in $C_{10}+$ selectivity when operating in this fashion. Experimentally, the observed methane and $C_{10}+$ selectivities were even better than predicted (see Table X.52).

A second configuration involves an interstage product separation step. A patent issued to Fiato (X.181) claims a two stage hydrocarbon synthesis process comprising reacting synthesis gas at reaction conditions in a first stage in the presence of a supported cobalt or ruthenium catalyst at a pressure $\geq$10 atmospheres, separating liquid from H_2 and CO, and reacting the remaining H_2 and CO at a pressure less than 10-12 atmospheres, but no greater than the first stage, in the presence of cobalt supported on alumina at reaction conditions. This process configuration takes advantage of the apparently higher activity of Co/Al_2O_3 catalysts at lower partial pressures of CO and H_2 relative to catalysts comprising Co or Re on other oxides supports, such as titania. 2-Stage processes having interstage separation of hydrocarbon product, in which the remaining H_2 and CO are recompressed, have the additional advantage of lower energy requirement.

Product Improvement through Feed Modification

Olefin Addition to Feed. Two patents were issued for processes that reduce methane formation in the FT process through injection of olefins. The first patent issued to Kim (X.182) claims a process with a catalyst comprising Group VIII (Fe, Co, Ru) metals supported on an inorganic oxide support wherein olefins are added to the feed to reduce methane formation. The second patent issued to Iglesia (X.183) claims further methane reduction by injecting the olefins at a point below the inlet of the reactor.

Kim (X.84) showed that injection of ethylene in the feed stream increased CO conversion and decreased methane selectivity. A 2/1 H_2/CO synthesis gas mixture gave a CO conversion of 8.4% and a methane selectivity of 6.4% when passed over a Ru/TiO_2 catalyst at 200^{o}C at 70 psig at a flow rate of 55 standard cm^3/3 g catalyst/min. When 8.2 mol % ethylene was injected into the feed stream, CO conversion increased slightly to 9.0% and methane selectivity dropped to 3.5%. When 20% ethylene was added, the methane selectivity dropped even further to 2.7%. In another case, when 4% 1-decene was substituted for ethylene, an approximate 20% decrease in methane selectivity occurred. Over a precipitated bulk Fe catalyst the introduction of 9.6% ethylene into the same synthesis gas mixture at the same temperature and pressure at a flow rate of 100 standard cm^3/10 g catalyst/min caused a 30% decrease in methane selectivity.

In the 2nd case, methane was further reduced through adding the ethylene downstream of the inlet of the reactor. A patent issued to Iglesia (X.58) claims that for a FT process using an Fe, Co or Ru catalyst, the methane yields are further reduced when the olefins are added to the reactor bed below a point equivalent to 10% of the distance from the top to the bottom of the reactor bed and above a point in the reactor bed equivalent to 10% of the distance from bottom to the top of the reactor bed. The addition level is stated as the amount sufficient to suppress methane formation. In the examples, for ruthenium and cobalt-ruthenium on titania catalysts, adding ethylene below the top 1/3rd of the catalyst bed decreased the amount of ethane produced relative to the amount of ethylene added to the feed. Likewise, the amount of C_3+ increased accompanied by a small decrease in methane yield, as shown in Table X.53.

Water Addition to Feed. A patent issued to Kim (X.184) claims enhanced CO conversion and C_5+ selectivity for a once-through, fixed or slurry bed FT process comprising contacting the synthesis gas containing 1-70 vol % water in a reaction zone with a catalyst consisting of cobalt, ruthenium and mixtures thereof on titania converting 90% of the CO to liquid hydrocarbons in the substantial absence of CO_2. This case involved numerous filings and abandonments over an eight year period from the time of the first filing on July 13, 1985. The long background discussion of numerous prior patents outlines the extensive number of related cases. Numerous examples were shown for a range of catalysts exhibiting increased CO conversion, decreased methane selectivity and increased C_{10}+ liquid yield in the presence of added water.

Reactor Design

Modified Gas Inlet System. Two patents were issued related to the design of FT reactors. One patent issued to Chang and Coulaloglou (X.185) claims a method for improving axial distribution and mixing of particulate catalyst in a slurry bubble column by introducing a secondary gas into the column at a location within the lower 20% of the vertical height of the column but above the gas distributor plate. This gas stream can be part of the synthesis gas feed, recycle gas, inert gas, condensed light hydrocarbons or light synthesis hydrocarbons which vaporize under conditions present in the column.

A figure is presented of experimental data taken in a 5 ft diameter by 30 foot high slurry bubble column that shows that the solids distribution in the reactor is more uniform when using this gas inlet configuration.

The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. The key to the method disclosed in this patent is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

Downcomers. A patent issued to Behrmann et al. (X.186) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry with the bottom near the bottom of the reactor and the top near the top surface of the slurry. The bottom is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (X.187) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure X.15.

A patent issued to Chang (X.188) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure X.16 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. A patent issued to Stark (X.189) claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity.

Tube-in-Shell Reactor. A patent issued to Koros (X.190) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in ID x 50 ft long pipe mounted in a 12 inch pipe cooling jacket was provided. Liquid heights varied between 12 and 32 feet with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H_2/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig, and steam jacket pressure of 140 psig, CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Reactor Start-up. A patent issued to Arcuri (X.35) claims a procedure for the start-up of a fixed-bed FT reactor that allows a flexible and more effective response to a potential temperature runaway. While elevating the temperature, pressure and feed flow rate to line-out levels, the composition of the H_2 and CO in the feed is maintained at a H_2/CO mole ratio not exceeding 90% of the mole ratio at lineout. After the temperature, pressure and feed flow rate reach normal operating levels, the H_2/CO ratio is gradually increased to the operating lineout mole ratio.

The patent illustrates the advantage of using this operating protocol relative to using temperature as the main control parameter. Comparative exotherms are provided for two different startup procedures used on a 1/2 inch ID, 6 foot long tubular pilot scale FT reactor that was submerged in a sand bath, as shown in Figure X.17. Following a conventional start-up procedure in which temperature is slowly increased to bring the reactor online, a very significant temperature runaway occurred. In this example, the final target operating conditions were 359^{o}F with a 2.08/1 H_2/CO synthesis gas mixture at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step were as follows:

1. Synthesis gas mixture and flow rate were established at lineout conditions at a pressure of 60 psig and a sand bath temperature of 337^{o}F. The maximum exotherm in the bed during this period was 5^{o}F.
2. Pressure was then increased to lineout pressure of 280 psig and held 3 days. A maximum exotherm of 12^{o}F resulted.
3. Then temperature was increased slowly from 337 to 353^{o}F and held 24 hours. During this period the maximum exotherm was 21^{o}F.
4. Afterwards, the temperature was increased 2^{o}F over a 40 min period to 355^{o}F. The magnitude of the maximum exotherm remained the same at 22^{o}F.
5. However, when the temperature was increased over a 2 hour period to 359^{o}F, which was a 4^{o}F change in temperature, the maximum exotherm increased to 242 F^o, indicating a severe temperature runaway.

By contrast, the exotherms were much less when the procedure taught in the patent was followed, namely using a decreased H_2 content in the feed gas. In this example, the target lineout reactor conditions were 380°F with a 2.1/1 H_2/CO synthesis gas mixture flowing at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step, as shown in Figure X.18, were as follows:

1. The H_2 feed gas (1.8/1 H_2/CO) rate was brought to 910 GHSV at 60 psig and 337°F. The maximum exotherm was 7°F.
2. The pressure was increased to the lineout pressure of 280 psig over 0.5 hours. The maximum exotherm was 9°F.
3. The temperature was increased almost to the lineout temperature of 374°F in 1 hour during which the maximum exotherm was 17°F.
4. H_2 in feed gas was increased to a 2.0/1 H_2/CO ratio in 1 minute as flow rate increased to 970 GHSV. Maximum exotherm was 23°F.
5. The H_2 in feed gas was increased to a 2.1/1 H_2/CO ratio as flow rate increased to the final 1000 GHSV. The maximum exotherm was 25°F.

During this sequence the exotherm remained under control and space time yield data was higher with a higher CO conversion. Another example was also given that illustrates how rapidly an exotherm can occur in a FT synthesis reactor.

Setting Operating Conditions. A patent issued to Herbolzheimer and Iglesia (X.191) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

(a) injecting gas at an average gas velocity >2 cm/sec;

(b) fluidizing the particulate catalyst having an average diameter >5 µm in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D, such that

$$0.5\ (U_s - U_L) \leq \frac{D}{H},\ where\ H > 3m$$

where

$$U_s = \frac{1}{18}\ d_p^2 \frac{\rho_s - \rho_l}{\mu}\ gf\ (C_p), where\ d_p > 5\ \mu m$$

(c) operating at plug flow at a gas velocity U_g, expanded liquid height H, and dispersion coefficient D such that

$$U_g\ \geq\ 0.2\ \frac{D}{H}\ where\ H\ > 3\ m, U_g > 2\ cm/\text{sec}.$$

In one example using a Co-Re/TiO_2 catalyst having a density of 2.7 g/cm^3, a liquid density of 0.7 g/cm^3, and a wax viscosity of 0.01 g◦cm/sec, the particle settling velocity is:

$$U_s\,(cm/\text{sec}) =\ 1.1 x 10^{-4}[d_p(\mu m)^2]$$

For a 60 µm average particle, U_s = 0.39 cm/sec. For a liquid velocity of 0.5 U_s, and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

Catalyst Pretreatment

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (X.192) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H_2 in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (X.193) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H_2 at hydrocarbon synthesis temperature and pressure with temperatures no lower than 40°C below hydrocarbon synthesis temperature. Another patent issued to Mitchell (X.194) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO_2-5% Al_2O_3 catalyst by reducing the catalyst with H_2 was given. Following reduction, catalyst was passivated with a CO/H_2 stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H_2. Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non-H_2 treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure X.19.

A patent issued to Pedrick et al. (X.89) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft diameter by 35 ft high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H_2, which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H_2/26% CO/13% CO_2/5% CH_4, by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO_2-5% Al_2O_3 slurry catalyst at 210-230°C and 20 atm. When operating the reactor with two-2 inch diameter and two-4 inch diameter flue-gas fed draft tubes and one-3 inch diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;
draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure X.20) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure X.21, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch rejuvenation tube was brought on line. Immediately upon addition of H_2 an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After lineout, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 10^{o}F, CO conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table X.54.

A patent issued to Hsia (X.195) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure X.22). Likewise, rejuvenated catalyst is fed to the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (X.196) claims a method for removing <1 μm particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The method comprises dispersing the particles to which the <1 μm particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the <1 μm particles in the supernatant liquid and separating the <1 μm particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims only apply to the latter (see Table X.55). Catalysts stirred with FT wax at 130^oC gave initially a filtration rate of 5.8 gal/ft^2/min which decreased to 0.05 gal/ft^2/min after stirring for 44 hours. Using the method of this invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to 14.5 gal/ft^2/min.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (X.92) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure X.23, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure X.24.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure X.25. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. THe bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec.). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C_{16}-C_{18} hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferrably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferrably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m^2/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferrably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76 i.d.) about 50 ft. tall mounted inside a 12" pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron dismeter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig) and higher reactor pressure (285 psig at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr^{-1}) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water, this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

This summarizes the patents abstracted through October 19, 1994; Appendix will cover later period.

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Table X.1. Activity of laser generated iron carbide catalysts
Reaction Conditions: 270°C, 2/1 H_2/CO, 200 sccm, 75 psig, in octacosane

	Carbide from Fe_3O_4	Laser derived carbide	Laser derived carbide + K	Laser derived carbide + Si
Preparation Method	Fe_3O_4 reduced in H_2@450°C/5-7 hrs and treated with H_2/CO/350°C	$Fe(CO)_5/C_2H_4$ laser feed	$Fe(CO)_5/C_2H_4$ laser feed/ impregnated with 2% K as K_2CO_3	$Fe(CO)_5/C_2H_4/SiH_2(CH_3)_2$ laser feed
V/V cat/hr	2000	4000	4000	500
% CO conversion	71.9	82.5	66.5	5.0
Selectivity, wt% CO_2 free basis				
CH_4	16.1	9.5	5.6	15.9
C_2-C_4 Paraffins	17.3	7.8	0.8	27.0
C_2-C_4 Olefins	18.9	27.0	11.5	19.0
% olefins in C_2-C_4	50.7	77.6	93.5	41.0

Table X.2. Activity of high and low surface-area Fe-Co spinels for synthesis gas conversion.
In situ catalyst reduced in slurry with H_2 at 200°C and 1 atm for 1 hr.
Ex situ catalyst reduced with H_2 at 300°C+ and then H_2/CO at 350°C+.
Run in slurry reactor at 250°C, 1200 v/v/hr, 2/1 H_2/CO, 70 psig, 600 rpm in octacosane;
time on stream not specified.

	Starting Spinel					
	$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K high surface area		Fe_3O_4/1%K high surface area		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K low surface area	
	in situ	ex situ	in situ[a]	ex situ	in situ	ex situ
Spinel surface area, m_2/g	>100	>100	>100	>100	0.29	<0.3
CO Conv, mol %	60	64	8.0	65	<4.0	42
CO_2	36	36	5.2	39	na	24
Hydrocarbons	24	28	2.8	26	na	18
HC Selectivity wt%						
CH_4	4.5	8.2	11.4	12.8	na	9.3
C_2-C_4 paraffins	2.5	3.6	8.6	8.0	na	5.5
C_2-C_4 olefins	17.5	27.4	34.3	32.2	na	27.0
C_5+	75.5	60.8	31.4	47.0	na	58.2

Taken from Example 3, Table III and Example 5, Table IV U.S. Patent 4518707 (X.4).
a. Taken from Table V of U.S. Patent 4518707 (X.4).

Table X.3. Activity of *ex situ* reduced and carbided high and low surface-area Fe-Co spinels. High and low-surface-area spinels were reduced *ex situ* with H_2 at 300°C+ followed by carbiding with H_2/CO at 350°C+. Reactions run in slurry reactor at 250°C, 1200 v/v/hr, 1/1 H2/CO, 70 psig, in octacosane.

	Starting Spinel x = 2.85	
	high >100 m^2/g	low < 5 m^2/g
CO conv, mol %	45	44
CO_2, mol %	26	29
HC yield, mol %	19	15
HC Selectivity wt%		
C_1	4.4	5.9
C_2-C_4	19.3	25
C_2-C_4 olefins	90	90
C_5+	76.3	69.1

Data taken from Example 2, Table II in U.S. Patent 4544672 and Ex 4, Table III in U.S. Patent 4518707 (X.4).

Table X.4. Activity of alloys in a slurry reactor prepared *ex situ* from high surface-area Fe-Co spinels Spinels reduced *ex situ* with H_2 at 350°C /12 hrs followed by 400°C/24 hrs, but not carburized. Run in slurry reactor at 270°C, 70 psig, 1200 v/v/hr, 600 rpm in octacosane.

	Fe_3O_4/1%K high surface area		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K high surface area	
H_2/CO	1.0	2.0	1.0	2.0
CO Conv, mol %	44	28	55	54
CO to CO_2, mol %	26	15	34	34
CO to HC, mol %	18	13	21	20
HC Selectivity Wt.%				
CH_4	4.4	2.1	5.8	6.5
C_2-C_4 paraffins	1.9	0.6	3.4	2.7
C_2-C_4 olefins	25.2	10	25.2	27.3
C_5+	68.7	87.2	65.0	63.4

Data taken from Example 7, Table VI, U.S. Patent 4518707 (X.4).

Table X.5. Activity of low-surface area spinel derived catalysts in a fixed-bed reactor. Catalysts treated with flowing 90% H2/N2 at 500^{o}C at 100 psig for 5-7 hrs. Run in fixed bed reactor with 1/1 H2/CO at 300 psig.

	Fe_3O_4/1%K		$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K	
Time on stream, hrs	1	12	1	12
V/V/hr	570	1000	570	1000
Furnace Temp^{o}C^{c}	305	305	270	270
CO Conv, mol %	79	67	98	98
CO to CO_2, mol %	36	31	42	40
CO to HC, mol %	43	36	56	58
Wt% selectivity				
C_1	8.5	5.8	9.1	7.4
C_2-C_4 paraffins	5.2	4.7	6.2	6.2
C_2-C_4 Olefins	26.6	30.6^{b}	39.4	50.3^{b}
C_5+	59.7	-	45.2	
C_6+	-	58.9	-	36.1

Data taken from Example 1 of U. S. Patent 4537867 (X.8). Catalysts prepared by sintering mixtures of metal oxides.

b. Applies to C_2-C_5 olefins.

c. Actual bed temperatures were not reported.

Table X.6. Effect of Co concentration on Fe-Co spinel catalyst performance after 12 hrs on stream. Catalysts treated with flowing 90% H_2/N_2 at 500^{o}C at 100 psig for 5-7 hrs. Catalysts run in fixed bed reactor at furnace temperature of 295^{o}C, 300 psig, 1000 v/v/hr, 1:1 H_2:CO.

x in $Fe_xCo_{3-x}O_4$	2.97	2.85	2.625	2.20
Time on stream, hrs	12	12	12	12
CO Conv, mol %	97	98	97	98
CO_2, mol %	27	40	41	42
HC, mol %	70	58	56	56
Selectivity				
CH_4	8.3	7.4	18.0	13.2
C_2-C_6 olefins	46.5	53.1	41.4	53.0
C_2-C_6 paraffins	6.9	7.2	13.3	10.6
C_7+	38.3	32.3	27.3	23.2

Data taken from Example 7, Table 7 of U. S. Patent 4537867 (X.8).

Table X.7. Effect of temperature on performance of Fe-Co spinels in fixed bed reactor
Samples for 1-12 hrs on stream at 300 psig, 1000 v/v/hr, 1/1 H_2/CO.

	Starting Spinel						
	$Fe_{2.625}Co_{0.375}O_4$/1 wt.% K					$Fe_{2.85}Co_{0.15}O_4$/1 wt.% K	
Furnace Temperature, °C	225	240	260	270	290	235	270
Bed Temperature, °C	230	248	304	325	340	na	na
CO Conv, mol %	30	31	97	98	98	29.4	98.0
CO_2, mol %	4	7	40	33	41	8.0	42.0
HC, mol %	26	24	57	55	57	21.4	56.0
Selectivity							
CH_4	8.1	8.2	19.1	16.7	19.1	2.6	5.2
C_2-C_5 olefins	42.3	55.3	37.1	31.9	24.8	18.1	33.6
C_2-C_5 paraffins	14.4	22.0	17.7	10.6	14.8	2.7	4.4
C_6+	35.2	34.5	26.1	40.8	41.3	76.8	55.9

Taken from Examples 8 and 12 of U.S. Patent 4537867 (X.8).
na = not available

Table X.8. Cu promoted high-surface area Fe-Co spinels as slurry catalysts.
Slurry reactor runs at 270°C, 2000 v/v/hr, 2/1 H2/CO, 75 psig, 600 rpm in octacosane.

	Fe_3O_4/2%K		$Fe_{2.85}Co_{0.15}O_4$/2 wt.% K	$Fe_{2.85}Co_{0.15}O_4$/2 wt.% K/1 wt% Cu	
	In-situ	Ex-situ	In-situ	In-situ	Ex-situ
CO Conv, mol %	67	49	77	86	54
Wt% Selectivity					
CH_4	2.0	3.8	4.4	4.2	4.5
C_2-C_4 Olefin %	47.5	77	91	87	85
C_{10} Distribution					
α-olefins		50	49	59	46
n-paraffins		8	14.9	15	18
n-alcohols		2	1.0	3	1
β-olefins		17	4.1	2	6.0
all else		23	31	21	29

Taken from Tables I and II, U.S. Patent 4607020 (X.6).

Table X.9. Effect of promoters on both high and low surface area $Fe_{2.25}Mn_{0.75}O_4$ spinels. Runs made at 270°C, 75 psi, 120 H2/60 CO/20 N2 cc/min flows, 70-80 g octacosane solvent, 20+ hrs on feed, 2 gm cat.

atomic % K	-	2.0	2.0	2.0	2.0	2.0
atomic % Cu	1.0	-	1.0	1.0	-	1.0
Surface area, m^2/g	>50	>50	>50	>50	<5	<5
gm catalyst	2	2	1	2	2	2
% CO conv	34	36	69	83[a]	nil	nil
wt Selectivity						
CH_4	8.8	3.5	1.7	2.3		
olefins in C_2-C_4	78	91	94	92		
olefins in C_{10}+	?	?	63	65		

Taken from Example 2, Table 2 of U.S. Patent 4618597 (X.11).
a. 30+ hours on feed

Table X.10. Effect of Fe-Mn ratio in $Fe_xMn_{3-x}O_4$ /2% K/ 1% Cu (>50 m^2/g) on synthesis gas conversion. Runs made at 270°C, 75 psi, 120 H2/60 CO/20 N2 cc/min flows, 72 g octacosane solvent, 30+ hrs on feed, 2 gm cat.

gm catalyst	2	2	2	8	8
x	0.25	1.5	2.25	2.25	2.85
CO Conv	nil	30	83	87	79
Selectivity					
CH_4	na	2.6	2.3	4.1	4.2
olefins in C_2-C_4	na	86	93	92	94

Taken from Tables 3-4 of U.S. Patent 4618597 (X.11).

Table X.11. Activity of $Fe_{2.25}Mn_{0.75}O_4$/2 at % K/1 at % Cu as catalysts for FT fixed bed and slurry reactors with 2/1 H_2/CO synthesis gas.

	Fixed-Bed		Slurry
Temperature, C	263	275	270
Pressure, psig	65	65	75
Cat mesh	40-100	40-100	>140
Fe-SV	2.0	9.0	11.2
CO Conv	50	43	69
Selectivity			
CH_4	8.6	9.5	1.1
C_2-C_4	26.4	25.0	1.8
C_5+	65	65.5	97
CO_2	35	44.0	38
Olefin % Content			
C_2-C_4 olefin fraction	82	84	93
C_{10}+ olefin fraction	65	67	63

Taken from Tables 2 and 4 of U.S. Patent 5118715 (X.13).

Table X.12. Activity of Fe-Zn Spinel. Catalysts pretreated to 500°C in a 9/1 H_2/N_2 mixture at 100 psi and 100 v/v/hr space velocity for 5-8 h. Runs made in 1.7/1 H_2/CO at 300 psi at 550 vol/vol/h, 270°C furnace temperature, 10.5 hrs on stream.

	1.0 Fe/0.065 Zn/0.030 Ce/0.030 K	Fe/1% K
CO conversion	98	96
wt% selectivity		
CH_4	3.0	9.4
C_2-C_6	36.0	50.1
C_7+	21.4	14.5
CO_2	39.6	26
Specific olefin/paraffin prodn. ratios were:		
C_2	3.1	2.5
C_3	7.5	8.0
C_4	15.0	8.3
C_5	7.5	3.7
C_6	4.6	2.0

Taken from Example 3, Table V of U.S. Patent 4639431 (X.16).

Table X.13. Activity of Fe-Zn spinels promoted with Cu and K prepared with glycolate. Runs made with 2 g catalysts in at 270°C in 2/1 H_2/CO, 75 psig at 180 cc/min in octacosane for 40-100+ hr periods.

	CO Conv	CH_4 selectivity	% olefins in C_4	% Olefins in C_2-C_4	% α-Olefin in C_{10}+
$Fe_{2.8}Zn_{0.2}O_4$·2 at% K	33	2	89		
$Fe_{2.8}Zn_{0.2}O_4$·1 at%Cu	34	10.1	81		
$Fe_{2.8}Zn_{0.2}O_4$·2 at%K+1 at%Cu	73	1.9	89		
$Fe_{2.8}Zn_{0.2}O_4$·2 at% K, 1 at% Cu	80	1.7		93	63
$Fe_{2.45}Zn_{0.55}O_4$·2 at% K, 1 at% Cu	84	1.7		92	61
$Fe_{2.3}Zn_{0.7}O_4$·2 at% K, 1 at% Cu	32	2.3		85	nd

Taken from Example 2, 6 and 7 of U.S. Patent 5100856 (X.17). Spinels having Fe concentrations greater than $Fe_{2.5}Zn_{0.5}O_4$ fall within claimed compositions.

Table X.14

Conversion of Synthesis Gas with $Fe_{3-x}Zn_xO_4$ in 0.3 L CSTR at 270°C, C_{28} Solvent, H_2/CO = 2, 75 psig (from U.S. Patent 5118715, (X.13)

Catalyst	$Fe_{2.8}Zn_{0.2}O_4$ A	$Fe_{2.55}Zn_{0.45}O_4$ B	$Fe_{2.3}Zn_{0.7}O_4$ C	$Fe_{2.79}Zn_{0.21}O_4$	$Fe_{2.79}Zn_{0.21}O_4$	$Fe_{2.79}Zn_{0.21}O_4$
% Fe	66.87	60.28	53.70	71.50	71.50	71.50
% g-atom K	---	---	---	2	2	0
% g-atom Cu	---	---	0	1	0	1
CO Conv., %	80	84	32	73	33	34
CH_4/% Carbon	1.7	1.7	2.3	1.9	2.0	10.1
Olefin, %						
C_2-C_4	93	92	85			
% α- in C_{10}	63	61	*			
% α- in C_4	---	---	---	89	89	81
NL/gFe-hr**	8.97 (7.18)	9.95 (7.96)	11.17 (8.94)	8.89 (7.11)	8.89 (7.11)	8.89 (7.11)
NL/g cat-hr	6.00	6.00	6.00	6.36	6.36	6.36

* Insufficient yield of liquids.
** NL total flow; parentheses, flow based on CO + H_2.

Table X.15. Comparison of Ce,K and K/Ce promoters for 1.0 Fe/0.30 Ti/0.065 Zn/0.03 Ce and/or 0.03 K in fixed-bed reactor. Pretreated at 500°C with 9/1 H_2/N_2 at 800 v/v/hr for 5-6 hrs. Runs made at 270°C, 1/1 H_2/CO at 2.6 MPa at 870 v/v/hr space velocity for time on stream of 30-50 hrs

	K	Ce	K/Ce
CO Conv	2	17	24
wt HC selectivity			
CH_4	42	24.5	14.8
C_2-C_3 paraffins	6	14.6	12.2
C_2-C_3 olefins	42	14.1	32.5
C_4+	10	46.8	40.5

Taken from Example 5, Table VII in U.S. Patent 4657885 (X.18).

Table X.16. Manganese Catalysts with Ce,K and K/Ce in fixed-bed reactor. Pretreated at 500°C with 9/1 H_2/N_2 at 800 v/v/hr for 5-6 hrs. Runs made with 1/1 H_2/CO, 870 v/v/hr, 305°C, 2.0 MPa

	K	Ce	K/Ce
CO Conv	18	62.5	54.9
HC selectivity, wt.%			
CH_4	10.2	17.5	7.5
C_2-C_3 paraffin	4.1	10.0	2.6
C_2-C_3 olefin	29.2	20.6	24.4
C_4+	56.5	51.9	65.5

Taken from Example 6, Table VIII in U.S. Patent 4657885 (X.18).

Table 17. Activity of a 10/1 Fe/Tl catalyst in a fixed bed reactor for synthesis gas conversion. Pretreated with 49 H_2/50 CO/1 N_2 at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made at 270 to 350°C, 1/1 H_2/CO at 120 psia and 150-1200 v/v/hr.

Temp, °C	270	300	325	350
CO Conv, %	90-20	65-40	96-80	97-90
Selectivity				
CH_4	6-4	6-3	6-10	9-15
C_5-C_{11}	50-54	51-57	50-51	42-51
C_4- (Gas)	35-30	34-26	35-39	39-50
Olefins in C_6+	21-26	23-26	21-16	14-8
Aromatics	2-3	2-3	4-8	7-14

Taken from Example 5, Tables 1 to 6 in U.S. Patent 4513104 (X.24).

Table X.18. Performance of Fe/Tl Catalysts in a fixed-bed reactor.
Pretreated with 49 H_2/50 CO/1 N_2 at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made with 1/1 H_2/CO at 300 GHSV and 0.9 MPa (130 psi).

	Fe/0.1 Tl			Fe/0.2 Tl	Fe/.04 K		NH_3 synthesis catalyst
Temp	350	350	270	350	350	270	350
GHSV	300	300	300	300	300	300	300
CO Conv	96.7	63.6	46.8	45.0	55.5	68.9	97.1
Selectivity to HC %	60.9	62.5	69.9	59.6	66.0	wax	69.5
C_1	10.1	13.0	3.4	16.6	11.1	3.0	3.3
C_1-C_5	38.4	44.7	30.4	46.6	31.8	-	42.2
C_6-C_{11}	45.3	45.4	44.8	39.0	32.5	-	42.3
C_{12}-C_{23}	16.0	9.7	23.8	13.6	24.9	-	14.8
C_{23}+	0.3	0.2	1.0	0.8	10.8	-	0.7
Aromatics	12.7	14.02	2.92	10.3	6.57	-	8.65
α-olefins	14.9	9.66	22.31	10.0	16.69	-	11.43

Taken from Example 9, Tables 10 and 11 in U.S. Patent 4513104 (X.24).

Table X.19. Activity of *in situ* prepared catalyst in a slurry reactor.
Runs made at 270°C, 1:1 H2/CO at 70 psig at 1200 V/V/hr in C16 paraffin solvent, 600 rpm.

Support	wt% support[a]		CO Conv	CO_2	CH_4	C_2-C_4 olefins	C_2-C_4 paraffins	C_5+
	Fe	Co						
None (Complexes only)	-	-	25	35.4	15.4	17.8	5.3	26.1
Fe_2O_3/1% K	9.5	3.2	54	50	3.0	7.2	1.1	38.5
Al_2O_3	4.8	1.6	21	25	20.0	18.3	9.0	27.7
Al_2O_3[b]	"	"	27	9.2	19.8	12.9	6.8	60.5
MgO	4.8	1.6	30	35	18.6	16.1	6.8	23.5
MgO/1% Cu	9.5	3.2	26	50	9.6	14.7	3.8	21.9

Taken from Example 1, Tables I and II, and Example 4, Table V, of U.S. Patent 4532229 (X.25).
a. Same weight of Fe and Co in reactor in all runs, except for Fe_2O_3/1% K run.
b. Product yield after 96 hours on stream.

Table X.20. Effect of air calcination on the crystalline form of titania

	Rutile content, wt%	Surface Area, m^2/g
Degussa P-25	28[a]-35[b]	60 m^2/g
500°C in air/16 hrs	55	33-36
500°C in air/16 hrs and H_2 at 450°C	67	22-26
560°C in air/ 4 hrs[d]	70	30
600°C in air/16 hrs	~100 (>30/1)	10-16
650°C in air/16 hrs[c]	97	14

a. From U.S. Patent 4711871 (X.32).
b. From U.S. Patent 4595703 (X.49).
c. From U.S. Patent 4663305 (X.57).
d. From U.S. Patent 4738948 (X.61).

Table X.21. Effect of calcination on rutile content of titanias

Source	Description	Binder/%	Hg PV[a], cc/g	Hg PD[b], Å	BET SA, m^2/g	% Rutile in titania	Calcination, °C/hr
Company A	-	none	0.253	140	45	27	-
Company A	-	none	0.162	270	15	92	700/1
Company A	-	none	0.134	250	14	95	700/1
Company A	-	none	0.120	481	5	100	840/1
Company A	Extrudate	none	0.154	389	8	98	650/16
$Ti(OC_3H_7)_4$ hydrolysis	-	none	0.160	n.a.	10	94	650/50
$Ti(OC_3H_7)_4$ hydrolysis	Extrudate	none	0.299	n.a.	41	n.a.	500/16
$Ti(OC_3H_7)_4$ hydrolysis	Extrudate	none	0.180	n.a.	15	n.a.	600/16
Company A	Extrudate	M/3.5	0.387	454	27	82	750/3
Company A	Extrudate	M/3.5	0.326	590	22	96	800/1
Company A	Extrudate	M/3.5	0.354	678	15	98	800/3
Company A	Extrudate	M/3.5	0.301	697	15	100	800/16
Company A	Extrudate	M/3.5	0.276	590	12	100	850/3
Company A	Extrudate	M/3.5	0.254	1151	13	100	850/10
Company A	Extrudate	M/3.5	0.237	1706	10	100	850/72

Taken from Example 1, Table 1 of U.S. Patent 4992406 (X.30).
M binder = 30 TiO_2/70 Al_2O_3
a. PV = pore volume.
b. PD = pore diameter.

Table X.22. Effect of rhenium on stability of Re/TiO_2 for synthesis gas conversion.
Conditions of run: 230°C, 280 psig, 2/1 H_2/CO, 1000 GHSV

	1% Ru and 0.5% Re/TiO_2	1% Ru/TiO_2
Half-life, days	231	26
CO Conv	97	97
HC Yield	90	94
Selectivities		
CH_4	3.7	3.5
CO_2	7.0	1.5

Taken from Example 1, Table I of U. S. Patent 4558030 (X.29).

Table X.23. Effect of Re/Ru ratios on Re promoted Ru/TiO_2 catalyst.
Conditions: 280 psig, 2/1 H_2/CO, 1000 GHSV

Wt.% Ru	Wt% Re	CO Conv	C_1 select	CO_2 select
0.1	1.0	11	4	20
0.5	0.5	33	7.5	5
0.75	0.5	43	9	6
1.0	0.5	82	5.6	6

Taken from Example 2, Table II of U. S. Patent 4558030 (X.29).

Table X.24. Effect of rutile content on activity of 1% Ru-0.5% Re on TiO_2.
Conditions: 230°C, 280 psig, 2/1 H_2/CO, 1000 GHSV at 90% CO conversion

Rutile/Anatase ratio wt	1.2/1	2/1	>30/1
Rutile, wt% in TiO_2	55	67	~100
C_1 selectivity	7	4.5	2
Half-life days	4	231	87
Deactivation, Δ *ln* k/day	−0.18	−0.003	−0.008
Pore Vol ml/g	0.4	0.2	0.15
SA m^2/g	35	24	12

Taken from Example 3, Table III of U. S. Patent 4558030 (X.29).

Table X.25. Selectivity of Ru Catalysts for synthesis gas conversion.
Conditions: Catalysts reduced in H_2 at 450°C for 1 hr before introducing 1/1 H2/Co at 980 kPa (9.5 psig),

	Temp	%CO Conv	Prod	Total wt%	Olefin, wt%	Paraffin wt%
2% Ru/TiO2	267	7	C1	14	-	-
			C_2-C_4	47	32	15
			C_5-C_7	39	23	16
			C8+	-	-	-
5% Ru/ηAl2O3	274	10	C1	24	-	-
			C_2-C_4	43	19	14
			C_5-C_7	32	6	6
			C8+	12		

Taken from Example 1, Table II of U. S. Patent 4042614 (X.31).

Table X.26. Methanol conversion over Ru/TiO_2.
Conditions: 230°C, 500 v/v/hr, fixed bed reactor

Methanol, psi	236	236	236[a]
H_2, psi	0	59	59
CO, psi	0	0	31
Methanol conv at 35 hrs, %	13	76	<3
Reactor effluent composition			
CO	38	1	84
CO_2	4	12	n.a.
CH_4	1	24	n.a.
C_2+	55	63	n.a.

Taken Example 4, Table IV and Example 6, Table VI of U.S. Patent 4513161 (X.36).
a. GHSV=560.

Table X.27. Activity of Ru on V, Nb and Ta oxides versus prior art.
Conditions: 3/1 H_2/CO, 1 atm, no other data provided.

	Temp C	CO Conv %	Hydrocarbon selectivities		
			CH_4	C_2-C_5 Olefins	C_2+
1% Ru/Nb_2O_5	234	7.8	48	22	52
1% Ru/Ta_2O_5	228	17.7	46	17	54
1% Ru/V_2O_5	243	4.1	45	28	55
1% Ru/SiO_2	232	4.1	87	2	13
1% Ru/Al_2O_3	244	14.1	71	10	29

Data taken from U. S. Patent 4171320 (X.37).

Table X.28. Reaction of a 0.76% Ru on TiO_2 in a fixed bed reactor.
Conditions: reduced at 400-450°C for 2-4 hrs in H_2. Run in 1.39/1 H_2/CO

Run No	3	5	7	14
Pressure,atm	3.0	3.0	5.0	4.3
^oC	206	224	218	213
GHSV	198	301	494	1240
H_2 Conv	84	84	89	26
CO Conv	84	84	89	30
Selectivity on CO_2 free basis				
CH_4	4.8	6.1	5.4	6.9
C_2/C_4	9.15	11.6	7.9	17.8
C_5-C_{20}	76.5	74.4	72.7	64.1
C_{20}-C_{40}	8.3	6.2	11.3	8.3
C_{41}+	0.15	0.13	1.5	0.2
Oxygenates	1.13	1.4	1.2	2.7
C_2= in C_2				40
C_3= in C_3				84
C_4= in C_4				82
Total olefin in C_7-C_{12}				39
Total olefin in C_4-C_{20}				31

Taken from U. S. Patent 4477595 (X.38).

Table X.29. Effect of support on activity of Ru catalysts
Fixed bed reactor with supported Ru, reduced at 400-450°C for 2-4 hrs in H_2

	0.76 Ru/ TiO_2	0.56 Ru/ Nb_2O_3	0.67 Ru/ Ta_2O_3	1.57Ru/ SiO_2	0.56Ru/ Nb_2O_3	1.1 Ru/ TiO_2	1.57Ru/ SiO_2	1.1Ru/ TiO_2	1.1Ru/ Al_2O_3
H_2/CO	1.39	1.39	1.39	1.39	2	2	2	2	2
Pressure, atm	5.0	5.0	5.2	21	7	4.6	4.6	2.1	2.1
°C	203	196	200	251	229	209	209	214	214
GHSV	298	300	303	200	1225	300	300	303	303
H_2 & CO Conv	86	88.3	79	88.7	81	82	5	87	32
Selectivity									
CH_4	2.9	2.0	5.5	7.5		4.3	10.6	6.7	16.6
C_2/C_4	6.2	2.5	18.5	17.4		12.5	34.0	12.8	19.5
C_5-C_{20}	65.5	62.1	66.5	71.3		81.6	51.1	68.8	59.2
C_{21}+	25.4	33.4	9.5	3.8		-	-	9.2	2.1

Taken from U. S. Patent 4477595 (X.38).

Table X.30. Activity of Ru on oxide modified titania surfaces.
Conditions: 230-250°C, 300 v/v/hr, H_2/CO=2, 60 psig, fixed bed reactor

	1% Ru/TiO_2	1% Ru/TiO_2 +10%Nb	1% Ru/TiO_2 +10%Ta	1% Ru/TiO_2 +1%Ta	1% Ru/TiO_2 +2%V	Physical Mixture 1% Ru/TiO_2 +10%Ta
Temp	238	230	235	232	252	240
H_2+CO conv	37	43	19.5	31.5	71.3	47.4
CO_2	3.8	1.9	3.7	3.2	3.5	5
CH_4	14.5	10.9	10.9	15.3	12.5	8.4
C_2	8.3	6.6	14.8	4.2	3.3	4.2
C_3+C_4	23.0	17.3	13.8	24.0	10.0	16.9
C_5+	50.4	63.3	56.8	53.3	70.7	65.5
HC products						
Alcohols	5.1	0	0	1.4	3.8	3.0
olefins	39.1	67.7	6.3	44.2	15.6	46.4
paraffins	34.	32.3	93.7	54.4	80.6	50.3

Taken from U. S. Patent 4711871 (X.32).

Table X.31. Activity of Ru/TiO_2 slurry catalyst.
Conditions: 1 g catalyst, 50 g octacosane, 6/3/1 $H_2/CO/N_2$, 1200 v/v/hr, 6 atm, 1 std L/g catalyst/hr

Catalyst 1% Ru	°C	% CO Conv	Selectivity			
			CO_2	CH_4	C_2-C_4	C_5+
Ru/TiO_2 Particulate, reduced 450°C	250	49	3.2	14.4	8.9	73.5
Ru/TiO_2 Particulate, not prereduced	260	10	2.0	20.0	30.0	48.0
Carbonyl based						
Ru	260	15	tr	4.7	19.5	75.8
Ru/CeO_2	240	<5	nil	na	na	na
Ru/Al_2O_3	240	25	3.0	19.3	9.4	68.3
Ru/TiO_2	240	55	6.7	12.3	17.5	63.5

Taken from U.S. Patent 4752600 (X.41).

Table X.32. Effect of steam treatment of Ru/TiO_2

Treatment of Ru/TiO_2	O/Ru ratio from O_2 chemisorption	Ru crystallite size Å
None	1.46	12
Air at 1 atm, 500°C/3 hrs	not reported	30
9/1 H_2O/H_2 at 280 psig, 300°C/4 hrs	1.08	15
9/1 H_2O/H_2 at 280 psig, 230°C/16 hrs	0.88	18
3% H_2O in N_2 at 1 atm, 500°C/3 hrs	0.98	16

Taken from Table 1, U.S. Patent 4647592 (X.43).

Table X.33. Effect of air treat on activity of Ru/TiO_2
Run in 2/1 H_2/CO, 210°C, 280 psig, and 1000 v/v/hr

Hrs	CO Conv	Selectivity to HC, %	wt.% selectivity		
			CH_4	CO_2	C_2+
No air treat					
0.7	84.8	80.3	7.3	5.3	87.4
1.4	94.8	90.8	4.9	4.2	90.9
2.4	94.7	88.2	3.6	6.9	89.5
3.0	98.3	89.6	3.6	8.8	87.6
3.7	97.7	89.5	3.8	8.4	87.8
Air treated sample					
0.7	78.6	72.1	3.0	8.3	88.7
1.3	91.9	85.0	2.3	7.5	90.2
2.2	94.5	88.5	2.3	6.4	91.3
3.0	93.7	88.6	2.5	5.4	92.1
3.7	93.1	88.9	2.5	4.5	93.0

Taken from Table II, U.S. Patent 4647592 (X.43).

Table X.34. Activity of Rh Catalysts for synthesis gas conversion.
Conditions: 1.6/1 H_2/CO, 100 kPa (1 atm), Catalyst reduced 450°C 1 hr,

	Temp	%CO Conv	CH_4 mol %	C_2-C_5 yield, mol %
2% Rh/TiO_2	248	1.3	74	26
2% Rh/Al_2O_3	265	3.5	15	85

Taken from U. S. Patent 4116994 (X.45).

Table X.35. Activity of rim-impregnated Co/TiO_2 catalysts
Conditions: 200°C, 2/1 H_2/CO, 2.1 MPa

Particle size, mm	2.2	2.2	0.1-0.2	2.2
Co Conc, wt%	13.0	13	13	20.9
Co Distribution	even	rim	rim	rim
Rim thickness, µm	-	80±30	80±30	120±30
Surface area, m^2/g	80	80	80	350
Hrs on stream	193	318	175	315
GHSV	420	650	940	1750
CO Conv, %	64.5	66.0	48.0	64.0
CO Conv, vol/vol/hr	90	150	210	342
Selectivity				
CH_4	12.0	8.3	4.7	12.7
C_2-C_4	5.1	4.4	4.7	5.3
C_5+	82.0	87.0	90.5	81.3
CO_2	0.9	0.4	0.1	0.7

Taken from Tables 1, 2, and 3 or U.S. Patent 5036032 (X.48).

Table X.36. Activity of Co/TiO_2 catalyst in a fixed-bed reactor.
Runs at 230°C, 150 psig, 400 GHSV, 2/1 H_2/CO

Cat		CO Conv	Selectivities			Schulz-Flory
			CO_2	CH_4	C_2+	
A	12 Co/TiO_2[b] (this invention)	88	1.1	8.6	90.3	0.91
B	100 Co/5 ThO_2/8 MgO/200 Kieselguhr[a] (known)	43	4.3	10.3	86.4	-
C	12 Co/SiO_2 (known)	72	1.6	8.7	89.7	0.85
D	25 Co/1.8 Ti/100 SiO_2 (known)	21	1.9	13.8	84.3	0.74

Taken from Example 7 in U. S. Patent 4542122 (X.46).
a. Conventional FT catalyst
b. Rutile/anatase ratio of 3.2. Reduced in H_2 at 450°C for 1 hr

Table X.37. Activities of Co and Co-Re on TiO_2 in a fixed-bed reactor. (Data shown in Figure 1 in Patent 4542122) Catalyst impregnated with nitrate/perrhenic acid and calcined in air at 500°C/3 hrs. Catalysts reduced in H_2 at 450°C for 1 hr. Runs made at 200°C, 2.15/1 H2/CO, 280 psig, GHSV=1000.

Metals, wt% on TiO_2	Rutile in TiO_2, wt%	Air treat°C for 3 hrs	O_2 chemisorp. μ mol O_2/ g cat	%CO Conversion	Surface area m^2/g	CH_4	CO_2	C_2+
12 Co	53	250	213	67	36	9.7	0.2	90.1
12 Co	100	250	265	79	10	11.5	0.7	87.8
12 Co	56	500	178	54	33	9.9	-	90.1
12 Co	100	500	202	67	10	11.7	0.3	88.0
12 Co-0.1 Re	100	500	145	67				
12 Co-0.5 Re	56	500	343	85				
12 Co-0.5 Re	100	500	285	82				
12 Co-3 Re	56	500	399	81				

Table I in U.S Patent 4568663 (X.51).

Table X.38. Effect of Anatase-Rutile Ratio on Co/TiO_2 catalyst.
Catalysts impregnated with cobalt carbonyl from pentane solution. Run conditions: 200°C, 280 psig, 1000 GHSV, H_2/CO=2.15/1

Co, wt%	10.1	9.2
Rutile in Titania, wt%	28	~100
Pretreatment Conditions:		
1st Stage	250°C/ air/3 hrs	250°C/ air/3 hrs
2nd Stage	450°C/ H_2/1 hr	450°C/ H_2/1 hr
CO Conv, mol %	5	97
CH_4 Yield, mol %	15.1	5.4
O_2 Chemisorption, umol/g cat	53	205

Example 9 in U.S. Patent 4542122 (X.46) and Example 3 in U.S. Patent 4595703 (X.49).

Table X.39. Effect of rutile content on Co/TiO_2.
Run at 230°C, 40 MeOH:2 H_2:1 CO_2:7 Ar, 400 psig, GHSV=500.

Rutile content, %	55	100
MeOH Conv	66	100
Carbon Product Distribution		
CO	2.6	0.8
CO_2	15.6	27.8
CH_4	9.0	17.1
C_2+	72.8	54.3

Taken from Example 6 in U.S. Patent 4542122 (X.46).

Table X.40. Activity and selectivity of Co on titania based catalysts for methanol conversion (rutile not specified).
Run conditions: 230°C, 400 psig, GHSV=500, 40 $_2$MeOH:2 H_2:1 CO_2:7 Ar

	12% Co/TiO_2	12% Co/2% ThO_2/TiO_2		100 Co/5 ThO_2/8 MgO/200 Kieselguhr[a]	12% Co/ SiO_2	12% Co/ Al_2O_3
MeOH Conv, 35 hr	52	70[b]		97	38	64
Carbon Product Distribution						
CO	5.5	3.1	2.9	1.0	4.3	2.8
CO_2	12.9	17.0	12.6	38.4	22.3	21.8
CH_3OCH_3	0.2	0.3	0.5	-	0.1	2.4
CH_4	11.2	8.6	7.4	19.5	7.0	9.9
C_2+	70.2	71.0	76.6	41.1	66.3	63.1
Schulz-Flory Alpha	0.86	0.88	n.p.	n.p.	n.p.	n.p.

Example 5 of U.S. Patent 4542122 (X.46).
a. Conventional FT catalyst
b. Two sets of data provided for the same conditions having the same MeOH conversion that was not otherwise specified.
n.p. = not provided

Table X.41. Effect of Re on MeOH conversion over Co/TiO_2 with or without ThO_2. Run conditions: 230°C, 400 psig, GHSV=500, MeOH/Argon=4. Catalysts calcined 500°C

	12 Co/ 2 ThO_2/TiO_2	12 Co/2 ThO_2/ 0.5 Re/TiO_2	12 Co/ 0.5 Re/TiO_2
Rutile Conc, %	56	56	56
MeOH Conv	49	100	87
Product Distribution			
CO	6	2	2
CO_2	14	28	22
CH_4	6	14	9
C_2+	74	56	67

Table III in U.S. Patent 4568663 (X.51).

Table X.42. Effect of H_2 partial pressure on MeOH conversion.
Co/ThO2/TiO2 (rutile and catalyst composition not specified) at 230°C, 500 GHSV, 400 psig

Partial Pressures, psig			
MeOH	332	332	332
Ar	83	66	0
H_2	0	17	83
MeOH Conv, wt%	38	52	83
Carbon Product Distribution			
CO	8.5	3.9	0.9
CO_2	11.3	8.9	12.2
CH_3OCH_3	1.0	0.4	0.1
CH_4	4.6	5.7	15.9
C_2+	74.6	81.1	70.9
CH_4 in hydrocarbon, wt%	5.8	6.6	18.3

Table IV in U. S. Patent 4542122 (X.46).

Table X.43. Effect of promoter on MeOH Conversion on Co/TiO_2.
Conditions: 230°C, 400 psig, LHSV=0.67, 20 MeOH/1 H_2/4 Argon

Catalyst composition					
Wt% Co	5.0	4.34	4.65	4.55	4.73
Promoter @ 1 wt%	none	Zr[a]	Hf	Ce	U
MeOH Conv	31	37	34	49	46
Rate MeOH Conv, g/hr/g Co	1.6	2.3	1.9	2.8	2.6
Carbon Prod Distribution					
CO	16	13	16	10	9
CO_2	8	9	7	9	13
CH_4	8	8	8	7	9
C_2+	68	70	69	74	69

Table IV, Example 2 in U.S. Patent 4663305 (X.57).
a. The Zr salt was $ZrO(O_2CCH_3)_2$.

Table X.44. Effect of silica promotion on CoRe/TiO_2 in a fixed-bed reactor.
Conditions: 200°C, 2.1 MPa, H_2/CO=2, run at space velocity to give ~60% CO conversion.

	(A) CoRe/TiO_2		(D) CoRe/TiO_2		(B) CoRe/TiO_2 +SiO_2		(C) CoRe/TiO_2 +SiO_2	
% SiO_2	0		0		4		5.2	
Steam treat H_2O (40 Torr)/He at 400°C/13 hrs	No		Yes		Yes		Yes	
reduction in H_2	250°C for 13 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs	
Hrs on stream	50	139	49	190	47	120	49	119
CO Conv	61.5	64	67	58	69	61	60	55
mol CO conv/g atom Co-hr	5.7	5.5	5.1	4.4	7.5	6.8	8.3	7.5
CH_4	5.3	5.1	4.6	5.0	5.2	5.6	5.4	5.8
C_2 (O/P)	0.6 (0.12)	0.6 (0.14)	0.6 (0.17)	0.6 (0.19)	0.7 (0.11)	0.7 (0.13)	0.6 (0.13)	0.6 (0.14)
C_3 (O/P)	2.1 (1.9)	1.9 (2.1)	2.2 (2.6)	2.1 (2.8)	2.4 (2.0)	2.5 (2.1)	2.3 (2.0)	2.3 (2.1)
C_4 (O/P)	2.3 (0.70)	2.16 (0.63)	2.0 (1.6)	1.9 (1.6)	2.4 (1.1)	2.6 (1.3)	2.6 (1.2)	2.5 (1.3)
C_5+	89.5	89.9	90.3	90.1	89.3	88.5	89.1	89.1
CO_2	0.2	0.2	0.3	0.3	0.07	0.06	0.05	0.04

Combined Table 1 and Table 2 of U.S. Patent 4794099 (X.58).
(O/P) = olefin/paraffin ratio

Table X.45. Effect of Precalcination on FT activity of Co-Ru/TiO_2 catalyst in fixed-bed reactor. Runs made at 200°C, $60H_2/30CO/7N_2$, 75 psia, space velocity adjusted; catalysts 70% rutile titania,

	D	A	B	C
	20% Co/ SiO_2	11.6% Co/ TiO_2	Reduced 11.6% Co/ 0.14% Ru/TiO_2	Calcined-reduced 11.6% Co/ 0.14% Ru/TiO_2
1st Calcination	none	400°C/16 hrs	400°C/16 hrs[a]	400°C/16 hrs[b]
Reduction/oxidation /reduction step[c]	No	No	No	Yes
CO Conv	65	50	64	68
CH_4 select	7.4	9.3	6.8	6.5
C_5+ select	82	80.2	87.3	87.8
Co time yield[d]	1	0.6	2.0	2.9

Taken from Table III in U. S. Patent 4738948 (X.61).
a. Ru impregnated to catalyst A after 1st calcination.
b. Started with catalyst B.
c. Calcined in air at 300°C/4 hrs and then reduced in H_2
d. moles CO converted per hr g-atom Co in catalyst.

Table X.46. H_2 Regeneration of Air-calcined-reduced Co-Ru/TiO_2Catalysts Aged 10-30 days

	CO Conv, %	Co time yield, hr^{-1}	CH_4	C_5+
Cat A. Co/TiO_2	At 560 kPa, 200°C, H_2/CO=1			
Initial	20	0.6	8.9	80.1
Aged	20	0.5	9.5	81
H_2 Treated	20	0.5	9.5	80.5
Cat. B CoRu/TiO_2	At 2060 kPa, 200°C, H_2/CO=1			
Initial	50-60	2.6	7.0	86
Aged	50-60	2.0	8.2	84
H_2 Treated	50-60	2.6	6.5	87
Cat. C. CoRu/TiO_2 Calc	At 2060 kPa, 200°C, H_2/CO=1			
Initial	50-60	4.5	5.5	91.0
Aged	50-60	3.9	6.4	88.8
H_2 Treated	50-60	4.8	4.9	91.5

Taken from Example 5, Table IV in U. S. Patent 4738948 (X.61).

Table X.47. Synthesis gas conversion activity of Fe-coated, vanadia and niobia modified titanias in a fixed-bed reactor. Runs made with 1:1 H_2/CO, 500 v/v/hr, 300 psig

	4% Fe/TiO_2			4% Fe/TiO_2+V			4%Fe/TiO_2+Nb
Temp	305	315	270	290	305	270	270
CO Conv	47	60	27.0	49	70	34.3	20.1
Selectivity (CO_2 free)							
CH_4	21.0	24.4	21.0	16.1	17.8	13.0	14.6
C_2-C_4 olefins	14.6	13.3		42.7	23.4		
C_2-C_4 paraffins	35.9	36.3	55.0	21.2	44.2	41.5	32.9
C_5+	27.5	26.0	24.0	20.0	14.6	45.5	52.5

Taken from Tables 1 and 2 in U. S. Patent 4559365 (X.68).

Table X.48. Selectivity of TiO_2 Promoted Nickel Catalysts for Synthesis gas conversion in a fixed-bed reactor.
Run conditions: 250°C, 3/1 H_2/CO, 1 atm., catalyst reduced in H_2 at 250°C/1 hr.

	CO Conv %	HC Selectivity, wt%			umol/min/g of Ni[a]		H_2 chemisorption umol/g	BET SA m^2/g	H/M
		CH_4	C_2-C_3	C_4-C_6	CH_4 formation rate	CO Conv rate			
Ni Powder	4.9	88	12	-	9.7(.0115)	11.0 (.0131)	7.0	0.41	0.0131
0.007% TiO_2 on Ni	11.6	74	16	9	19.1(.0295)	26.3 (.0406)	5.4	0.48	0.00063
0.07% TiO_2 on Ni	27.2	38	42	19	21.9(.0468)	60.2 (.129)	3.9	0.60	0.00046
0.20% TiO_2 on Ni	25.4	39	44	17	21.2 (.0281)	56.6 (.0748)	6.4	1.15	0.00075
1.66% TiO_2 on Ni	15.9	36	44	21	11.7 (.0244)	34.7 (.0723)	4.0	7.69	0.00047
8.40% TiO_2 on Ni	18.8	33	42	24	14.3	46.0			
10% Ni on TiO_2	49.0	37	34	28	14.6 (0.0194)	41.6 (0.0550)			
1/1 Ni powder + TiO_2	2.1	92	8	-	7.6 (0.0101)	8.3 (0.0110)			

Taken from U.S. Patent 4273724 (X.70).

a. ( ) numbers in parenthesis are reactions/site/sec or turnover number.

Table X.49. Activity of Cu-promoted Co-Mo spinel catalysts in a slurry reactor. Conditions: CSTR: 2/1 H_2-CO feed, 270°C, 75 psig, and 2000 h^{-1} gas space velocity in octacosane. Catalyst first reduced *in situ* at 100-270°C with H_2/CO at 1000-2000 v/v/hr flow rate at 75 psig.			
	Co_2MnO_4/1% Cu	Co_3O_4/1% Cu	Co_2MnO_4
CO Conv	45	23	nil
wt% Prod Select			
CO_2	16	54	-
CH_4	7	40	-
C_2-C_4	26	6	-
C_5+	51	nil	-
%olefins in C_2-C_4	83	52	-
Taken from U. S. Patent 5162284 (X.73).			

Table X.50. Synthesis gas conversion for making alcohols Conditions: 1/1 H_2/CO, 50 atm.. GHSV 1832			
	$Cu_{0.5}Mg_5CeO_x$	0.9%K on $Cu_{0.5}Mg_5CeO_x$	$Cu_{0.45}NdCeMgO_x$
Temp, °C	290	320	290
CO conv, %	25.5	15.5	20.6
CO_2	22.5	31.0	17.1
Selectivity, % C exclusive of CO_2			
Methanol	70.7	57.2	82.6
Isobutanol	8.2	10.4	8.2
Other alcohols	4.9	6.9	2.4
Methane	8.4	11.5	3.7
Higher Hydrocarbons	4.1	12.8	2.7
DME	3.3	1.2	1.6
Taken from U. S. Patent 5387570 (X.81).			

Table X.51. Synthesis gas reaction in dual fixed-bed reactors with different catalysts . First stage bed: 20g Fe/Zn/Ce/K Second stage bed: 1.5 g Ru/TiO_2 + quartz	
Temp, ^oC	220
Pressure, atm	6.47
H_2/CO mole ratio	1.64
Flow rate, sccm/min	36.5
CO Conv	59.0
CO_2 Selectivity in upper bed	26
CH_4 Selectivity	2.5
HC Selectivity in upper bed	33
HC Selectivity in lower bed	41
Taken from U. S. Patent 4624968 (X.82).	

Table X.52. Hydrocarbon selectivity from one and two-stage beds

	First stage Fe/Zn/Ce/K	Second stage Ru/TiO_2	2-Stage Beds	
			Predicted	Observed
CH_4	3.5	6.1	4.9	3.9
C_2-C_4	18.5	11.0	15.4	13.8
C_5-C_9	22.9	24.7	23.9	22.6
C_{10}+	55.1	58.2	56.8	60.3

Taken from U. S. Patent 4624968 (X.82).

Table X.53. Effect of adding ethylene to the feed

	Catalyst					
	Ru-Co/TiO_2			Ru/TiO_2		
C_2H_4 in feed, %	0	2.5	2.5	0	6.2	6.2
Location of C_2H_4 Addition[a]	-	inlet	below top one-third	-	inlet	below top one-third
CO Conv %	25-27	25-27	25-27	35-45	35-45	35-45
C_2H_4 Conv		99.5	89.5		97	45.3
C_2H_4 Selectivity	-			-		
to C_2H_6	-	86.5	69.5	-	82	44
to C_3+	-	13.5	30.5	-	18	56
Added C_2H_4 that appears as C_3+ %		13.5	27.3	-	17	26
% Selectivity[b]						
CH_4	9.4	8.3	7.2	5.5	4.3	3.9
C_2	1.3	-	-	0.7	-	-
C_3	2.7	3.3	3.7	2.1	2.6	3.4
C_4	2.4	2.9	3.7	3.5	4.0	5.1
CO_2	0.4	0.5	0.4	0.7	0.7	0.7
C_5+	83.8	92.9	99.3	87.5	105.6	117.0

Example 3 in U.S. Patent 4754092 (X.85).

a. Downflow reactor.

b. Selectivity defined as percent CO converted. When ethylene is added, the sum of selectivities is >100%.

Table X.54. Effect of heating rejuvenation tubes on catalyst activation.

Heat addition	no	Yes
Gas rate in tube, scfh	5100	4800
Avg reactor temp, °F	427	427
Avg rejuvenation temp, °F	430	440
CO conv, start to end of run, %	32 to 26 (over 12 hrs)	26 to 36 (over 24 hrs)
Conv, change/day	-12.4	+10.4

Example 4 in U.S. Patent 4754092 (X.85).

Table X.55. Improvement in catalyst/wax separation in slurry FT processes by removal of catalyst fines.

Classification Solvent	Catalyst/solvent wt/wt	Other	Cycles	Acetone cycles	Filter time	Filter rate	
						(gm/min)	gal/ft^2/min
0.45 μm Millipore filter paper							
Blank	-	-	-	-	95.0	0.5	
Water	15/85	-	6	2	0.9	55.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% Oleic acid added	7	2	1.0	50.0	
i-C_3H_6OH/n-C_7H_{16} (1/9)	10/150	1% Aerosol OT-100 added	7	2	1.0	50.0	
0.3 μm glass fiber filter							
FT wax @ 130°C	2/98	Stirred 5 min	none	none	-	-	5.8 @ 14 psig
		Stirred 44 hrs	none	none	-	-	0.05 @ 14 psig
FT wax @ 120°C	2/98	Stirring per cycle19/48/24	3	none	-	-	14.5 @ 14 psig

Taken from U.S. Patent 5070064 (X.98).

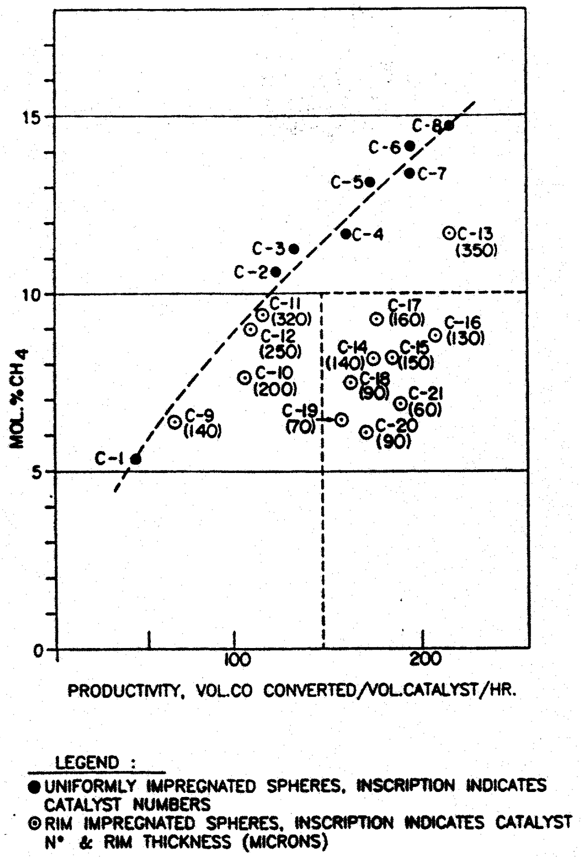

Figure X.1. Plot of methane production for various catalysts (from ref. X.50).

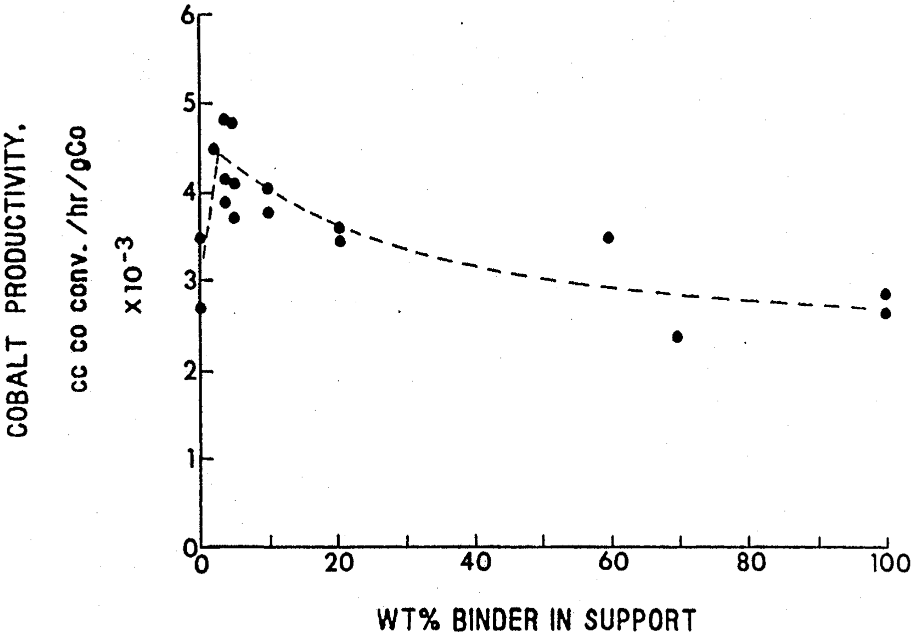

Figure X.2. Plot of cobalt productivity versus binder content in the titania support (from ref. X.30).

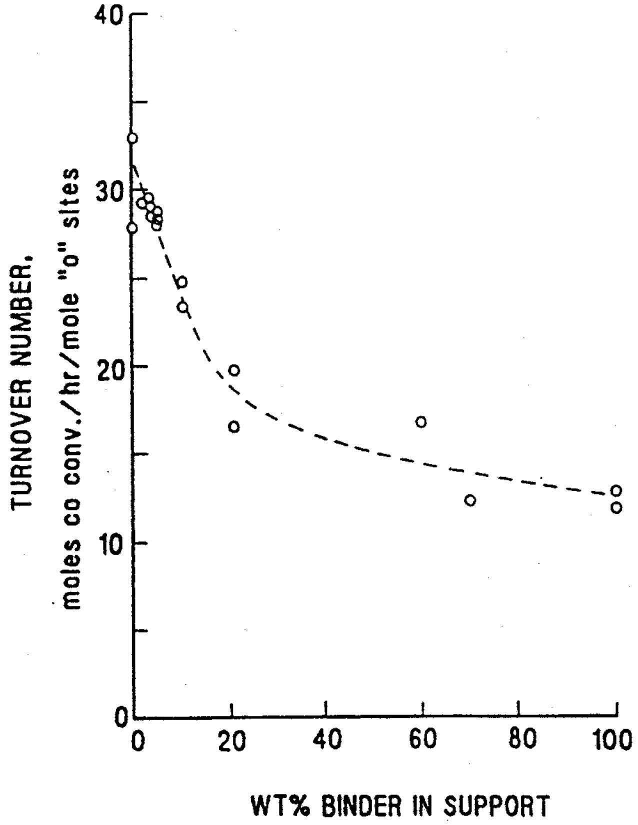

Figure X.3. Plot of wt.% of binder versus turnover number (TON) (from ref. X.30).

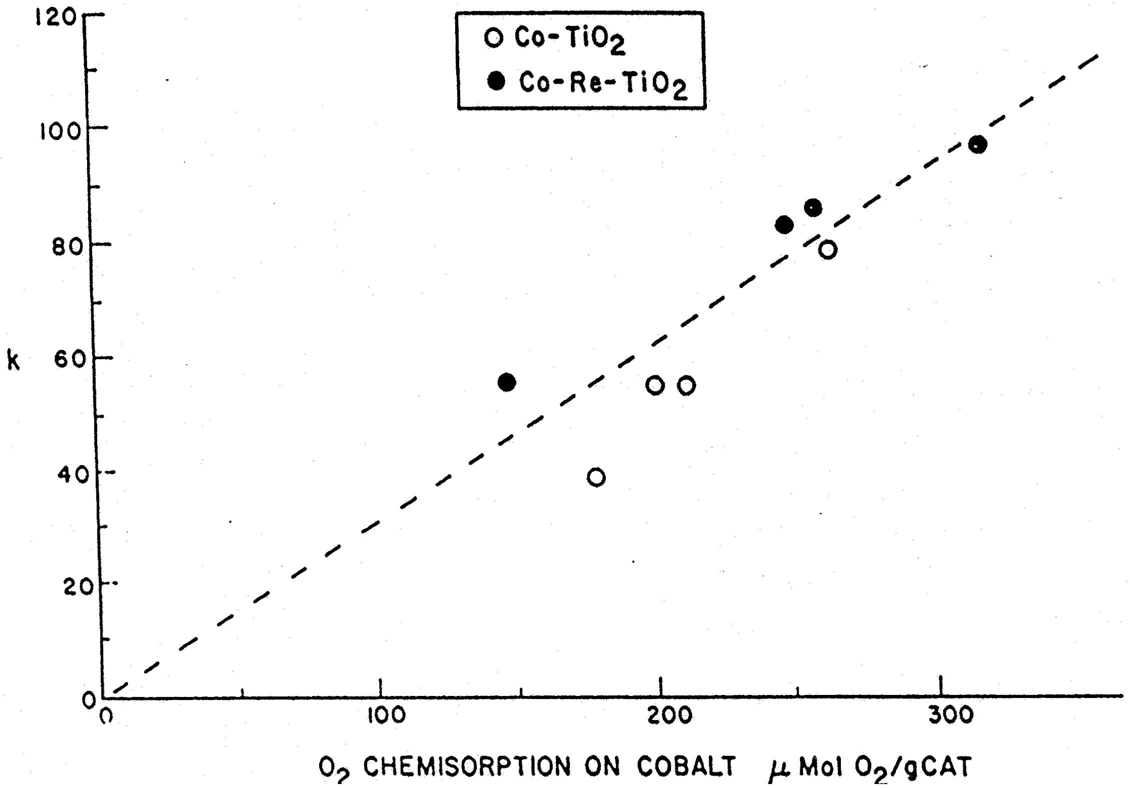

Figure X.4. Effect of dispersion on cobalt catalyst activity (from ref. X.51).

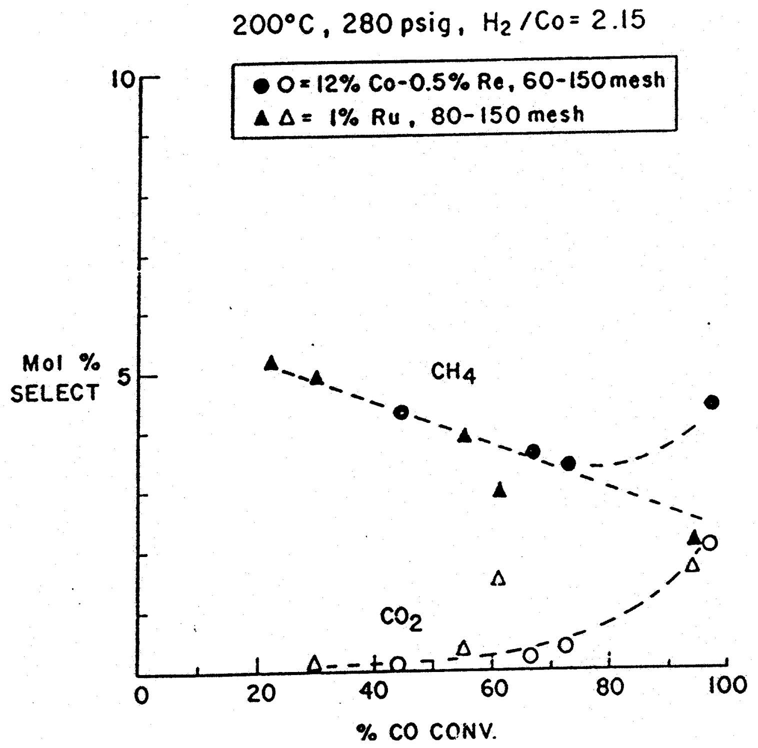

Figure X.5. Dependence of CH_4 and CO_2 production on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

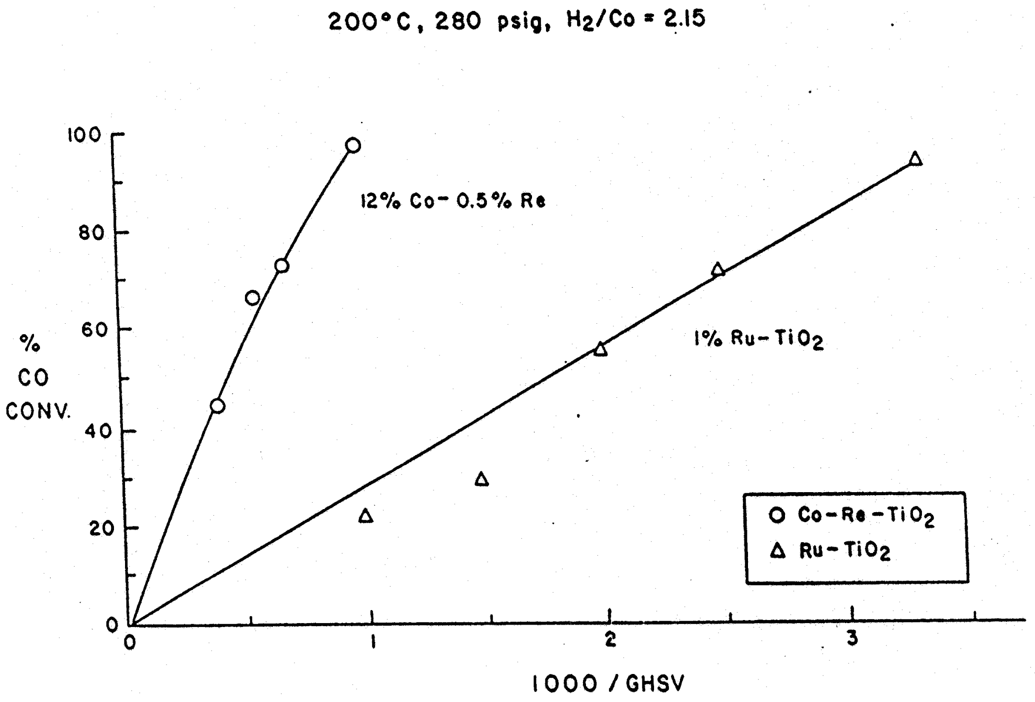

Figure X.6. Dependence of CO conversion on presence of ruthenium or rhenium in the cobalt catalyst (from ref. X.51).

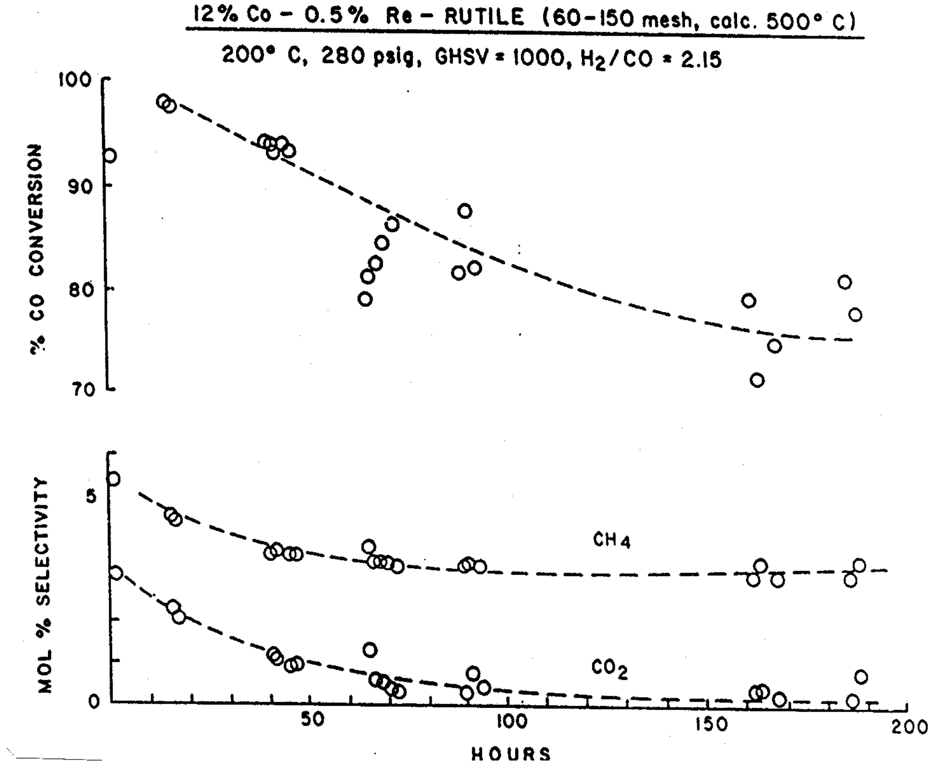

Figure X.7. The CO conversion and the methane and CO_2 production at increasing conversion time using a Co-Ru-TiO_2 catalyst (from ref. X.51).

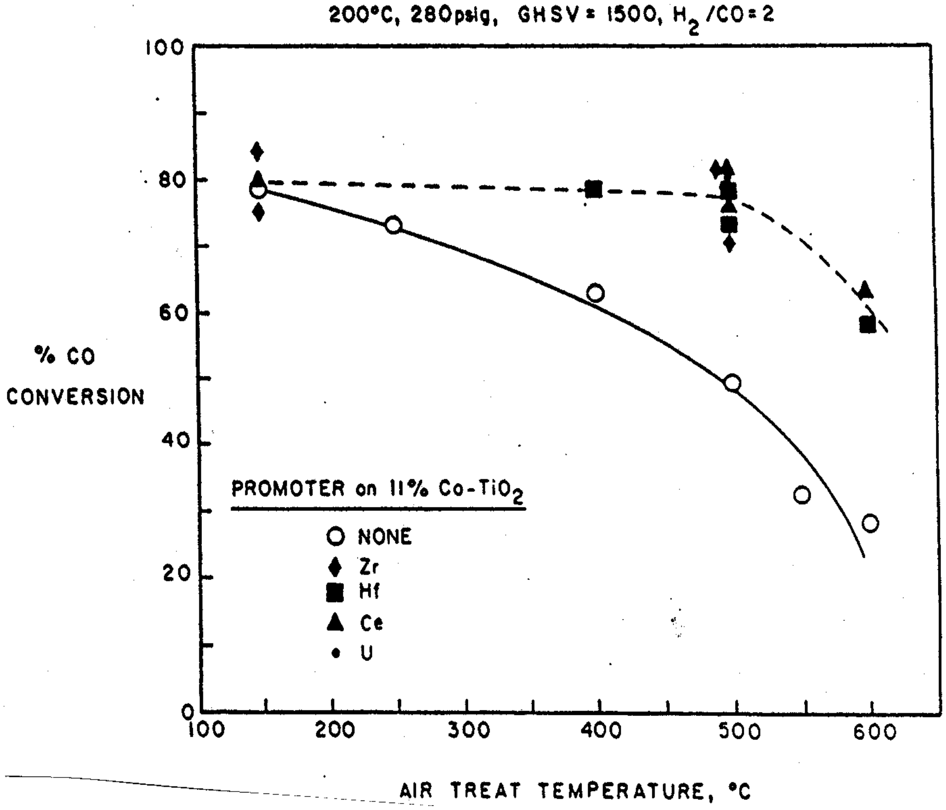

Figure X.8. Comparison of activity for Zr, Hf, Ce and U promoted Co-TiO_2 catalysts and unpromoted catalysts after simulated catalyst regeneration (from ref. X.57).

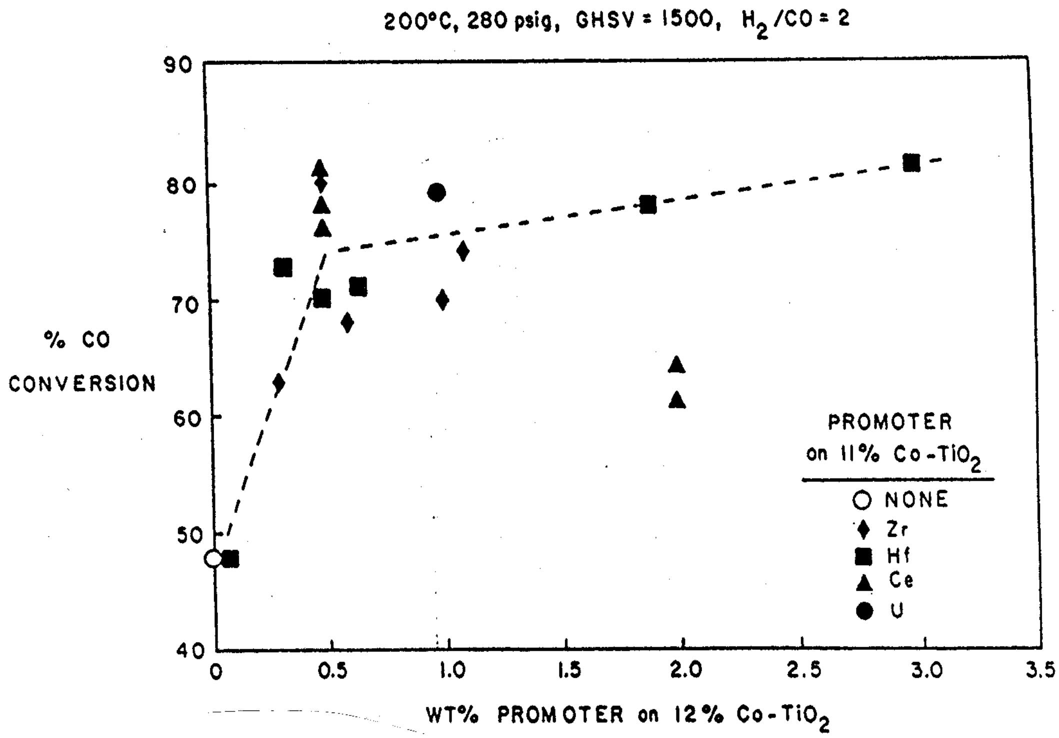

Figure X.9. Effect of promoter loading on Co-TiO_2 catalyst after simulated regeneration at 500°C (from ref. X.57).

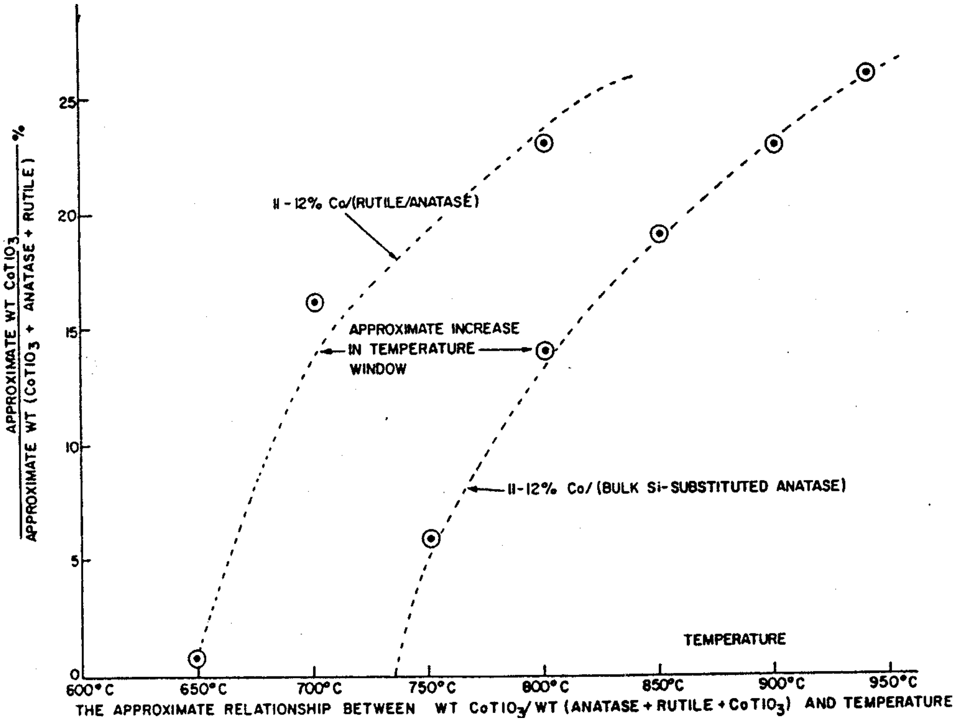

Figure X.10. Relationship between wt.% Co-TiO_3 and total TiO_2 versus temperature (from ref. X.60).

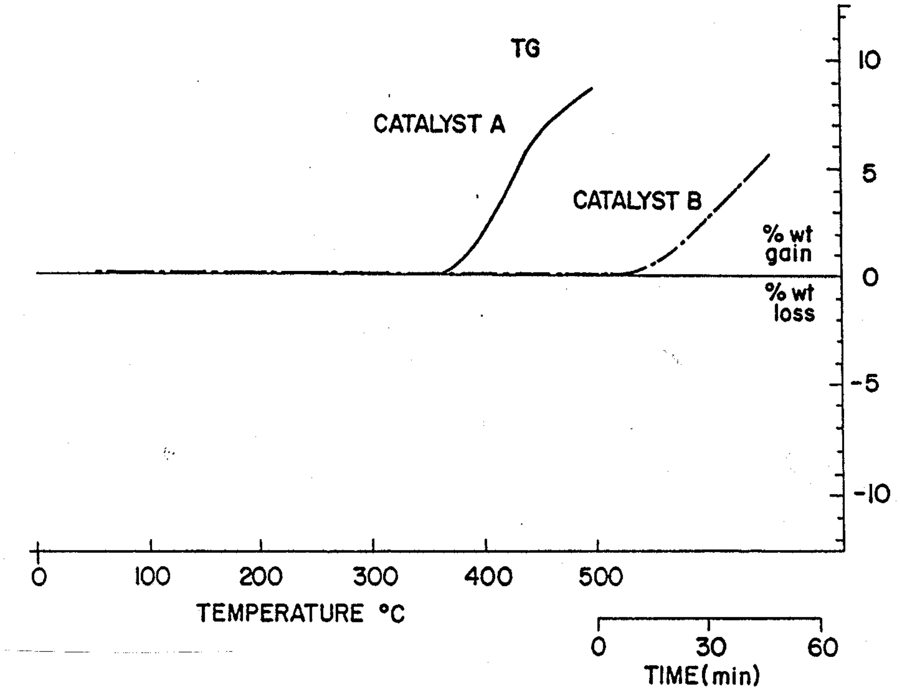

Figure X.11. Effect on catalysts A and B (see text) of carburization showing that silica suppresses carbon growth (from ref. X.58).

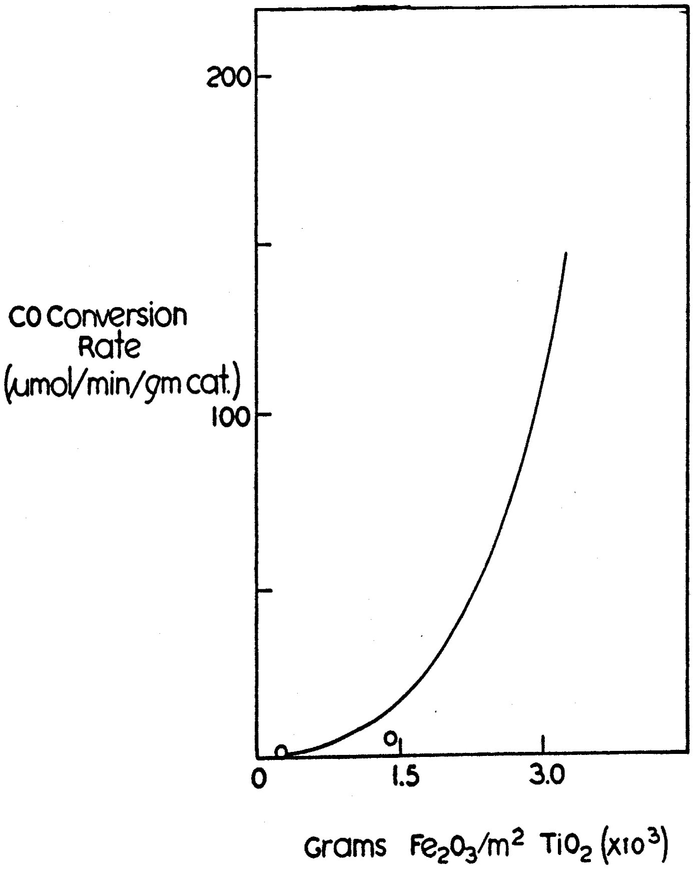

Figure X.12. Plot of CO conversion rate as a function of the iron loading on titania (from ref. X.64).

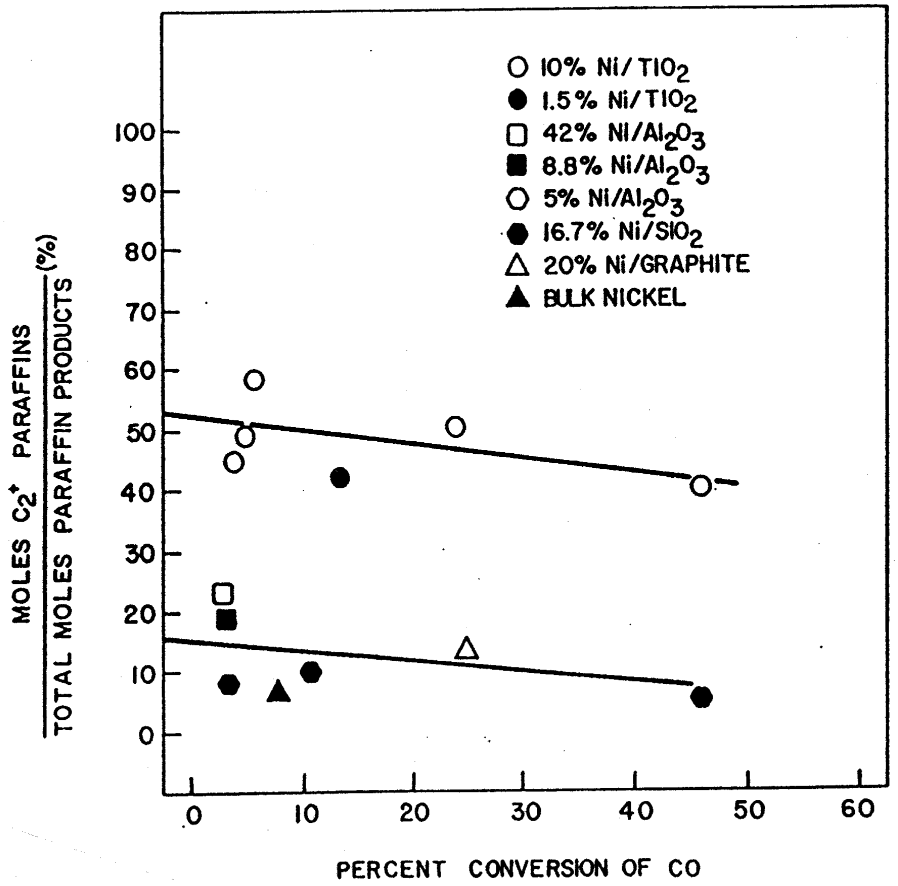

Figure X.13. C_{2+} selectivity for increasing conversion with nickel catalysts (from ref. X.69).

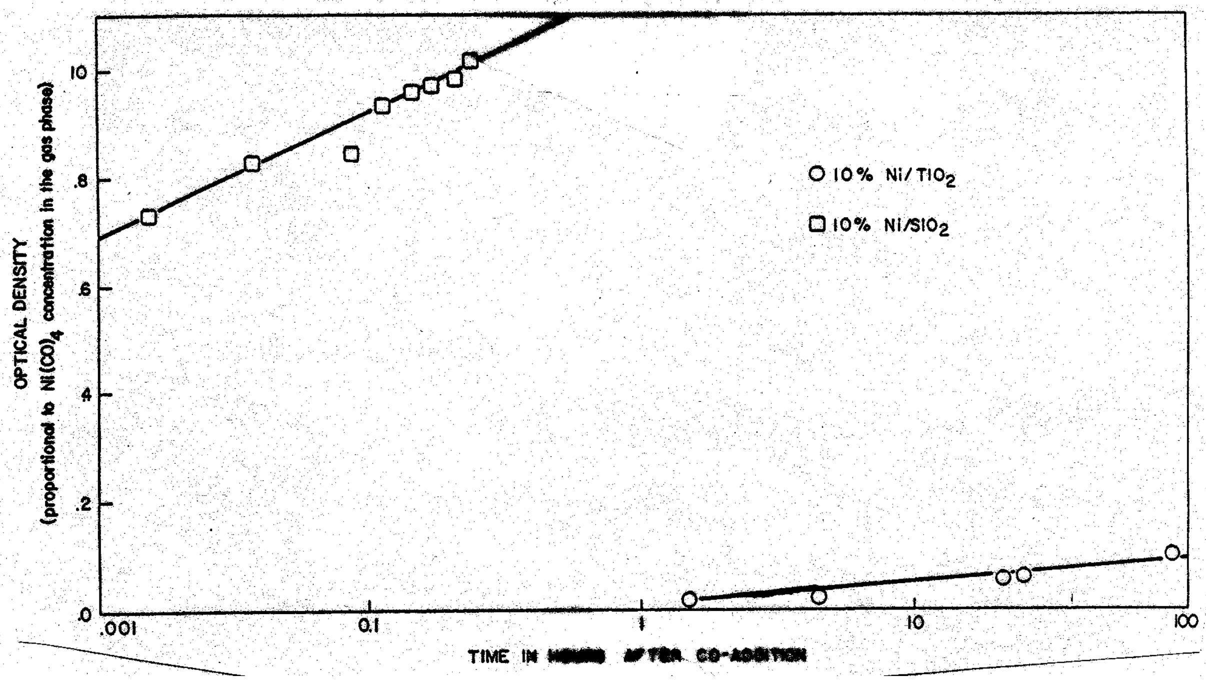

Figure X.14. Impact of support on the rate of nickel carbonyl fraction (from ref. X.69).

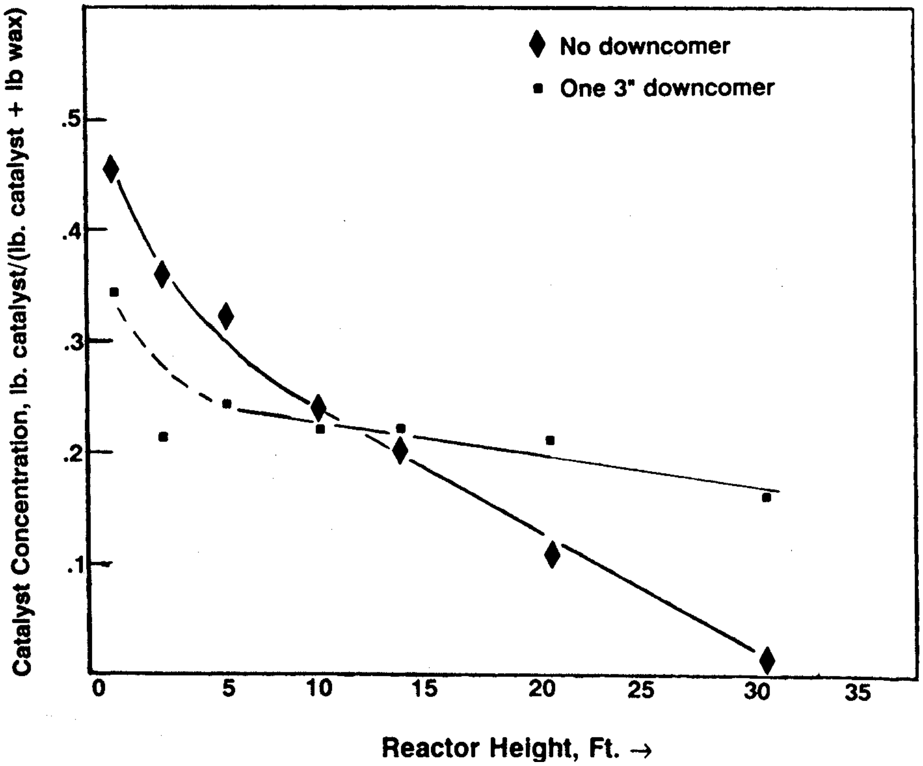

Figure X.15. Catalyst concentration versus reactor height for (!) no downcomer and for one 3" downcomer (Q).

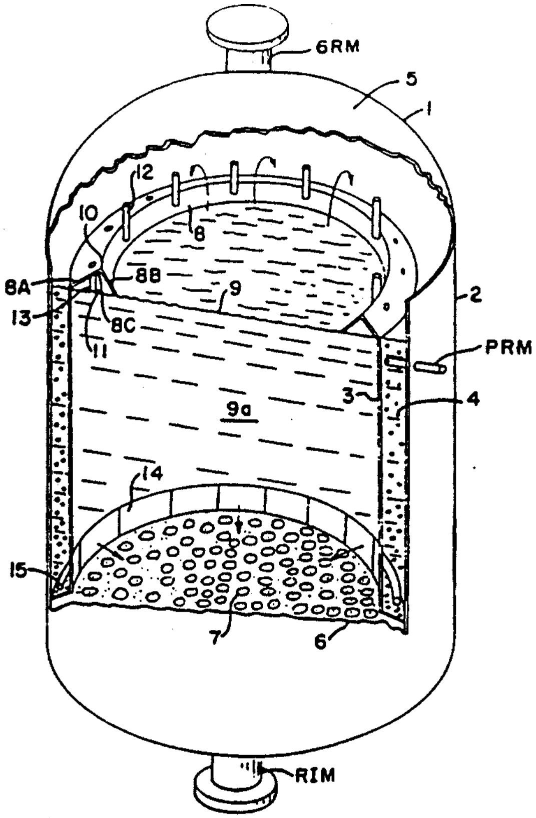

Figure X.16. Schematic of reactor for enhanced gas separation for bubble column draft tubes (from ref. X.90).

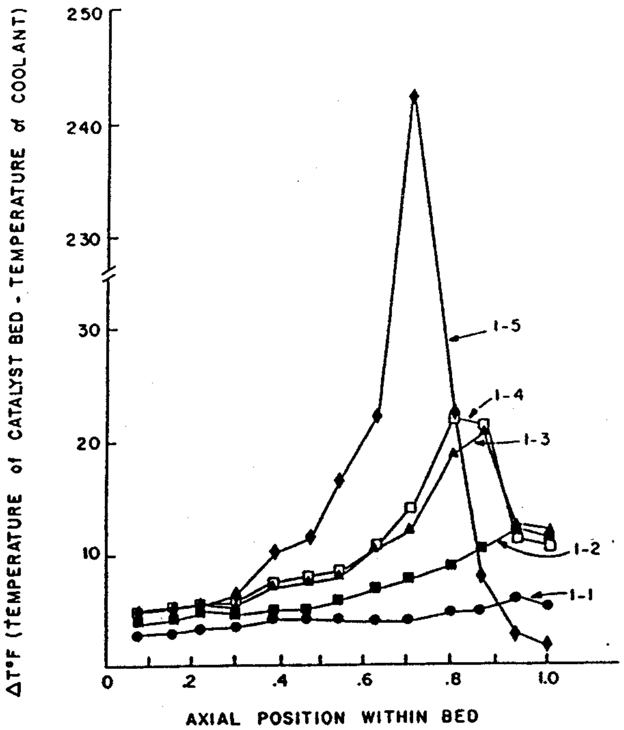

Figure X.17. Temperature exotherm within bed position for different start-up procedure (see text) (from ref. X.35).

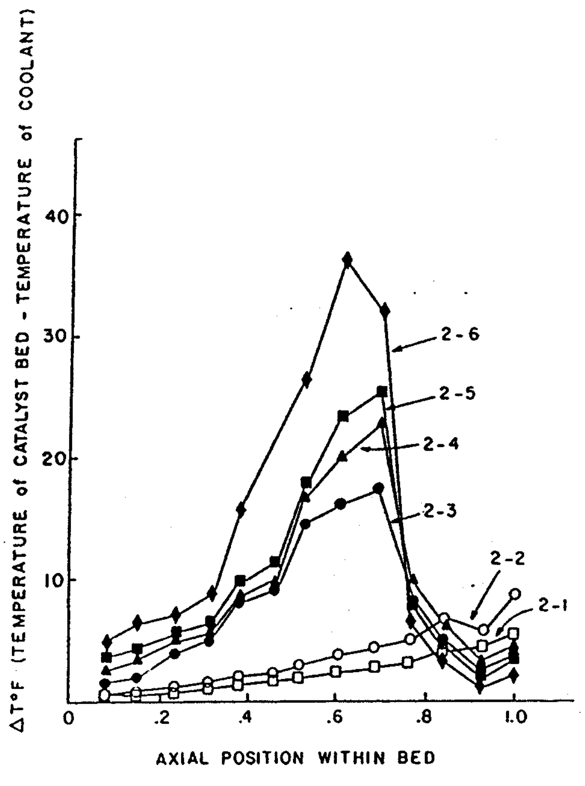

Figure X.18. Temperature exotherm within bed position for low H_2:CO ratio start-up (from ref. X.35).

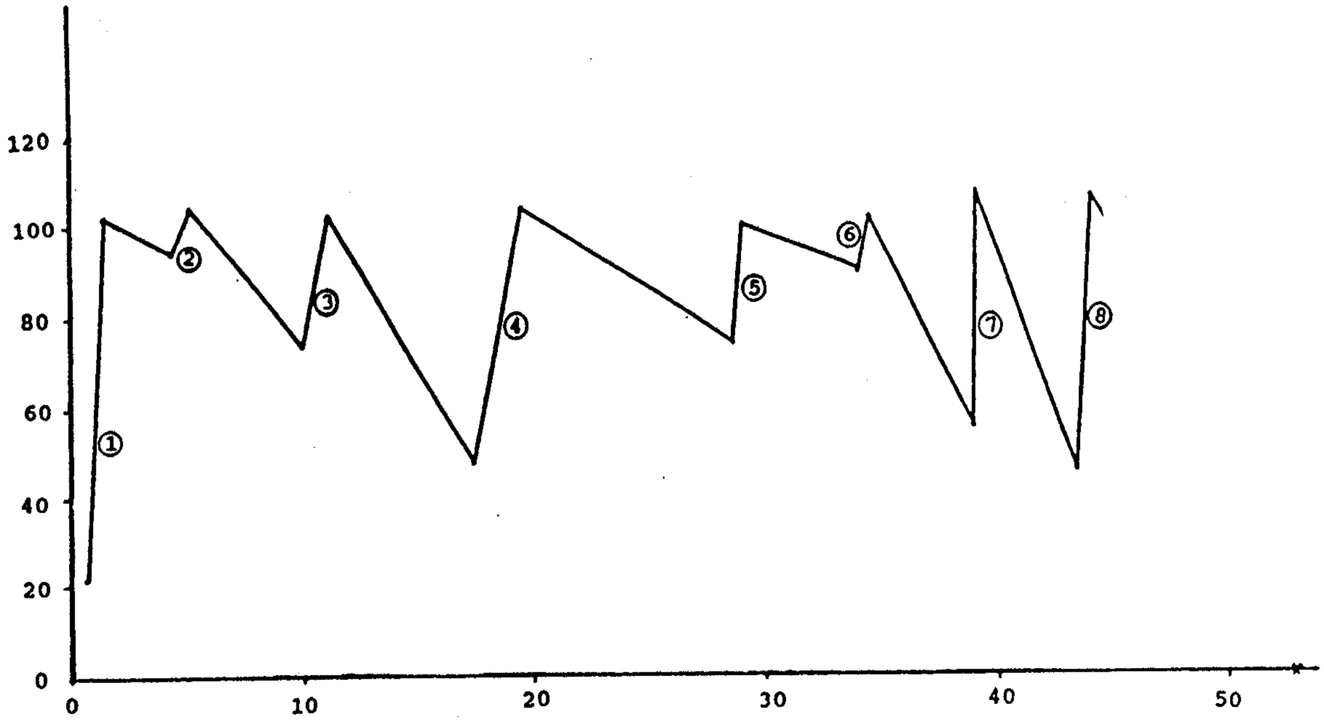

Figure X.19. Relative volumetric productivity represented by activity with days on stream with intervals of hydrogen rejuvenation (12 wt.% Co on titania with 6 wt.% Al_2O_3 as binder (from ref. X.96).

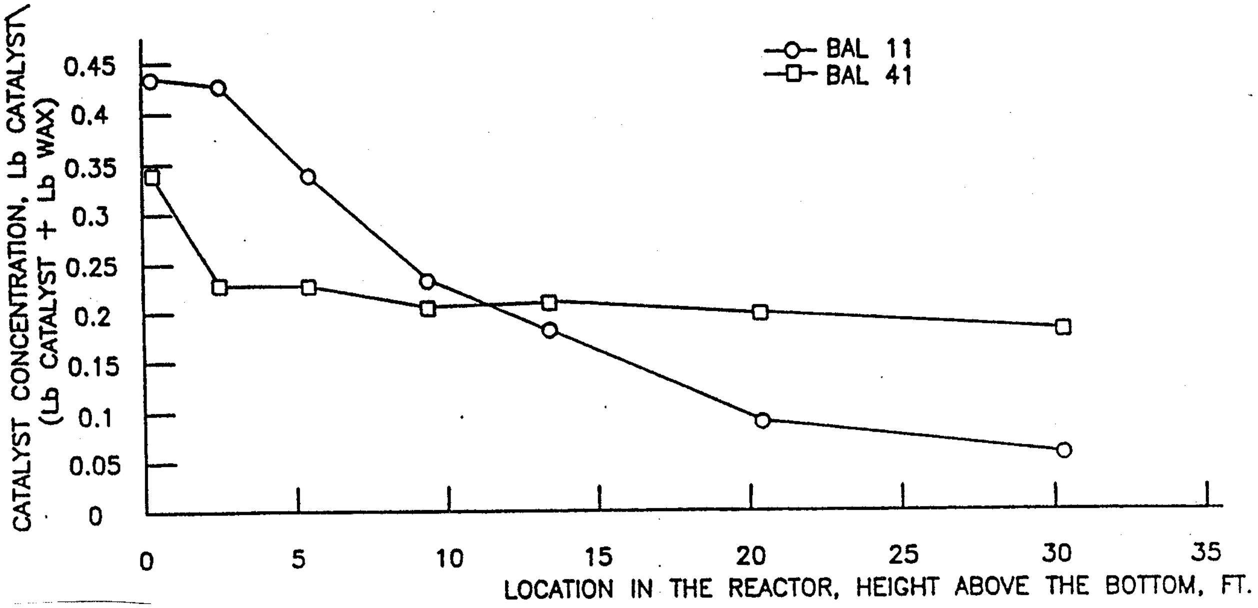

Figure X.20. Catalyst concentration versus elevation in the reactor with (Q) and without (F) use of draft tubes (from ref. X.89).

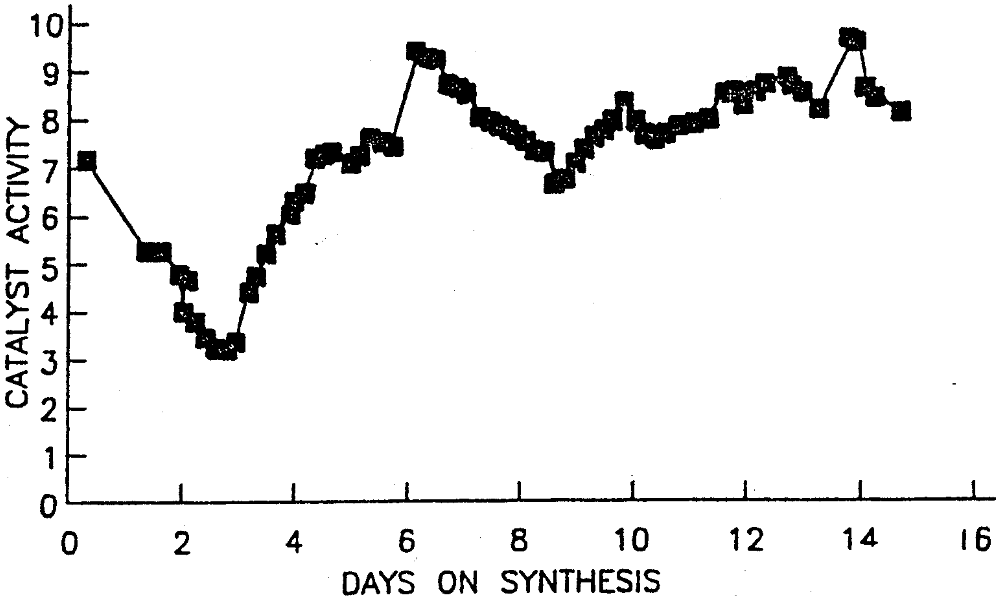

Figure X.21. Conversion using hydrogenation rejuvenation (to day 3 no rejuvenation; rejuvenation after day 3) (from ref. X.89).

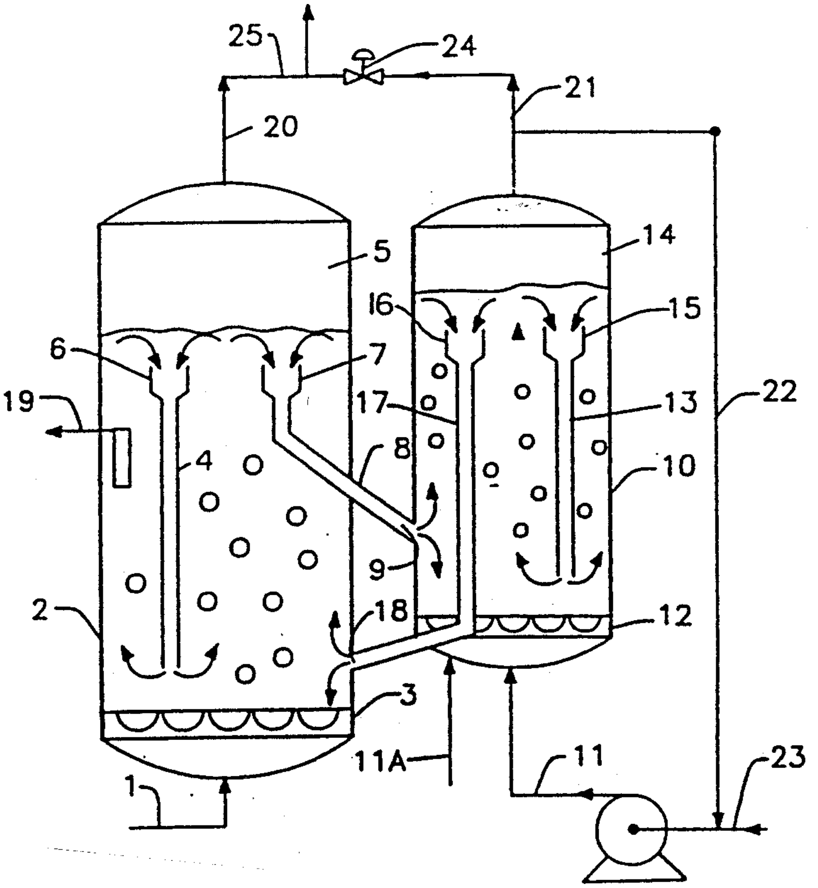

Figure X.22. Schematic of multiple vessels for catalyst rejuvenation (from ref. X.97).

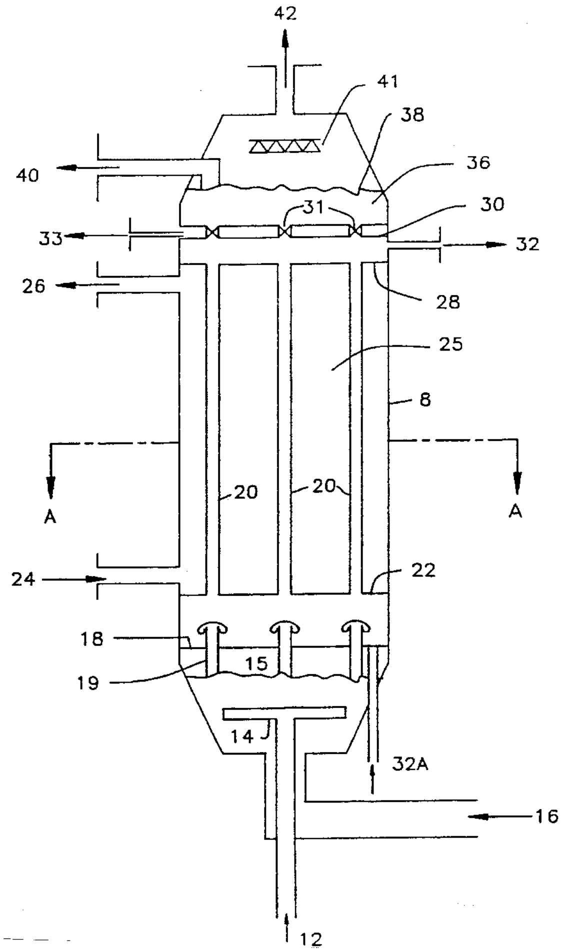

Figure X.23. Elevation of a shell and tube reactor arrangement showing the gas, liquid, catalyst interconnection both above and below the upper and lower tube sheets.

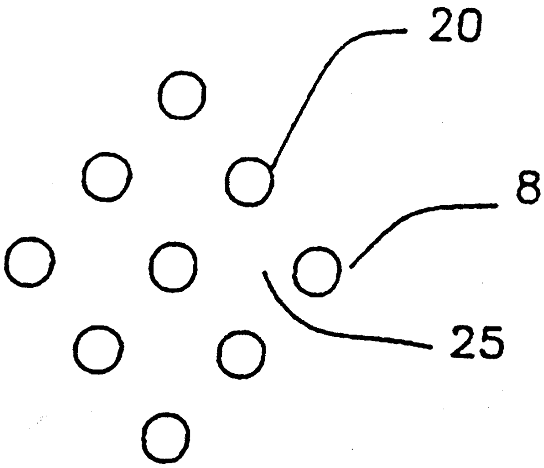

Figure X.24. Horizontal Section A - A through the elevation of Figure 23 showing a possible arrangment of tubes, that is, reaction zones.

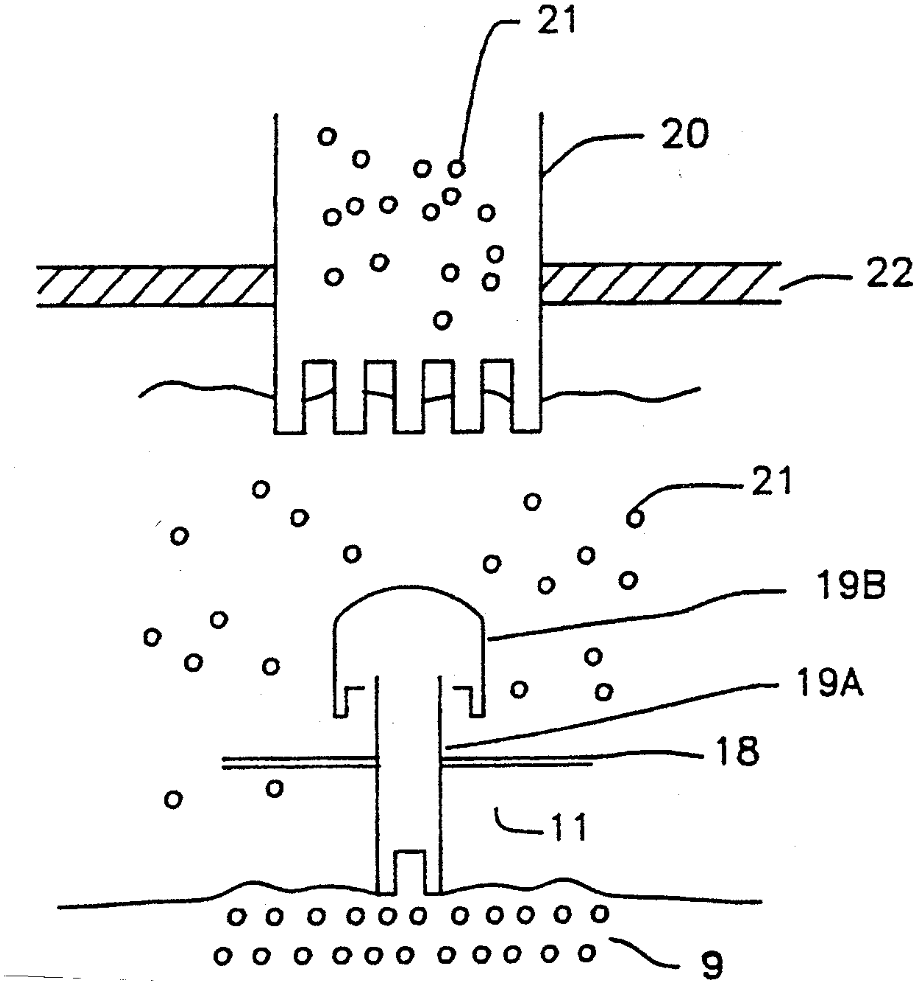

Figure X.25. Detail of a possible distribution zone for one reaction tube/zone.

APPENDIX - EXXON PATENTS

The following provides a listing of the primary claim from the patents reviewed during the preparation of this document. It is intended to provide a scope of the coverage of the initial report and the first addendum.

1. Gates, William, R. Fiato; Catalysts in FT process for producing olefins; Patent 4,639,431 (1987). **Claim 1:** A hydrocarbon synthesis catalyst comprising a sintered combination of metal oxides having the following components: (a) an oxide of a Group VIII metal; (b) an oxide of a Group IIB metal; (c) an oxide of a Group IA alkali metal; and (d) an oxide of a lanthanide metal, such that said sintered combination comprises a series of the Group VIII metal and the Group IIB metal spinels and the alkali metal oxide dispersed in a lanthanide metal oxide matrix.

2. Kim, Chang; R. Fiato; Multi-state FT process, patent 4,624,968, (1986). **Claim 1:** A process for producing paraffinic hydrocarbons from carbon monoxide and hydrogen comprising: (a) introducing carbon monoxide and hydrogen into a reaction zone wherein the carbon monoxide and hydrogen contact in a first bed a first catalyst having a high olefin selectivity selected from the group consisting of Fe/Ce/Zn/K, Fe/Mn/K and Fe/Co/K; and (b) contacting the resulting olefin in a second bed with a second catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons selected from the group consisting of Ru/TiO_2, Ru/SiO_2 and Ru/Al_2O_3.

3. Fiato, Rocco; S. Soled; FT hydrocarbon synthesis with high surface area Cu and K-promoted reduced-carbided iron/manganese spinels; Patent 4,621,102, (1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising contacting a catalyst composition, comprising at least one unsupported, single phase, iron-manganese spinal dual promoted with both copper and a Group IA and IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/G and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_2-C_{20} olefins.

4. Soled, Stuart, R. Fiato; Copper promoted iron/cobalt spinels and their preparation; patent 4,607,020 (1986). **Claim 1:** A composition of matter comprising a reduced and carbided, copper promoted iron-cobalt alloy, said composition being substantially isostructural with chi-Fe_5C_2, as determined by X-ray diffractometry and possessing a BET surface area of greater than 5 m^2/g, said composition produced by contacting, with a carbiding atmosphere for a time sufficient to produce said composition, said copper-promoted iron cobalt alloy, being isostructural with metallic alpha iron as determined by powder X-ray diffractometry, possessing a BET surface area of greater than 5 m^2/g, wherein said alloy was produced by contacting, with a reducing atmosphere, an

unsupported Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4, and possessing a BET surface area greater than 5 m^2/g and an iron-cobalt atomic ratio of 4 to 1 or above.

5. Iglesia, Enrique, S. Soled, R. Fiato, J. Baumgartner; Selective fixed-bed FT synthesis with high surface area Cu and K promoted, iron/manganese spinels; Patent 5,118,715 (June 1992). **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-400°C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

6. Soled, Stuart, S. Miseo, E. Iglesia, R. Fiato; Iron-zinc based catalysts for the conversions of synthesis gas to alpha-olefins; patent 5,100,856 (Mar. 1992). **Claim 1:** A composition comprising of iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, or mixtures thereof, wherein the iron:zinc atomic ratio is at least about 5:1, and the alkali metal:copper atomic ratio is at least about 2:1.

7. Fiato, Rocco; G.McVicker, A. Montagna; Process for preparing a Fe-CO catalyst slurry system for alpha olefin production; Patent 4,532,229 (Jul 1985). **Claim 1:** A process for preparing a slurry Fischer-Tropsch catalyst system comprising the steps of: (a) heating a slurry mixture comprised of a Fischer-Tropsch slurry liquid, an iron carbonyl compound, a cobalt carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in an atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound; and (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating and slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products.

8. Cody, Ian; D. Brown; Wax isomerization using small particle low fluoride content catalysts; patent 4,923,588 (May 1990). **Claim 1:** A method for the isomerization of waxes into liquid hydrocarbons comprising passing the wax to be isomerized in the presence of hydrogen and under isomerization conditions over an isomerization catalyst comprising a noble Group VIII metal on small particle size, fluorided, refractory metal oxide wherein the catalyst possesses a fluoride content in the range of 0.1 to up to but less than 2.0 wt.% and the small particle size refractory metal oxide has a particle diameter of less than 1/16 inch.

9. Pedrick, Larry; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; Patent 5,268,344 (Dec. 1993); **Claim 1**: A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst int the top of the slurry phase in the slurry phase reactor through the open to of the draft tube means.

l0. Kugler, Edwin, S.Tauster, S. Fung; Ruthenium supported on manganese oxide as hydrocarbon synthesis catalysts in Co/H2 reactions; patent 4,206,134 (June 1980). **Claim 1:** A process for the enhanced synthesis of C_2-C_4 olefins with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO ratio of from about 10 to about 0.1 over a catalyst reduced at a temperature greater than about 300°C comprising ruthenium on a manganese-containing oxide support, wherein said manganese-containing oxide support is selected from the group consisting of MnO, Al_2O_3-MnO, SiO_2-MnO, MnO-carbon, Group IVB-manganese oxide, Group VB-manganese oxides, Group IA-manganese oxides, Group IIA-manganese oxides, rare earth-manganese oxides and mixtures thereof, at a space velocity of from about 100 hr^{-1} to about 50,000 hr^{-1}, at a temperature of from about 100°C to about 500°C at a pressure of from about 103 to about 1.03×10^5 kPa for a time sufficient to effect the generation of the desired olefinic product, wherein the concentration of said ruthenium in said catalyst is from about 0.01 to about 15% by weight.

ll. Madon, Rostam; Liquid hydrocarbon synthesis using supported ruthenium catalysts; patent 4,477,595 (Oct. 1984). **Claim 1:** A process for selectively producing paraffins comprising (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon,TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates,V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-NbO_5, SiO_2-Ta_2O_5, V_2O_3-carbon,

Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth Group VB oxides, alkali-group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at Fischer-Tropsch conditions such that the temperature ranges from about 100 to 400°C, the pressure ranges from about 0.2 to 10 MpaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/hr, and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/MPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5-C_{40} hydrocarbons, containing C_5-C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least about 1.5.

12. Wachs, Israel, C. Chersich; Catalysts comprising tantala supported on titania; patent 4,544,649 (Oct. 1985). **Claim 1:** A catalyst composition comprising an oxide of tantalum supported on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

13. Kim, Chang; Reducing methane productions in FT reactions; patent 4,547,525 (Oct. 1985). **Claim 1:** A process for reducing methane formation in a Fischer-Tropsch process for synthesizing hydrocarbons which comprises contacting, at an elevated temperature of 100-500°C and a pressure of from about 100-10,000 kPa, a H_2/CO feed mixture with a heterogeneous catalyst comprising one or more Group VIII metals supported on an inorganic refractory oxide support for a time sufficient ro produce hydrocarbons, including methane, wherein one or more olefins is added to the H_2/CO feed mixture in an amount sufficient to reduce said methane formation to a level lower than it would be without adding said olefin to said feed.

14. Mauldin, Charles; Cobalt catalysts for the conversion of methanol to hydrocarbons and for FT synthesis; patent 4,568,663 (Feb. 1986). **Claim 1:** A catalyst useful for the conversion at reaction conditions of methanol or synthesis gas to hydrocarbons by contact with a catalyst which comprises cobalt and thoria in catalytically active amounts and ruthenium, composited with an inorganic oxide support in weight ratio of ruthenium:cobalt ranging from about 0.025:1 to about 0.10:1.

15. Arcuri, Kym; C. Mauldin, D. Shaw; Ruthenium rhenium catalyst on titania support for FT synthesis; patent 4,558,030 (Dec. 1985). **Claim 1:** A catalyst composition useful for the synthesis of hydrocarbons from admixtures of carbon monoxide and hydrogen at reaction conditions which comprises: ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

16. Payne, Virgil; C. Mauldin; Preparation of hydrocarbons from synthesis gas; patent 4,959,703 (June 1986). **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

17. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalyst in CO/H2 FT synthesis reactions; Patent 4,154,751 (May 1979). **Claim 1:** In a Fischer-Tropsch process reaction for the production of hydrocarbons from CO and H_2 wherein CO and H_2 are passed over a catalyst the improvement comprising using as the catalyst a supported potassium or rubidium-Group VIII metal cluster catalyst which catalyst is prepared by depositing a known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complex on a high surface area support, drying the carbonyl cluster complex impregnated support in the absence of oxygen and reducing the supported complex at elevated temperatures, wherein using this catalyst in Fischer-Tropsch processes results in the selective formation of higher molecular weight paraffinic and olefinic hydrocarbons.

18. Fiato, Rocco; S. Soled; Cobalt promoted catalyst for use in FT slurry process; patent 4,544,672 (Oct. 1985). **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2-C_4 olefins comprising the step of contacting a liquid slurry catalyst system, comprised of a slurry liquid and a carbided and reduced, unsupported iron-cobalt single phase spinel catalyst containing a Group IA or IIA metal salt promoter agent, and said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the provisos that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a single phase X-ray diffraction pattern substantially isostructural with that of Fe_3O_4 and said spinel having a measured BET surface area of up to 5 m^2/g, said process being conducted with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said product C_2-C_4 olefins.

19. Fiato, Rocco, S. Soled, A. Montagna; Cobalt promoted FT catalysts patent 4,544,674 (Oct. 1985). **Claim 1:** A fixed bed process for synthesizing a hydrocarbon mixture containing C_2-C_6 olefins comprising the step of contacting a fixed bed of a catalyst composition comprised of an unsupported Group IA or IIA metal salt promoted iron-cobalt spinel: said spinel exhibiting a single spinel phase, being isostructural with Fe_3O_4 as determined by X-ray diffractometry and possessing a BET nitrogen surface area of up to 5 m^2/g, and an iron-cobalt atomic ratio of 7:1 or above; with a mixture of CO/hydrogen under process

conditions of pressure, space velocity (SHSV) and elevated temperature for a time sufficient to produce said C_2-C_6 olefins.

20. Vaughan, David; K. Strobmaier; Synthesis of ECR-26(C-2646); patent 5,283,047 (Feb. 1994). **Claim 1:** A synthetic transition metal aluminosilicate crystalline zeolite having the gmelinite structure and a chemical composition in the dehydrated form: 0.8 to 1.3 $M_{2/n}O:(Al,Fe,Cr)_2O_3:4$ to 8 SiO_2, where n is the valence of metal M; the atoms of Al$\geqq$ atoms of

$$(Cr + Fe), \frac{Cr}{Cr + Al + Fe} \geq 0.05$$

and characterized by an X-ray diffraction pattern having the following essential lines:

dD	I/Io
11.9	VS
6.8	S
5.0	VS
5.59	M
4.11	MS
3.44	MS
2.97	MS
2.85	M
2.59	M

21. Iglesia, Enrique, S. Soled, R. Fiato; SiO2 promoted cobalt catalyst on a support of TiO2 for converting synthesis gas to heavy hydrocarbons; patent 4,794,099 (Dec. 1988). **Claim 1:** A hydrocarbon synthesis catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprised of a major portion of titania to which a lesser portion up to about 15 wt.% of silica in the form of silica or a silica precursor has been added.

22. Iglesia, Enrique, R. Madon; Reducing methane production and increasing liquid yields in FT reactions; patent 4,754,092 June (1988); **Claim 1**: A process for reducing methane formation and increasing liquid (C_5+) yields in a Fischer-Tropsch hydrocarbon synthesis process comprising adding an olefin to a gas feed and contacting said gas feed comprising a mixture of H_2 and CO with a catalyst at an elevated temperature of at least about 100^oC, said addition of said olefin and said contacting with said gas feed occurring within the reactor bed in the area of the reactor bed below 10% of the distance from the top to the bottom

of the reactor bed and above 10% of the distance from the bottom to the top of the reactor bed in an amount sufficient to reduce said methane formation, wherein said catalyst comprises a catalytic metal selected from the group consisting of iron, cobalt and ruthenium supported on an inorganic refractory oxide support.

23. Fiato, Rocco, S. Miseo; Process for the preparation of slurried CO hydrogenation catalysts; patent 4,749,677 (June 1988) **Claim 1**: A process for forming a slurry catalyst composition produced by the steps of: (a) adding to a stirred slurry reactor TiO_2, ruthenium carbonyl complex and an inert alkane hydrocarbon; (b) sealing said stirred slurry reactor and adding a gas mixture of N_2:CO at room temperature and one atmospheric pressure to said stirred slurry reactor to purge said stirred slurry reactor; (c) heating said stirred slurry reactor t o about 100^oC and raising the pressure of said stirred slurry reactor to about 4 to about 10 atmospheres and adding a gas mixture of $N_2:H_2$ to said stirred slurry reactor; and (d) increasing the temperature of said stirred slurry reactor to about 230^oF to about 270^o and the pressure of said stirred slurry reactor from about 4 to about 20 atmospheres for about 2 to about 6 hours to cause the decomposition of said ruthenium carbonyl complex to form said slurry catalyst composition.

24. Iglesia, Enrique, S. Soled, R. Fiato; Cobalt-ruthenium catalysts for FT synthesis and process for their preparation; patnet 4,738,948 (Apr. 1988). **Claim 1**: A hydrocarbon synthesis catalyst prepared by a process comprising impregnating a refractory support comprising titania with solutions of catalytically active amounts of cobalt and ruthenium salts, drying the impregnated support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

25. Wachs, Israel, D. Yang; Catalysts comprising ruthenium on titania surface modified with group VA oxide of vanadium, niobium or tantalum; patent 4,711,871 (Dec.1987). **Claim 1:** A process for preparing a catalyst comprising ruthenium supported on a surface-modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania wherein said process comprises the sequential steps of: (a) forming said support comprising titania whose surface has been modified with and supports an oxide of a metal selected from the group consisting of niobium, tantalum, vanadium or mixture thereof wherein said supported, modifying oxide is a non-crystalline form; (b) impregnating said so-formed surface modified titania support with a solution of a ruthenium precursor compound; and (c) converting said ruthenium precursor compound to ruthenium to form said catalyst.

26. Mauldin, Charles, S. Davis, K. Arcuri; Cobalt catalysts for the conversion of methanol and for FT synthesis to produce hydrocarbons; patent 4,663,305 (May 1987). **Claim 1:** A regeneration stable catalyst for the conversion at reaction conditions of methanol or synthesis gas to liquid hydrocarbons which consists

essentially of from about 2% to about 25% cobalt, based on the weight of the catalyst composition, composited with titania, or a titania-containing support, to which is added sufficient of a zirconium, hafnium, cerium, or uranium promoter to provide a weight ratio of the zirconium, hafnium, cerium, or uranium metal:cobalt greater than about 0.101:1.

27. Fiato, Rocco, R. Bar-Gadda, S. Miseo; Cerium promoted FT catalysts; patent 4,657,885 (Apr. 1987). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising sintered combination metal oxides having the following components in the stated weight percentage of the catalyst composition: (a) about 5 to about 80 wt.% of a Group VIII metal oxide; (b) about 4 to about 40 wt.% of a Group IIB metal oxide; (c) about 10 to about 40 wt.% of a Group IVB and/or VIIB metal oxide; (d) about 1 to about 5 wt.% of a Group IA metal oxide; and (e) about 1 to about 10 wt.% of a Lanthanum Group metal oxide, such that where the catalyst contains a Group VIII metal, said sintered combination comprises a series of spinels of a Group VIII metal, a Group IIB metal, and/or a Group IVB metal, and/or a Group VIIB metal, and a Group IA metal oxide in a lanthanum Group metal oxide matrix.

28. Mauldin, Charles; Start-up with ruthenium catalysts; patent 4,647,592 (MAR. 1987). **Claim 1:** In a process for the conversion of synthesis gas to hydrocarbons by contacting at reaction conditions a feed characterized as an admixture of carbon monoxide and hydrogen with a bed of particulate ruthenium catalyst constituted of a catalytically active amount of ruthenium composited with titania, or a titania-containing support, the improvement comprising contacting and pretreating the catalyst, prior to initiating the conversion reaction, with an admixture of steam and hydrogen at temperatures ranging from about 200^{o}C to about 550^{o}C sufficient to mildly agglomerate and ruthenium and form on the particles of catalyst larger agglomerates of ruthenium of average crystallize size from about 15 D to about 25 D approximating that obtained on completion of the startup portion of a synthesis gas operating run.

29. Arcuri, Kym; Process for the start-up of a FT reactor; patent 4,626,552 (Dec. 1986). **Claim 1**: In a process for the startup of a reactor wherein a feed comprised of hydrogen and carbon monoxide is contacted with a bed of hydrocarbon synthesis catalyst in which perturbations of the temperature profile across the bed can develop, and which, at line-out conditions defined by feed flow rate, pressure, temperature, and the molar ratio of hydrogen:carbon monoxide of the feed is sufficient to synthesize hydrocarbons from the hydrogen and carbon monoxide, the improvement which comprises: elevating, while maintaining the molar feed ratio of hydrogen:carbon monoxide at below about 90% of its line-out value, the feed flow rate, pressure and temperature to values approaching line-out feed flow rate, line-out pressure and line-out temperature and then gradually increasing the molar feed ratio of hydrogen:carbon monoxide to essentially that employed at line-out.

30. Davis, Stephen M.; Silica modified hydroisomerization catalyst; U.S. patent 5,187,138 (Feb. 1993). **Claim 1:** A catalyst composition comprising: a Group VIII metal; a support therefore of alumina or silica-alumina wherein the silica content is less than about 35 wt.%; at least about 0.5 wt.% silica other than the support silica; and a surface area of about 180-400 m^2/gm.

31. Hamner, Glen P.; Process for the isomerization and hydrocracking of FT waxes to protect a syncrude and upgraded hydrocarbon products; patent 4,832,819 (May 1989). **Claim 1:** A process for producing a pumpable syncrude from a Fischer-Tropsch wax containing oxygenate compounds, which comprises: (1) separating the FT wax into (a) a low-boiling fraction which contains most of the oxygenate compounds and (b) a high-boiling fraction which is substantially free of water and oxygenate compounds, (2) reacting the high-boiling fraction from step (1) with hydrogen at hydroisomerization and mild hydrocracking conditions in the presence of a fluorided Group VIII metal-on-alumina catalyst to produce a C_5+ hydrocarbon product, and (3) combining the C_5+ hydrocarbon product from step (2) with the low-boiling fraction from step (1) to produce a pumpable, refinery processable syncrude that can be transported at atmospheric conditions.

32. Hsia, Stephen J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; patent 5,260,239 (Nov. 1993). **Claim 1**: A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel means to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by means of a first downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down this first downcomer C conduit means from the top of the first vessel means to the bottom of a reactivation C rejuvenation second vessel means, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catalyst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated C rejuvenated in said second vessel means, collecting reactivated C rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer C conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated C rejuvenated catalyst down the second downcomer C conduit means from the top of the second vessel means to the bottom of the first vessel means, all catalyst downward flows on both the first and second downcomer means occurring solely under the influence of gravity.

33. Mitchell, Willard N.; Activation of hydrocarbon synthesis catalyst; patent 5,292,705 (Mar. 1994). **Claim 1:** A method for activating an essentially fresh, reduced cobalt containing FT catalyst which comprises treating the catalyst with

hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

Examples. In a hydrocarbon synthesis process demonstration unit, lhydrogen treatment of the catalyst to enhance initial activity for slurry phase operations was demonstrated. In the unit, fresh catalyst 12 st% Co, 1 wt% Re on a titania support with 6 wt% Al_2O_3 as a binder material, was activated by first reducting the catalyst in hydrogen to reduce the cobalt oxide to the cobalt metal. This was accomplished in a **fluid bed reactor** at temperatures up to about 375°C. The H_2 treat gas rate was 8-18 SCFH H_2/lb catalyst with a H_2 concentration of 18-25% in N_2. Following the reduction the catalyst was passivated with 0.25-1.3 SCFH of CO in N_2+H_2 for 1-2 hours.

The dry reduced catalyst [presumably they mean the dry reduced and passivated catalyst] with was combined with a wax to form a slurry in a slurry mix vessel. The slurry was transferred to the hydrocarbon synthesis reactor and synthesis was initiated. Followingg a shor test to measure initial catalyst productivity, a hydrogen treat was conducted in the slurry reactor ("super" activation). The following table shows two samples of this "super" activation:

	Relative Productivity	
	Before	After
Example 1	60	100
Example 2	25	100

In the first example the relative productivitry increased from 40% to 100% and the second case from 25% to 100%. The conditions for the H_2 treat of the slurry were typical of conditions described earlier.

In order to determine the real increase in initial activity, the catalyst had to be run at synthesis conditions for a period sufficient to obtain an initial activity or productivity. However, this minimal operation at synthesis conditions is not believed to change or effect the catalyst in any substantive way and the catalyst may be considered as essentially fresh catalyst.

34. Chang, Min; C. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); patent 5,252,613 (Oct. 1993). **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributing catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas

distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

35. Kim, Chang J.; Water addition for increased Co/N2 hydro-carbon synthesis activity over catalysts comprising cobalt, ruthenium and mixtures thereof which may include a promoter metal; patent 5,227,407 (Jul 1993). **Claim 1:** A once-through, fixed or slurry bed FT process with CO conversion activity and C_5+ liquid hydrocarbon selectivity comprising contacting a feed mixture of carbon monoxide and hydrogen in a reaction zone with about 1 vol.% to about 70 vol.% water based on the total volume of feed mixture, at a pressure above one atmosphere and a temperature ranging from about 150^{o}C to about 300^{o}C, wit a catalyst selected from the group consisting of cobalt, ruthenium, and mixtures thereof on a titania support, wherein said titania support is less than 40 m^2/g, converting at least 90 vol.% of the carbon monoxide to liquid hydrocarbons, and in the substantial absence of CO_2 formation.

36. Soled, Stuart, E. Iglesia, R. Fiato, G. Ansell; Method for stabilizing titania supported cobalt catalyst and the catalyst for use in FT process; patent 5,169,821 (Dec. 1992). **Claim 1:** A method of preparing a 400-750^{o}C regeneration stable catalyst composition comprising: (a) coprecipitating a titanium metal complex from a solution of a titanium alkoxide and a metal alkoxide or a solution of titanium chloride and a metal chloride wherein said metal is selected from the group consisting of silicon, zirconium and tantalum; (b) recovering the coprecipitate and calcining at temperatures of 400-750^{o}C, to form a ternary metal oxide support; (c) depositing a cobalt compound onto said calcined ternary metal oxide support; (d) activating said cobalt calcined support to form a catalyst comprised of cobalt on a substituted ternary metal oxide support of titania having the general formula $Co/Ti_xM_{1-x}O_2$ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum, wherein the titania is an anatase polymorph.

37. Soled, Stuart, E. Iglesia, R. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for FT synthesis; patent 5,162,284 (Nov. 1992). **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2.

38. Mauldin, Charles, K. Riley; Process for the preparation of surface impregnated dispersed cobalt metal catalysts; patent 4,977,126 (Dec. 1990). **Claim 1**: In a process for the production of catalysts wherein a catalytically effective amount of cobalt is impregnated and dispersed on the outer surface of a particulate porous inorganic oxide support to form a catalyst useful for the conversion of synthesis gas to hydrocarbons, and the support particles are contacted with a spray containing a decomposable compound of cobalt, the improvement comprising: maintaining a bed of the support particles in a fluidized state at temperature ranging from about 50^{o}C to about 100^{o}C by contact with a gas at temperature ranging from about 50^{o}C to about 100^{o}C; spraying the bed of the heated support

particles with a liquid in which a cobalt compound is dispersed at flow rate sufficient to provide a ratio between the flow rate of the liquid: flow rate of the fluidizing gas below about 0.6 grams liquid/ft^3 of fluidizing gas to form on the particles a surface layer of cobalt compound in average thickness ranging from about 20 microns to about 250 microns, with the loading of cobalt compound ranging from about 0.01 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst.

39. Iglesia, Enrique; S. Soled, R. Fiato; Synthesis gas to heavy hydrocarbons on SiO2 promoted Co/TiO2; patent 4,960,801 (Oct. 1992). **Claim 1:** A process for preparing C5+ hydrocarbons which comprises reacting hydrogen and carbon monoxide at hydrocarbon synthesis reaction conditions in the presence of a catalyst comprising cobalt in a catalytically active amount composited with an inorganic refractory support comprising a major portion of titania to which a lesser portion up to about 15 qt.% silica in the form of silica or a silica precursor has been added.

40. Pedrick, Larry E.; C. Mauldin, W. Behrmann; Draft tube for catalyst rejuvenation and distribution; patent 5,268,344, (Dec. 1993). **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the open bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

45. McVicker, Gary; M. Albert Vannice; Preparation and use of supported potassium (or rubidium)-group VIII metal cluster catalysts in CO/H2 FT synthesis reactions; patent 4,192,777 (Mar. 1980). **Claim 1:** Supported, highly dispersed, high activity potassium or rubidium-Group VIII metal cluster catalysts demonstrating improved selectivity olefinic and paraffinic hydrocarbons in CO/H_2 reactions prepared by the process which comprises depositing known, well-characterized potassium or rubidium-Group VIII metal carbonyl cluster complexes and mixtures thereof on a high surface area support material, drying the carbonyl cluster complex impregnated support in the absence of oxygen, and reducing the supported complex at elevated temperatures to effect the essentially complete reduction of the supported potassium or rubidium-Group VIII metal carbonyl cluster complexes to discrete potassium or rubidium-Group VIII clusters of metals on the support surface.

46. Wright, Franklin; M. Richard, J. Pirkle; Process using iron-thallium catalysts in CO hydrogenation; patent 4,513,104 (Apr. 1985). **Claim 1:** A process for producing liquid hydrocarbons, including those in the C_6-C_{11} hydrocarbon range,

comprising the steps of: (a) first depositing thallium on the surface of a supported or unsupported iron catalyst wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compounds contain iron value substantially in the trivalent state; (b) contacting said iron-thallium catalyst with a mixture of CO and H_2 in a volume ratio of about 1:4 to 4:1, respectively, at a temperature ranging from 270 to 550°C, a pressure ranging from 0.1 to 10 MPa and a space velocity ranging from 10 to 10,000 v/v/hr, or equivalent conditions, for a sufficient time to substantially convert said thallium compounds to metallic thallium and said iron compounds to reduced and carbided iron; and (c) continuing said contacting as described in step (b) at a pressure above 0.1 MPa, a temperature ranging from 230 to 550°C, to produce liquid hydrocarbons comprising about 40 wt.% and greater C_6-C_{11} liquid hydrocarbons and below about 5 wt.% C_{23}+ hydrocarbons.

47. Wright, Franklin; Iron-thallium catalysts for use in CO hydrogenation and process of preparing the catalysts, Patent 4,436,834 (Mar. 1984). **Claim 1:** A catalyst composition consisting essentially of a mixture of an iron compound and a thallium compound, being supported or unsupported, said compound of iron and thallium being selected from the group consisting of an oxide, hydroxide, carbonate, sulfate, carbide, halide, nitrate, or mixtures thereof, wherein the weight ratio of iron-thallium, taken as the free metals, is from about 100:1 to 1:100, and wherein said iron compound contains iron value substantially in the trivalent state, and wherein said thallium compound is substantially deposited on the surface of said iron compound.

48. Soled, Stuart, R. Fiato; Process for preparing high surface area iron/cobalt FT slurry catalysts; patent 4,518,707 (May 1985). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal salt promoted iron-cobalt spinel, or mixture thereof, said spinel exhibiting a single phase powder X-ray diffraction pattern substantially isostructural with Fe_3O_4, and possessing a BET surface area greater than 5 m^2/g and an iron-cobalt atomic ratio of 4 to 1 or above.

49. Soled, S. L. and R. A. Fiato; Process for preparing high surface area iron/cobalt Fischer-Tropsch slurry catalysts; U.S. Patent 4,544,671, Oct. 1, 1985. **Claim 1:** A slurry process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising the step of contacting a catalyst composition, comprised of an unsupported iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial BET surface area greater than 5 m^2/g and an Fe:Co atomic ratio of 7:1 and above, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

50. Fiato, Rocco; S. Soled, A. Montagna; Promoted iron-cobalt spinel catalyst for FT process; patent 4,537,867 (Aug. 1985). **Claim 1:** A hydrocarbon synthesis catalyst composition comprising an unsupported, Group IA or IIA metal salt

promoted iron-cobalt single phase spinel, said spinel having the initial empirical formula: $Fe_xCo_yO_4$, wherein x and y are integer or decimal values, other than zero, with the proviso that the sum of x+y is 3 and the ratio of x/y is 7:1 or above, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and said spinel having an initial BET surface area of up to about 5 m^2/g.

51. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ni supported on a titanium oxide; U. S. Patent 4,042,615, Aug. 16, 1977. **Claim 1:** A process for the synthesis of higher molecular weight paraffins comprising the steps of passing CO and H_2 in a CO/H_2 ratio of 10 to 0.1 over a catalyst comprising nickel on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 tp 50,000 v/v/hr and a temperature of from 100 to 500 and ^oC at pressure of from 103 to 1.03×10^5 kPa for a time sufficient to effect the generation of the desired paraffinic products in the desired ratio, wherein the concentration of said nickel in said catalyst is from 0.01 to 75% by weight.

52. Tauster, S. J. and S. C. Fung; Group VIII metals on manganese-containing oxide supports which exhibit strong supports which exhibit strong metal support interactions; U.S. Patent 4,402,869, Sept. 6., 1983. **Claim 1:** Improved catalytic compositions comprising catalytic metal selected from the group consisting of iron, nickel, cobalt and mixtures thereof supported on a manganese-containing oxide support, the improvement comprising as a final step before use, contacting said catalyst composition with a reducing atmosphere at a temperature of at least about 300^{o}C to produce at catalyst composition which exhibits suppressed hydrogen chemisorption.

53. Wachs, Israel; R. Fiato, C. Chersich; Iron carbide on titania surface modified with group VA oxides as FT catalysts; patent 4,559,365 (Dec. 1985). **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous feed mixtures of CO and H_2 comprising contacting said feed, at a temperature ranging from about 200 to 350^{o}C and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum and mixture thereof supported on titania wherein at least a portion of said supported oxide is in a non-crystalline form.

54. Soled, Stuart, R. Fiato; FT hydrocarbon synthesis with copper promoted iron/cobalt spinel catalyst; patent 4,584,323 (Apr. 1986). **Claim 1:** A process for synthesizing a hydrocarbon mixture containing C_2-C_{20} olefins comprising contacting a catalyst composition, comprising an unsupported, copper promoted iron-cobalt spinel, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing an initial

BET surface area greater than 5 m^2/g and an Fe:Co atomic ratio of 4:1 and above, with a mixture of CO and hydrogen in a slurry liquid under conditions of pressure, space velocity and elevated temperature, for a time sufficient to produce said C_2-C_{20} olefins.

56. Kugler, E. L. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using titanium promoted bulk nickel catalysts; U.S. Patent 4,273,724, June 16, 1981. **Claim 1:** A process for the synthesis of higher molecular weight paraffinic hydrocarbons of from C_2 to C_7 carbon number comprising the steps of passing CO and H_2 at a CO/H_2 ratio of from 10 to 0.1 at a space velocity of from 100 hr^{-1} to 50,000 hr^{-1}, at a temperature of from 100 to 500°C and at pressures of from 103 to 1.03×10^5 kPa over a catalyst comprising bulk nickel promoted with from 0.07 to 10 wt.% titanium containing oxide (calculated as TiO_2) for a time sufficient to effect the generation of the desired paraffinic products.

57. Vannice, M. A. and S. J. Tauster; Hydrocarbon synthesis from CO and H_2 using Ru supported on group VB metal oxides; U.S. Patent 4,171,320, Oct. 16, 1979. **Claim 1:** A process for the synthesis of olefins of from C_2 to C_5 chain length inclusive, said process comprising the steps of passing H_2 and CO at a H_2/CO ratio of 0.1 to about 10 over a catalyst comprising ruthenium on a support selected from the group consisting of V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth group VB oxides, alkali Group VB oxides, rare earth Group VB oxides, Group IVB-Group VB oxides and mixtures thereof, at a space velocity of from 100 to 50,000 hr^{-1}, at a temperature of from 100 to 500°C, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic products wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15 wt.% based on total catalyst weight.

58. Fiato, Rocco; S. Soled; High surface area dual promoted iron/manganese spinel compositions; patent 4,618,597 (Oct. 1986). **Claim 1:** A composition of matter comprising an unsupported, Group IA or IIA metal and copper promoted, single phase, iron-manganese spinel, said spinel exhibiting a powder X-ray diffraction pattern substantially isostructural with Fe_3O_4 and possessing a BET surface area greater than 30 m^2/g and an iron-manganese atomic ratio greater than about 2:1.

59. DeLuca, J. P., L. L. Murrell, R. P. Rhodes and S. J. Tauster; Stabilized ruthenium catalysts for selective reduction of oxides of nitrogen; U.S. Patent 3,922,235, Nov. 25, 1975. **Claim 1:** A stabilized supported ruthenium catalyst, said catalyst comprising ruthenium metal in combination with an oxide support, said support being one selected from the group consisting of zirconium titanate, and zirconium titanate mixed with titania, the ruthenium being present in an amount which does not exceed 0.003 grams of ruthenium per gram of oxide support.

71. Kugler, E. L. and S. J. Tauster; Catalyst comparison nickel supported on tantalum oxide or niobium oxide and their use as hydrocarbon synthesis catalysts in CO/H_2 reactions; U.S. Patent 4,206,135, June 3, 1980. **Claim 1:** A process

for the enhanced synthesis of paraffinic hydrocarbons of from 2 to 6 carbon atoms inclusive with reduced production of methane comprising the steps of passing H_2 and CO in an H_2/CO mole ratio of from about 0.1 to about 10 over a catalyst reduced at a temperature of at least 375°C comprising nickel on a tantalum or niobium-containing oxide support wherein said tantalum or niobium-containing oxide support is selected from the group consisting of tantalum oxides, niobium oxides, Al_2O_3-Ta_2O_5, Al_2O_3-Nb_2O_5, SiO_2-Ta_2O_5, SiO_2-Nb_2O_5, Ta_2O_5-carbon, Nb_2O_5-carbon, alkaline earth-tantalum oxides, alkaline earth-niobium oxides, alkali-tantalum oxides, alkali-niobium oxides, rare earth-tantalum oxides, rare earth-niobium oxides, Group IVb-tantalum oxides, Group IVb-niobium oxides, and mixtures thereof, at a space velocity of from 100 hr^{-1} to about 50,000 hr^{-1}, at a temperature of from about 100°C to about 500°C, at a pressure of from about 100 to about 1×10^5 kPa, for a time sufficient to effect the generation of the desired paraffinic product, wherein the concentration of said nickel in said catalyst is from about 0.01 to about 75 wt.%.

72. Murrell, L. I. and S. J. Tauster; Catalytic process for NO_x reduction under lean conditions; U.S. Patent 4,039,622, Aug. 2, 1977. **Claim 1:** A process for effecting the selective reduction of NO_x in lean effluent waste streams containing NO_x, CO, O_2, H_2, CO_2 and water, wherein the concentration of CO is at least equivalent to the concentration of NO_x present in the waste stream, a lean effluent waste stream being defined as one in which the concentration of oxygen is in excess over the concentration of reductants to a level as high as 8%, i.e,. about 800% excess oxygen, over the total of reductants present, said reductants being selected from the group comprising CO and H_2 so that when such a waste stream is reacted to completion, the residuum is oxidizing in character, said process comprising the steps of contacting said lean exhaust stream in a reaction zone with an iridium catalyst, said contacting occurring at a temperature between 300OC to 750°C thereby effecting the selective reduction by CO of the oxides of nitrogen to molecular nitrogen.

73. ;Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and $_2$ using Rh supported on titanium oxides; U.S. Patent 4,116,994, Sept. 26, 1978. **Claim 1:** A process for the enhanced synthesis of olefins and paraffins, wherein said paraffins are other than methane, comprising the steps of passing H_2 and CO in a H_2/CO ratio of 0.1 to 10 over a catalyst comprising rhodium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr and at a temperature of from 100 to 500°C, at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic and paraffinic products in the desired ratio, wherein the concentration of said rhodium in said catalyst is from 0.01 to 10% by weight.

74. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO, H_2 mixtures and process for maintaining catalytic activity; U.S. Patent 4,093,643,

June 6, 1978. **Claim 1:** A process to produce low molecular weight organic compounds comprising substantially methane, said process consisting of the steps of passing a mixture of CO and H_2 over palladium supported on an acidic metal oxide selected from the group consisting of alumina and hydrogen-y-zeolite wherein the palladium metal particle size is maintained at less than 100 A by running at a reactor bed temperature of less than 350^oC, at a pressure ranging from 1 to 500 atm. and a GHSV of from 1200-4600 hr^{-1}.

75. Voorhies, Alexis, Jr., Hydrocarbon synthesis process, U.S. Patent 2,479,439, Aug. 16, 1949. **Claim 1:** An improved hydrocarbon synthesis process which comprises reacting together, under synthesis conditions, hydrogen and carbon monoxide initially in the presence of an unpromoted powdered iron catalyst in the form of a fluidized bed contained in a reaction zone, adding an alkali metal compound to the reaction zone at a slow rate during such a period of time as to cause a slow and homogeneous impregnation of said alkali metal compound within said catalyst, and to the extent that the desired yields or normally liquid hydrocarbons are obtained from the reaction zone, whereupon the feeding of the alkali metal compound is discontinued, the amount of said promoter with respect to the catalyst and contained thereon lying within the limits of from about 0.1 to 5 wt.% after the initial period, and adding water to the reaction zone to repress carbon formation in an amount such that the feed to the reaction zone contains 5 to 25 mols of hydrogen per mol of water.

76. Aldridge, C. L. and T. Kalina; Shift process for new catalysts; U.S. Patent 3,850,841, Nov. 26, 1974. **Claim 1:** A process for the preparation of hydrogen and carbon dioxide which comprises introducing a gas mixture containing monoxide and steam at a temperature varying from about 300 to 700^oF, and introducing at least a portion of said cooled reaction mixture to at least one additional shift reaction stage and contacting the same therein with a catalyst, the temperature within each said reaction stage being maintained above the dew point temperature of the reaction mixture and the pressure within each said reaction stage being maintained below the dew point pressure of said reaction mixture and ranging from about atmospheric to about 3000 psig, the catalyst in each reaction stage comprising (i) an alkali metal compound derived from an acid having an ionization constant of less than about $1x10^{-3}$ and (ii) a hydrogenation-dehydrogenation component selected from the group consisting of (a) a metal composition comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof or (b) mixtures of materials comprising vanadium, molybdenum, tungsten, cobalt, tantalum or niobium materials or mixtures thereof with a nickel, iron or chromium material or mixtures thereof, the weight ratio of said hydrogenation-dehydrogenation component to said alkali metal compound, each calculated on the basis of the oxides thereof, being less than 5:1.

77. Vannice, M. A. and R. L. Garten; Catalytic formation of hydrocarbons from CO hydrogen mixtures; U.S. Patent 3,941,819, March 2, 1976. **Claim 1:** A process for producing substantial amounts of dimethyl ether, said process comprising the

step of passing CO and H_2 over platinum supported on alumina, wherein the amount of platinum ranges from 0.3 to 2 wt.% based on total weight of the support including platinum at a temperature ranging from 200 to 300°C and a pressure ranging from 10.10 to 40 atm. and wherein the mol ratio of hydrogen to CO ranges from 0.1 to 2.

78. Kwang, K. K., R. E. Pennington, L. W. Vernon and N. C. Hahas; Methane production, U. S. Patent 3,958,957, May 25, 1976. **Claim 1:** A method for the production of a methane-rich gas which comprises introducing a gaseous mixture of hydrogen and at least one carbon oxide into a reaction zone containing a carbon-alkali metal catalyst at a temperature between about 800°F and about 1500°F and at a pressure between about atmospheric and about 2000 psig, said catalyst being prepared by heating an intimate mixture consisting essentially of a carbonaceous solid and an alkali metal constituent to an elevated temperature sufficient to produce a reaction between the carbon and alkali metal in said mixture and form a carbon-alkali metal reaction product, and recovering a methane-rich gas from said reaction zone.

79. Vannice, M. A.; Method for the direct preparation of halogenated hydrocarbons by the reaction of CO, H_2 and halogen in the presence of a catalyst; U.S. Patent 4,041,087, Aug. 9., 1977. **Claim 1:** method for the preparation of halogenated hydrocarbons of the formula $C_AH_{2A+2-B}X_B$ wherein x is a halogen selected from the group consisting of fluorine, chlorine, bromine and iodine, A is an integer ranging from 1 to 4 inclusive and B is an integer ranging from 1 to 10 inclusive, except that 2A+2-B may not be less than zero, which method comprises the steps of: (1) preparing a system comprising CO, H_2 and a source of halogen wherein the source of halogen is selected from the group consisting of molecular halogen and hydrogen halides; (2) passing said system over a catalyst metal selected from the group consisting of Group VIII metals, rhenium, and platinum-iridium and platinum-rhenium alloys, which catalyst metal is in combination with an acidic inorganic oxide material; (3) heating the system containing the CO, H_2 and halogen source over the catalyst to a temperature in the range of 200-1000°C; and (4) pressurizing the system to a level in the range of 0.1 atm to 500 atm.

80. Vannice, M. A. and R. L. Garten; Hydrocarbon synthesis from CO and H_2 using Ru supported on a titanium oxide; U.S. Patent 4,042,614, Aug. 16, 1977. **Claim 1:** A process for the selective synthesis of olefins from C_2 to C_{10} chain length inclusive, said process comprising the steps of passing H_2 and CO at a H_2/CO ratio of 0.1 to 10 over a catalyst comprising ruthenium on a titanium-containing oxide support, wherein said titanium-containing oxide support is selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof, at a space velocity of from 100 to 50,000 v/v/hr at a temperature of from 100 to 500°C at a pressure of from 100 to 10^5 kPa for a time sufficient to effect the generation of the desired olefinic products in the desired ratio wherein the concentration of said ruthenium in said catalyst is from 0.01 to 15% by weight.

81. Yates, D. J. C. and L. L. Murrell; Method for preparing a highly dispersed supported nickel catalyst; U.S. Patent 4,073,750, Feb. 14, 1978. **Claim 1:** A highly dispersed nickel catalyst having a nickel surface area of from 200 to 400 m^2/g nickel prepared by the method which comprises slurrying a nickel metal precursor dissolved in a nonaqueous organic liquid solvent with a high surface area refractory oxide support, removing the solvent to obtain a composite of said nickel metal precursor and said support, and activating said composite by reducing in hydrogen or hydrogen dilutes with an inert gas at conditions sufficient to convert substantially all of the nickel metal precursor to nickel metal.

82. Tauster, S. J., L. L. Murrell and S. C. Fung; Supported metal interaction catalysts; U. S. Patent 4,149,998, April 17, 1979. **Claim 1:** Improved catalytic composition consisting of a metal selected from the group consisting of iridium, osmium, rhodium, and mixtures thereof and an oxide of titanium support prepared by depositing said iridium, osmium, rhodium and mixtures thereof on the oxide of titanium and pretreating the composition prior to use, the improvement comprising, as a final step before use, reducing the composition in a hydrogen atmosphere at a temperature of at least 200^oC, thereby producing a composition which exhibits suppressed hydrogen chemisorption.

83. Wheelock, K. S., Catalyst and a process for its preparation; U.S. Patent 4,219,447, Aug. 26, 1980. **Claim 1**: A catalyst useful for the conversion of a hydrocarbon feed by contact thereof at hydrocarbon conversion conditions which comprises a cluster of titanium metal oxide and a Group VIII noble metal deposited on the surface of an inorganic oxide support.

84. Murrell, L. L., C. J. Kim, and D. C. Grenoble; Acid catalyzed hydrocarbon conversion process utilizing a catalyst comprising a group IVB, VB or VIB metal oxide on an inorganic refractory oxide support; U.S. Patent 4,233,139, Nov. 11, 1980. **Claim 1:** In a hydrocarbon conversion process wherein hydrocarbon fractions are cracked over acid catalysts at elevated temperatures, the improvement comprising using as the catalyst a material comprising a catalytic metal oxide selected from the group consisting of the oxides of tungsten, niobium and mixtures thereof and tungsten or niobium oxides in combination with one or more additional metal oxides selected from the group consisting of tantalum oxide, hafnium oxide, chromium oxide, titanium oxide and zirconium oxide supported on an inorganic refractory metal oxide base selected from the group consisting of alumina, zirconia, boria, thoria, magnesia, zirconium-titanate, titania, chromia, kieselguhr and mixtures thereof, said catalyst being steamed prior to use.

85. McCandlish, L. E. and E. L. Kugler; CO hydrogenation process using molybdenum oxycarbonitride catalyst; U.S. Patent 4,418,154, Nov. 29, 1983. **Claim 1:** A process for preparing paraffinic hydrocarbons including linear and branchedC_1-C_{10} carbon chain numbers comprising contacting a gaseous mixture of CO and H_2 in a CO/H_2 volume ratio of 10:1 to 1:10, respectively, with a catalyst comprised of face-centered cubic molybdenum oxycarbonitride, in which the

interstitial oxygen, carbon and nitrogen atoms are distributed throughout the bulk structure, at a temperature of about 100 to 600^{o}C, a pressure of about 0.1 to 50,000 v/v/hr and recovering product paraffinic hydrocarbons.

86. Hallulin, A. P. and A. E. Burnett; Coprecipitated Si-Al-metal-particle catalyst; U. S. Patent 4,497,907, Feb. 5, 1985. **Claim 1:** A calcined support catalyst comprised of: (a) one or more metals which are catalytically active for the hydrogenation of organic compounds, (b) alumina and silica at a weight ratio of 0.45:1 to 1:0.45, respectively, and (c) solid porous particles, the catalyst being characterized as having a BET total surface area ranging from about 150 to about 350 m^2/g wherein the total amount of catalytically active metal in the catalyst ranges from about 10 wt.% to about 70 wt.% and wherein the catalyst has been prepared by: (aa) coprecipitating ions of one or more catalytically active metals, aluminum ions and silicate ions, with the solid porous particles, (bb) drying the coprecipitated catalyst and (cc) calcining the dried coprecipitated catalyst at a temperature from about 300 to 450^{o}C.

87. Mauldin, C. H.; Conversion of methanol to hydrocarbons; U.S. Patent 4,513,161, Apr. 23, 1985. **Claim 1:** A process useful for the conversion of methanol to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of methanol and hydrogen, in methanol:hydrogen molar ratio equal to or greater than about 2:1 at total pressure equal to or greater than about 160 psig, over a catalyst which comprises ruthenium in catalytically active amount composited with titania or titania-containing support.

88. Soled, S. L., A. Wold and R. Kershaw; Reduction process for forming powdered alloys from mixed metal iron oxides; U.S. Patent 4,525,206. **Claim 1:** A process for producing a powdered metal-based iron alloy comprising the steps of: (a) heating a mixture comprised of a powdered mixed metal iron oxide, being difficulty reducible in hydrogen gas, with at least a stoichiometric amount of calcium metal, in a non-oxidizing atmosphere, at a temperature below the melting point of the mixed metal iron oxide for a time sufficient to substantially reduce all the metal oxide present, and form said product metal-based iron alloy, as determined by X-ray diffractometry, (b) contacting said reduced mixed metal iron oxide with aqueous acid to remove calcium impurities and by-products; and (c) recovering said product metal-based iron alloy.

89. Payne, V. L. and C. H. Mauldin; Cobalt catalysts for the preparation of hydrocarbons from synthesis gas and from methanol; U.S. Patent 4,542,122, Sept. 17, 1985. **Claim 1:** A catalyst composition useful for the conversion of methanol or synthesis gas to hydrocarbons which consists essentially of cobalt, or cobalt and thoria in catalytically active amount composited with titania or a titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

90. Wachs, I and C. C. Chersich; Catalysts comprising tantala supported on titania; U.S. Patent 4,544,649, Oct. 1, 1985. **Claim 1:** A catalyst composition comprising

an oxide of tantalum support on titania wherein at least a portion of the supported tantalum metal oxide is in a non-crystalline form.

91. Madon, R. J.; Liquid hydrocarbon synthesis using supported ruthenium catalysts; U.S. 4,477,595, Oct. 16, 1984. **Claim 1:** A process for selectively producing paraffins comprising: (a) first contacting a mixture of H_2 and CO for at least 10 hours with a reduced and supported ruthenium catalyst, said ruthenium catalyst comprising ruthenium on a support selected from the group consisting of TiO_2, $ZrTiO_4$, TiO_2-carbon, TiO_2-Al_2O_3, TiO_2-SiO_2, alkaline earth titanates, alkali titanates, rare earth titanates, V_2O_3, Nb_2O_5, Ta_2O_5, Al_2O_3-V_2O_3, Al_2O_3-Nb_2O_5, Al_2O_3-Ta_2O_5, SiO_2-V_2O_3, SiO_2-Nb_2O_5, SiO_2-Ta_2O_5, V_2O_3-carbon, Nb_2O_5-carbon, Ta_2O_5-carbon, alkaline earth Group VB oxides, alkali-Group VB oxides, rare earth-Group VB oxides, Group IVB-Group VB oxides, and mixtures thereof, at FT conditions such that the temperature ranges from about 100 to 400^{o}C, the pressure ranges from about 0.2 to 10 mPaA, the gas hourly space velocity, GHSV, ranges from about 100 to 50,000 v/v/he and wherein the ratio of GHSV/pressure is below about 24,000 v/v/hr/mPaA, and at least about a 20% CO conversion is effected; and (b) continuing said contacting as in step (a) at a H_2/CO molar ratio from about 0.1 to 4 and thereafter recovering a hydrocarbon mixture comprising C_5-C_{40} hydrocarbons, containing C_5-C_{20} paraffins and olefins in a paraffins to olefins weight ratio of at least 1.5

92. Fiato, R. A. and E. L. Kugler; Production of alkanes from mixtures of CO and H_2; U.S. Patent 4,548,953, Oct. 22, 1985. **Claim 1:** A process for producing hydrocarbons, including alkane hydrocarbons, from gaseous mixtures of CO and H_2 comprising contacting said mixture, at a temperature ranging from about 200 to 350^{o}C and for a time sufficient to convert at least a portion of said feed to alkane hydrocarbons, with a catalyst comprising a mixture of iron carbide and ilmenite supported on titania wherein the amount of said supported iron present in said supported iron carbide and ilmenite, calculated as Fe_2O_3, is at least about 2 x 10^{-3} grams per square meter of titania support surface.

93. Arcuri, K. B., C. H. Mauldin and D. H. Shaw; Ruthenium catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,567,205, Jan. 28, 1986. **Claim 1:** A process useful for the synthesis of hydrocarbons at reaction conditions from a feed constituting an admixture of carbon monoxide and hydrogen, which comprises contacting said feed with a catalyst which comprises ruthenium in catalytically active amount composited with titania, or titania-containing support, having a rutile:anatase ratio of at least about 2:3 and rhenium in amount sufficient to provide a weight ratio of rhenium:ruthenium which ranges from about 2:1 to about 1:4, sufficient at corresponding reaction conditions to obtain improved activity maintenance vis-a-vis a ruthenium catalyst otherwise similar except that it does not contain rhenium.

94. Halluin, A. P. and A. E. Barnett; Catalyst support compositions; U.S. Patent 4,593,014, June 3, 1986. **Claim 1:** A catalyst support composition consisting essentially of alumina and titania at a weight ratio of about 0.3:1 to 1:0.3

respectively, and solid porous particles selected from the group of kieselguhr, infusorial earth, diatomaceous earth and siliceous earth.

95. Fiato, R. A. and E. L. Kugler; Improving activity of iron carbide and ilmenite on titania Fischer-Tropsch catalyst; U.S. Patent 4,594,331, June 10, 1986. **Claim 1:** A process for improving the activity of a FT catalyst present in a FT reaction zone wherein said catalyst comprises a mixture of iron carbide and ilmenite supported on a titania support wherein the amount of iron present in said supported iron carbide and ilmenite mixture, calculated as Fe_2O_3, is at least about 2×10^{-3} grams per square meter of titania support surface and wherein said reaction zone contains a FT feedstream comprising a mixture of H_2 and CO, said process comprising reducing or eliminating the hydrogen content of the FT feedstream, raising the temperature in said reactor between about 50 to about 150°C above the FT reaction temperature for from about 1 to 6 hrs. and then lowering the temperature back to the reaction temperature and reestablishing the hydrogen content of the feedstream.

96. Payne, V. L. and C. H. Mauldin; Preparation of hydrocarbons from synthesis gas; U.S. Patent 4,595,703, June 17, 1986. **Claim 1:** A process useful for the conversion of synthesis gas to hydrocarbons which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with titania or titania-containing support, wherein the titania support is one having a rutile:anatase ratio of at least about 2:3.

97. Wachs, I. E., R. A. Fiato and C. C. Chersich; Iron carbide on titania surface modified with Group VA oxides as Fischer-Tropsch catalysts; U.S. Patent 4,608,359, Aug. 26, 1986. **Claim 1:** A catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof supported on said titania wherein at least a portion of said supported oxide of niobium, vanadium, tantalum or mixture thereof is in a non-crystalline form, wherein the amount of said supported oxide ranges from about 0.5 to 25 wt.% metal oxide on the titania support based on the total support composition and wherein the catalyst contains at least about 2 milligrams of iron, calculated as Fe_2O_3 per square meter of support surface.

98. Fiato, R. A., G. B. McVicker and A. A. Montagna; Fe-Co catalyst slurry system for use in alpha olefin production; U.S. Patent 4,624,967, Nov. 25, 1986. **Claim 1:** A process for synthesizing hydrocarbons containing alpha olefins comprising contacting a gaseous feed mixture of H_2 and CO, in a reaction zone, with a slurry catalyst system at elevated temperature for a time sufficient to convert at least a portion of said gaseous feed to said alpha olefins, wherein said catalysts slurry system is prepared by a process comprising the steps of: (a) heating a slurry mixture comprised of: a FT slurry liquid, an iron carbonyl compound, a cobalt

carbonyl compound, or iron and cobalt compounds capable of forming carbonyl complexes in a atmosphere of CO, and mixtures thereof, and a powdered support, wherein said iron and cobalt compounds are present in a total iron:cobalt atomic ratio of about 35:1 to 1:10, taken as free metals, and wherein the cobalt carbonyl compound has a lower melting point/decomposition temperature than the iron carbonyl compound; in a carbon monoxide atmosphere under pressure, at a temperature above the melting point/decomposition temperature of the cobalt compound for a time sufficient to substantially decompose the cobalt compound, (b) heating said slurry mixture from step (a) at a temperature above the melting point/decomposition temperature of the iron compound in said CO atmosphere under pressure, to substantially decompose the iron compound; and (c) heating said slurry mixture from step (b) in an atmosphere of hydrogen gas to substantially reduce said iron and cobalt carbonyl compounds and their decomposition products to form said catalyst.

99. Rice, G. W., R. A. Fiato and S. L. Soled; Promoted iron-carbon-based catalysts produced in the presence laser radiation; U.S. Patent 4,659,681, April 21, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm, and which particles are subsequently impregnated with at least 2% of a promoter selected from the group of the salts and oxides of alkali and alkaline earth metals.

100. Rice, G. W., R. A. Fiato and S. L. Soled; Iron carbide-based catalyst produced in the presence of laser radiation; U.S. Patent 4,668,647, May 26, 1987. **Claim 1:** A composition of matter comprising finely divided non-pyrophoric iron-carbide catalytic particles comprising iron and carbon in the substantial absence of silicon, a substantial portion of which is cementite, produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron compound reactants selected from the group consisting of iron carbonyls, iron acetyl-acetonate, and ferrocene, and pressure sufficient to produce non-pyrophoric iron-carbon particles having average diameters between 1 and 100 nm.

101. Mauldin, C. H.; Improved cobalt catalysts, and use thereof for Fischer-Tropsch synthesis; U.S. Patent 4,670,475, June 2, 1987. **Claim 1:** A process useful for the conversion or synthesis gas feed comprised of hydrogen and carbon monoxide to hydrocarbons which comprises contacting said feed at reaction conditions with a catalyst which comprises cobalt, or cobalt and thoria in catalytically active amount composited with a titania or titania-containing support, to which is added sufficient rhenium to obtain, with a similar feed at

corresponding process conditions, improved activity, as contrasted with a catalyst composition otherwise similar except that it does not contain rhenium.

102. Fiato, R. A. and E. L. Kugler; Iron on titania Fischer-Tropsch catalyst; U.S. Patent 4,689,313, Aug. 25, 1987. **Claim 1:** A catalyst composition consisting essentially of catalytic components being selected from the group consisting of a mixture of iron carbide and ilmenite and a mixture of iron carbide and ilmenite containing at least one alkali metal promoter wherein the ratio of supported iron present in said supported iron carbide and ilmenite, calculated as FE_2O_3, to the surface area of said titania support ranges between about 2 to 25 milligrams per square centimeter, and wherein said catalyst has been formed by depositing an iron precursor salt of said catalytic component on said titania support, calcining said deposited salt and support to form a calcined composite and sequentially contacting said composite with a hydrogen containing reducing gas free of CO at elevated temperatures of from about 300 to about 500^{o}C for a time sufficient to reduce the calcined composite followed by contacting said reduced composite with CO at a temperature from about 100 to about 200^{o}C lower than the temperature used for said hydrogen contacting.

103. Fiato, R. A., R. Bar-Gadda and S. Miseo; Cerium promoted Fischer-Tropsch catalysts; U.S. Patent 4,719,240, Jan. 12, 1988. **Claim 1:** A hydrocarbon synthesis process comprising contacting a feed stream of CO and H_2 in a molar ratio of about 0.5 to about 4:1 with a catalyst at a temperature in the range of about 200 to 350^{o}C, a pressure in the range of about 1 to 50 atm, a space velocity in the range of about 10 to 10,000 v/v/hr to produce a hydrocarbon product containing ethylene and ethane in which the ethylene/ethane mole ratio is greater than one, and recovering the product; the catalyst being comprised of a sintered composition containing: (a) about 5-80 wt.% Fe oxide; (b) about 4-20 wt.% Zn oxide, (c) about 10-40 wt.% Ti and/or Mn oxide, (d) about 1-5 wt.% of a Group IA metal oxide selected from the group consisting of K, Rb and Cs, and mixtures thereof, (e) about 1-10 wt.% Ce oxide such that said sintered combination comprises a series of spinels of Fe, Zn and/or Ti and/or Mn and said Group IA metal oxide in a cerium oxide matrix.

104. Fiato, R. A.; Slurried CO hydrogenation catalysts; U.S. 4,752,600, June 21, 1988. **Claim 1:** A slurry catalyst composition consisting essentially of: (a) TiO_2, (b) the decomposition product of a ruthenium carbonyl complex which is $Ru_3(CO)_{12}$, said decomposition product being formed by the decomposition of said $Ru_3(CO)_{12}$ in the presence of a gas mixture of $CO:H_2N_2$ at a temperature of about 230^{o}C to about 270^{o}C and a pressure of about 230 to about 270^{o}C and a pressure of about 4 to about 20 atm. for a sufficient period of time to form said decomposition product, said decomposition product being supported on said TiO_2, and (c) an inert alkane hydrocarbon.

105. Iglesia, E., S. L. Soled and R. A. Fiato; Cobalt-ruthenium catalysts for Fischer-Tropsch synthesis; U.S. 4,822,824, April 18, 1989. **Claim 1:** A hydrocarbon synthesis process which comprises reacting hydrogen and carbon monoxide in

the presence of a catalyst comprised of cobalt and ruthenium on titania, at reaction conditions suitable for the formation of higher hydrocarbons, the catalyst being prepared by impregnating titania with solutions of cobalt and ruthenium salts, drying the impregnating support, reducing the cobalt and ruthenium, treating the reduced metals with an oxygen containing stream at conditions sufficient to form oxides of cobalt and oxides of ruthenium and reducing the cobalt and ruthenium oxides.

106. Wachs, I. E. and D. B. Yang; Catalysts comprising ruthenium on titania surface modified with Group VA oxide of vanadium, niobium or tantalum; U.S. 4,861,747, Aug. 29, 1989. **Claim 1:** A catalyst comprising ruthenium supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from the group consisting of niobium, vanadium, tantalum or mixture thereof, in a non-crystalline form, supported on said titania.

107. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts; U.S. Patent 4,962,078, Oct. 9, 1990. **Claim 1:** A catalyst composition useful for the conversion of synthesis gas to liquid hydrocarbons which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support, the support being at least about 80% by weight titania, the layer ranging in average thickness from about 0.2 mm to about 0.20 mm with the cobalt loading being about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalysts, and having a productivity and methane selectivity at 200^{o}C of at least 150 hr^{-1} and no more than 10 mole %, respectively.

108. Mauldin, C. H. and K. L. Riley; Titania-supported catalysts and their preparations for use in Fischer-Tropsch synthesis; U.S. Patent 4,992,406, Feb. 12, 1991. **Claim 1:** A support composition for forming a catalyst useful for the conversion of synthesis gas to hydrocarbons which comprises titania in which there is incorporated from 0.1 to about 20 wt.% of an inorganic oxide binder selected from the group consisting of alumina and zirconia based on the weight of the titania-binder support, to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.5 cc/g, and surface area ranging from about 8 m^2/g to about 70 m^2/g.

109. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U. S. Patent 5,004,862, April 2, 1991. **Claim 1:** A process for purifying a condensate stream from a hydrocarbon synthesis or alcohol synthesis process which comprises: (a) contacting the condensate with a hot gaseous mixture comprising methane and steam to strip contaminants comprising lower molecular weight hydrocarbons and oxygenates; (b) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (c) separately recovering purified water.

110. Hildinger, H. W. and E. D. Carlson; Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process; U.S. Patent 5,053,581, Oct. 1, 1991. **Claim 1:** A process for producing heavy hydrocarbons which comprises: (a) reacting CO and H_2 over a catalyst at reactive conditions in a hydrocarbon synthesis to form heavy hydrocarbons and a product condensate; (b) separately recovering the heavy hydrocarbons from the product condensate; (c) contacting the product condensate with a hot gaseous mixture comprising CH_4 and steam to strip the product condensate of contaminants, said contaminants comprising lower molecular-weight hydrocarbons and oxygenates; (d) recovering a gaseous stream comprising the contaminants and the gaseous mixture; and (e) converting the gaseous stream recovered in step (d) to CO and H_2 and utilizing at least a portion of said CO and H_2 in step (a).

111. Fiato, R. A.; Two stage process for hydrocarbon synthesis; U.S. Patent 5,028,634, July 2, 1991. **Claim 1:** A two stage hydrocarbon synthesis process comprising:
(a) reacting in a first stage, hydrogen and carbon monoxide in the presence of a supported cobalt or ruthenium catalyst and obtaining a CO conversion to C_2+ hydrocarbons of at least 50% at reaction conditions including a pressure of at least 10 atmospheres;
(b) recovering a reaction product comprisiong hydrogen and carbon monoxide and separating liquid therefrom;
(c) reacting in a second stage, at a pressure below 10-12 atmospheres and no greater than the outlet pressure of the first stage, the remaining reaction products in the presence of a catalyst comprising catalytically effective amounts of cobalt supported on alumina at reaction conditions and
(d) wherein the second stage catalyst is at least as active for CO conversion to C_2+ hydrocarbons as the first stage catalyst at second stage reaction presssure.

112. Iglesia, E., H. Vroman, S. Soled, J. Baumgartner and R. A. Fiato; Selective catalysts and their preparation for catalytic hydrocarbon synthesis; U.S. Patent 5,036,032, July 30, 1991. **Claim 1:** A method for preparing a supported cobalt catalyst particle which comprises: (a) contacting a support particle with a molten cobalt salt, for a period sufficient to impregnate substantially all of the molten cobalt salt on the support to a depth of less than about 200 :m; (b) drying the supported cobalt salt obtained in step (a); and (c) reducing the cobalt of the supported cobalt salt in step (b) to metallic cobalt by heating the salt in the presence of H_2, wherein the heating is conducted at a rate of less than about 1^oC/min up to a maximum temperature ranging from about 200^oC to about 500^oC to produce a supported cobalt catalyst particle.

113. Hsu, E. C. and J. L. Robbins; Catalyst pretreatment method; U.S. Patent 5,070,064, Dec. 3, 1991. **Claim 1:** A liquid phase method for removing sub-1 micron particles adhering to catalyst particles the catalyst containing a Group VIII metal supported on an inorganic refractory oxide as a result of preparation of the

catalyst which comprises: (a) dispersing the catalyst particles to which the sub-1 micron particles adhere within a liquid comprising a FT; (b) agitating the dispersion and separating the sub-1 micron particles from the catalyst particles, and concentrating the sub-1 concentrating the sub-1 micron particles in the liquid phase; and (c) separating the sub-1 micron containing liquid phase from the particulate material.

114. Mauldin, C. H. and K. L. Riley; Titania catalysts,. their preparation, and use in Fischer-Tropsch synthesis; U.S. Patent 5,140,050, Aug. 18, 1992. **Claim 1:** A process for the conversion of synthesis gas to hydrocarbons at high activity which comprises contacting at reaction conditions a feed comprised of an admixture of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than 0.5:1 at pressure greater than or equal to 80 psig, over a catalyst composition comprised of a catalytically effective amount of a Group VIII non-noble metal catalytically active for the conversion of synthesis gas to hydrocarbons dispersed upon a titania support in which there is incorporated from about 0.1% to about 10% of an inorganic oxide binder selected from the group consisting of alumina, and zirconia based on the weight of the titania-binder to support to provide a titania-binder support having a pore volume ranging from about 0.2 cc/g to about 0.55 cc/g and surface area ranging from about 8 m^2/g to about 70 m^2/g.

115. Soled, S. L., G. B. McVicker and W. E. Gates; Metal on rare earth modified silica alumina as hydrocarbon conversion catalyst; U.S. 5,248,409, Sept. 28, 1993. **Claim 1:** A catalytic hydroconversion process which includes hydroisomerization of at least a feedstream comprising: contacting and feedstream with a catalyst composition comprising an amorphous silica-alumina support having at least about 50 wt..% silica, a rare earth oxide, and a metal selected from the group consisting of Group VIII noble metals, rhenium, and mixtures thereof.

116. Herbolzheimer, E. and E. Iglesia; Slurry bubble column; U.S. Patent 5,348,982, Sept. 20, 1994. **Claim 1:** A method for optimally operating a large diameter three phase (gas, liquid, solid) slurry bubble column having a diameter greater than 15 cm for FT synthesis over a supported cobalt catalyst in which solid particles are fluidized in the liquid phase by bubbles of the gas phase, comprising: (a) injecting the gas phase into said column at an average gas velocity along said column, U_g>2 cm/sec, such that the flow regime is in the substantial absence of slug flow; (b) fluidizing the solid supported cobalt catalyst particles of average diameter, d_p>5 :m, to the height, H>3m, of the expanded liquid in the column by operating with a catalyst settling velocity, U_s, and dispersion coefficient, D, such that

$$0.5\ (U_s - U_L) \le \frac{D}{H},\ where\ H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu}\ g f(C_p),\ where\ d_p > 5 \mu m$$

and (c) maintaining plug flow in said column by operating with a gas phase velocity, U_g, expanded liquid height, H, and dispersion coefficient, D, such that $U_g \geq 0.2$ D/H, where H >3m, $U_g > 2$ cm/sec, wherein D_s = effective density of the particles; D_l = density of the liquid; : = viscosity of the liquid; $f(C_p)$ = hindered settling function; = volume fraction of solids in the slurry (liquid plus solids); U_L = liquid velocity along the column; H = height of the expanded liquid in said reactor; g = gravitational constant; d_p = diameter of particles; m = meters.

117. Agesteguia, C. R., S. L. Soled and S. Miseo; Catalysts for iso-alcohol synthesis from CO + H_2, U.S 5,387,570, Feb. 7, 1995. **Claim 1:** A catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof, and wherein said second oxide is a Group IIA oxide and a Group IB metal.

118. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Structurally modified alumina supports, and heat transfer solids for high temperature fluidized bed reactions; U.S. 5,395,406, March 7, 1995. **Claim 1:** A composition of matter which comprises: a support components comprising particulate alpha alumina solids of fluidizable particle size of 30-150 microns modified by compositing a metal therewith to form particles represented by formulas (1) and (2), a composite particle being represented by formula (1), as follows;

$$M_xAl_2O_{3+Y} \qquad \textbf{(1)}$$

with the core of the particle being represented by formula (2), as follows:

$$M_yAl_2O_{3+Y} \qquad \textbf{(2)}$$

where in formulas (1) and (2), M is a Group IIA metal, x is a number ranging from about 0.01 to about 0.4 and is representative of the number of moles of the metal M per mole of Al_2O_3, y is a number equal to or greater than zero, and x is greater than y.

119. Pruett, R. L. and J. S. Bradley; Transition metal bimetallic clusters of ruthenium with thallium, indium and gallium, U.S. 4,360,475, Nov. 23, 1982. **Claim 1:** A composition of matter comprising a bimetallic cluster compound of the formula $[M]_n[(Ru_6C\text{-}(CO)_{16})_2L]$ where M is alkali metal cation, alkaline earth metal cation, N(RN)4+, P(RN)4+ or As(R^o)4+ where RN is C_1-C_{20} aliphatic, C_3-C_8 cycloaliphatic, C_7-C_{14} aralkyl or C_6-C_{10} aryl, n is a number which satisfies valence requirements and L is Tl, In or Ga.

120. Iglesia, E., S. L. Soled and J. E. Baumgartner; Selective fixed-bed Fischer-Tropsch synthesis with high surface area Cu and K promoted, iron/manganese spinels; U.S. 5,118,715, June 2, 1992. **Claim 1:** A hydrocarbon synthesis process for preparing a product containing C_5+ hydrocarbons and less than about 30% CO_2 comprising contacting in a fixed-bed a pelletized catalyst composition

wherein the particle size is greater than about 200 microns average diameter, at a temperature of 200-240°C, the catalyst comprising at least one unsupported, single phase, iron-manganese spinel dual promoted with both copper and a Group IA or IIA metal, said spinel exhibiting a single phase being isostructural with Fe_3O_4 as determined by powder X-ray diffractometry, and possessing a BET surface area greater than 30 m^2/g and an Fe:Mn atomic ratio of at least 2/1, with a mixture of CO and hydrogen under conditions of pressure, space velocity, and elevated temperature for a time sufficient to produce said C_5+ hydrocarbons.

121. Behrmann, W. C., C. H. Mauldin and K. B. Arcuri; Cobalt-titania catalysts. Process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas, and process for the preparation of said catalysts (C-2448); U.S. 5,128,377, July 7, 1992. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons, which comprises contacting at reaction conditions a feed comprising carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition which comprises cobalt dispersed and impregnated as a catalytically active layer upon the surface of a support containing at least about 80 wt% titania ranging in average thickness from about 0.02 mm to about 0.20 mm, with a cobalt loading of about 0.04 g/cc to about 0.15 g/cc, calculated as metallic cobalt per packed bulk volume of catalyst and with a productivity and methane selectivity at 200°C of at least 150 hr^{-1} and no more than 10 mole%, respectively.

122. Say, G. R., J. H. Taylor, D. C. Long and R. A. Fiato; Synthesis gas generation of startup process (C-2556); U.S. 5,143,647, Sept. 1, 1992. **Claim 1:** A method for starting up a fluidized bed or spouted bed steam reforming partial oxidation process for converting a feed gas comprising methane to a product comprising hydrogen and carbon monoxide and unconnected methane which comprises the sequential steps of: (a) heating to reaction temperature the fluidized bed or spouted bed comprised of essentially inert particles, in the presence of oxygen, in an oxiding atmosphere, and in the substantial absence of a reforming catalyst; (b) converting to a reducing atmosphere; and (c) introducing into the fluidized or spouted bed sufficient Group VIII metal containing catalyst and converting, in the presence of oxygen, the feed gas to the product.

123. Soled, S. L., E. Iglesia and R. A. Fiato; Copper promoted cobalt-manganese spinel catalyst and method for making the catalyst for Fischer-Tropsch synthesis; U.S. 5,162,284, Nov. 10, 1992. **Claim 1:** A composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula: $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2.

124. Soled, S. L., S. Miseo, E. Iglesia and R. A. Fiato; Iron-zinc catalysts for the conversion of synthesis gas to alpha-olefins; U.S. 5,185,378, Feb. 9, 1993. **Claim 1:** A process for preparing a liquid product containing olefins and paraffins wherein the olefin/paraffin ratio is at least about 2.5/1, and the C_5+/C_4-ratio is at least about 4.5/1 which comprises reacting in a slurry liquid, at suitable reaction

conditions, hydrogen and carbon monoxide in the presence of a catalyst comprising: iron, zinc, copper, an alkali metal selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof, wherein the iron:zinc atomic ratio is at least a 5:1, and the alkali:copper atomic ratio is at least 2:1.

125. Soled, S. L., E. Iglesia and R. A. Fiato; Substituted cobalt catalysts for Fischer-Tropsch synthesis; U.S. 5,248,701, Sept. 28, 1993. **Claim 1:** A FT process for the conversion of synthesis gas to hydrocarbons which comprises activating a copper promoted, cobalt-manganese spinel catalyst having the formula $Co_{3-x}Mn_xO_4$, where x is from about 0.5 to about 1.2 by contacting the catalyst with a reducing atmosphere and contacting the activated catalyst in a reactor with hydrogen/carbon monoxide synthesis gas.

126. Chang, M. and C. A. Coulaloglou; Enhanced catalyst mixing in slurry bubble columns (OP-3723); U.S. 5,252,613, Oct. 12, 1993. **Claim 1:** A method for improving the axial distribution of catalyst in a hydrocarbon synthesis slurry bubble column which uses rising synthesis gas introduced by means of synthesis gas distribution means located at the bottom of said column to provide the majority of the energy used in distributiong catalyst in said column, the improvement in axial distribution of catalyst being achieved by using a secondary fluid introduction means in said slurry bubble column at a location above the synthesis gas distribution means located at the bottom of said column to introduce a secondary fluid stream into said column.

127. Hsia, S. J.; External catalyst rejuvenation system for the hydrocarbon synthesis process; U.S. 5,260,239, Nov. 9, 1993. **Claim 1:** A process for practicing catalytic hydrocarbon synthesis and reactivation rejuvenation of deactivated hydrocarbon synthesis catalyst on a continuous basis, said process comprising combining catalyst and synthesis feed and hydrocarbon liquid in a hydrocarbon synthesis first vessel menas to produce a reactor slurry comprising catalyst, synthesis feed and synthesis product, collecting deactivated catalyst from the top of the reactor slurry by menas of a first downcommer-conduit means the top of which is fitted with gas disentrainment means and which is located just below the top surface of the reactor slurry, passing the deactivated catalyst down the first downcomer-conduir means from the top of the first vesssel means to the bottom of a reactivation-rejuvenation second vessel menas, said second vessel means having rejuvenating gas introduction means located at its bottom, forming a reactivating slurry of catlayst in reaction product and rejuvenating gas, wherein the deactivated catalyst is reactivated-rejuvenated in said second vessel menas, collecting reactivated-rejuvenated catalyst from the top of the reactivating slurry by means of a second downcomer-conduit means to theop of which is fitted with gas disentrainment means and which is located just below the top surface of the reactivation slurry and passing the reactivated-rejuvenated catalyst down the second downcommer-conduit means from the top of the second vessel means to the bottom of the first vessel means, all catlayst downward flows on both the first and second downcomer means occurring solely inder the influence of gravity.

128. Pedrick, L. E., C. H. Mauldin and W. C. Behrmann; Draft tube for catalyst rejuvenation and distribution; U.S. 5,268,344, Dec. 7, 1993. **Claim 1:** A method for rejuvenating reversibly deactivated particulate hydrocarbon synthesis catalyst in a slurry phase reactor, said method comprising the use of substantially vertical draft tube means, open at both ends, fully immersed in the slurry containing the catalyst and injecting a hydrogen containing gas at or substantially near the bottom of said draft tube means thereby lifting catalyst in slurry from the bottom of the slurry phase reactor into and through the oppen bottom end of the draft tube means, rejuvenating catalyst in the presence of said hydrogen containing gas in the vertical draft tube means and ejecting the rejuvenated catalyst into the top of the slurry phase in the slurry phase reactor through the open top of the draft tube means.

129. Mitchell, W. N.; Rejuvenation of hydrocarbon synthesis catalyst; U.S. 5,283,216, Feb. 1, 1994. **Claim 1:** A method for rejuvenating a partially deactivated, Group VIII metal containing Fischer-Tropsch catalyst having an initial catalyst activity which comprises: suspending the catalyst in slurry liquid hydrocarbons and treating the suspended catalyst with hydrogen or a hydrogen containing gas at elevated temperatures and pressures and recovering a substantial portion of the metal catalyst activity.

130. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,292,705, March 8, 1994. **Claim 1:** Amethod for activating an essentially fresh, reduced cobalt containing Fischer-Tropsch catalyst which comprises treating the catalyst with hydrogen or a hydrogen containing gas in the presence of hydrocarbon liquids for a period sufficient to increase substantially the initial catalyst productivity.

131. Chang, M.; Enhanced gas separation for bubble column draft tubes; U.S. 5,332,552, July 26, 1994. **Claim 1:** A slurry bubble column reactor comprising a double walled vessel defined by an inner vessel wall having a peripheral circumferential top rim and a bottom edge, and an outer main containment vessel wall surrounding said inner vessel wall, said outer main containment vessel having a top and a bottom, and wherein the inner vessel wall and the outer vessel wall are substantially co-axial and have a space between them forming an annulus between said respective walls, the outer main containment vessel wall having a synthesis gas inlet means at the bottom, gas outlet means and product recovery means at the top, and a floor above the gas inlet means which floor is fitted wigh gas distribution means, the inner vessel wall serving as a main reactor zone, the peripheral circumferential top rim of the inner vessel wall having attached to it an inverted channel having an apex and two edges, the point of attachment of the inverted channel to the inner wall being along a first one of said two edges of said inverted channel, a second of said two edges of said inverted channel extending over the main reaction zone thereby creating a gas space within its inverted contour and which inverted channel has a gas vent extending out of, and upwardly from, said inverted channel, and having a liquid by-pass pipe extending from a point on one side of the inverted channel below the apex

of said inverted channel and between said apex and the edge of attachment to the inner vessel wass, to under said top rim of said inner vessel wall and which by-pass pipe empties into the annulus, and liquid exit means at the bottom of the annulus defined by openings in the bottom edge of the interior vessel wall and above the gas distributor means of the main containment vessel.

132. Clavenna, L. R., S. M. Davis, G. R. Say and R. A. Fiato; Synthesis gas from particulate catalysts, and admixutres of particulate catalysts and heat transfer solids; U.S. 5,348,717, Sept. 20, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of oxygen, or both stean and oxygen, the improvement wherein the fludizing bed is comprised of an admixture of
a particulate consisting essentially of a non-leachable barium hexaaluminate solids of fluidizable particle diameter in concentration ranging from about 10 percent to about 99.9 percent, based on the weight of the admixture, and a catalyst comprised of a carrier component composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons when contacted with a fluidized bed of the catalyst, in concentration ranging from about 0.1 percent to about 90 percent, based on the weight of the admixture.

133. Clavenna, L. R., S. M. Davis and B. E. Beasley; Process for the reactivation of nickel-alumina catalysts; U.S. 5,356,845, Oct. 18, 1994. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of nickel-on-alumina catalyst at elevated temperature in the presence of steam and oxygen, in a reaction zone operated in a net reducing atmosphere, the steps comprising: withdrawing a portion of said catalyst and contacting said catalyst with an oxygen-containing gas at a temperature elevated sufficiently to convert the nickel component of said catalyst to nickel aluminate, and disperse said nickel aluminate within the alumina support, without sintering and alumina support; and reducing said catalyst after contact with the oxygen-containing gas to the reaction zone to reduce the nickel aluminate component of the catalyst, and increase the activity of the catalyst vis-a-vis that of the catalyst initially withdrawn from the reaction zone.

134. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U.S. 5,360,778, Nov. 1, 1994. **Claim 1:** In a process for the preparation of a particulate heat transfer solid characterized as particulate refractory inorganic oxide solids containing silicon, or boron, or both silicon and boron impurities, the steps comprising: contracting, and treating, said particulate refractory inorganic oxide solids containing silicon in concentration no greater than about 0.5%, based on the total weight of the solids, and boron in concentration no greater than about 500 parts, per million parts by weight total solids, with an acid sufficient to reduce the concentration of silicon and boron in the outer peripheral surface layer of the

particles to no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer.

135. Behrmann, W. C., C. H. Mauldin and L. E. Pedrick; Hydrocarbon synthesis reaction employing vertical downcomer with gas disengaging means; U.S. 5,382,748, Jan. 17, 1995. **Claim 1:** A method for uniformly redistributing particulate catalyst in a slurry phase reactor, said method comprising using a substantially vertical conduit means open at both ends, fully submerged in the slurry of the slurry phase reactor, the bottom end of the substantially vertical conduit means is near the bottom of the slurry phase reactor and the top of the conduit means is topped by gas disengaging means which are below the top surface of the slurry in the slurry phase reactor and wherein the bottom of the substantially vertical conduit means is shielded by a baffle means which diverts gases rising from the botytom of the slurry phase reactor from entering into the bottom of the substantially vertical conduit whereby catalyst in slurry which passes down the substantially vertical conduit and is ejected from the bottom of said conduit near the bottom of the slurry phase reactor.

136. Koros, R. M., Bubble column, tube side slurry process and apparatus; U.S. 5,384,336, Jan 24, 1995. **Claim 1:** A hydrocarbon synthesis process comprising reacting a gaseous mixture of hydrogen and carbon monoxide at a pressure of 1 to 100 atmospheres and a temperature of about 175^{o}C to about 400^{o}C in the presence of a hydrocarbon synthesis catalyst dispersed in a liquid thereby forming a slurry liquid, wherein the catalyst dispersion is disposed in a plurality of vertically arranged elongated reaction tubes having an L/D (length/diameter) of at least about 10, each tube being surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not being in fluid communication with the slurry liquid.

137. Mitchell, W. N.; Activation of hydrocarbon synthesis catalyst; U.S. 5,389,690, Feb. 14, 1995. **Claim 1:** A FT process which comprises activating an essentially fresh, reduced cobalt containing FT catalyst with hydrogen or a hydrogen containing gas, the catalyst being dispersed in hydrocarbon liquids and subsequently using the catalyst in a FT process at FT reaction conditions.

138. Soled, S. L., E. Iglesia, R. A. Fiato and G. B. Ansell; Method for stabilizing titania supported cobalt catalyst; U.S. 5,397,806, March 14, 1995. **Claim 1:** In a FT process, under FT reaction conditions, including contacting with a feedstream comprising a CO and H_2 reaction mixture, a 400-750^{o}C regeneration stable catalyst composition comprising cobalt on a substituted ternary metal oxide of titania having the general formula $Co/Ti_{l-x}M_xO_2$ wherein x is from 0.01 to 0.14 and M is selected from the group consisting of silicon, zirconium and tantalum, wherein the titania is an anatase polymorph.

139. Stark, T. M.; Pentane energy transfer medium in gas conversion; U.S. 5,409,960, April 25, 1995. **Claim 1:** A method for removing heat from a slurry FT hydrocarbon synthesis process reaction zone which comprises passing a cooling

medium comprising a C_4-C_{10} normal, iso- or cyclic paraffin liquid in cooling tubes in indirect heat exchange through the slurry reaction zone, thereby vaporizing the cooling medium at its boiling point, the cooling medium being inert for FT processes, condensible, and vaporizing at a pressure greater than the pressure in the reaction zone, and recovering the vaporized cooling medium heat.

140. Wittenbrink, R. J., S. M. Davis and K. L. Riley; Supported Ni-Cu hydroconversion catalyst; Int. Pub. No. WO 97/03750, Feb. 6, 1997. **Claim 1:** A hydroconversion catalyst comprising nickel in an amount of less than about 15 wt.% catalyst and copper in a copper:nickel ratio of less than about 1:2 supported on an amorphous silica-alumina carrier having less than about 30 wt.% alumina, the carrier having a surface area of greater than about 200 m^2/gm and a pore volume of less than about 1.0 mL/gm.

141. Davis, S. M. and D. F. Ryan; Distillate fuel production from Fischer-Tropsch wax; U.S. 5,378,348, Jan. 3, 1995. **Claim 1:** A process for producing middle distillate transportation fuel components from the waxy product of a hydrocarbon synthesis process which comprises: (a) separating the waxy product into a heavier fraction and at least one lighter fraction; (b) catalytically isomerizing the heavier fraction in the presence of hydrogen and recovering products with improved cold flow properties; (c) catalytically hydrotreating the lighter fraction and removing hetero atom compounds therefrom: (d) catalytically isomerizing the product of step (c) to produce jet fuel component having a freeze point of -30^{o}F or lower.

144. Behrmann, W. C., K. B. Areuri and C. H. Mauldin; Surface supported cobalt catalysts, process utilizing these catalysts for the preparation of hydrocarbons from synthesis gas and process for the preparation of said catalysts; U.S. Patent 5,545,674, August 13, 1996. **Claim 1:** A process useful for the conversion of synthesis gas to liquid hydrocarbons less than about 10 mole% methane which comprises contacting at reaction conditions a feed comprised of carbon monoxide and hydrogen, in H_2:CO molar ratio equal to or greater than about 0.5:1 at total pressure equal to or greater than about 80 psig, over a catalyst composition having a productivity of at least 150 hr^{-1} at 200^{o}C and which comprises cobalt dispersed as a catalytically active layer upon the outer surface of an inorganic oxide support of a thickness of less than about 200 microns, with the loading of cobalt at least about 0.04 g/cc in said catalytically active layer, calculated as metallic cobalt per packed bulk volume of catalyst.

145. Davis, S. M., L. R. Clavenna, G. R. Say and R. A. Fiato; High surface purity heat transfer solids for high temperature fluidized bed reactions; U. S. Patent 5,496,531, March 5, 1996. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed constituted of a catalyst and particulate alpha alumina containing both silicon and boron impurities, at high temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the alpha alumina is comprised of particles of alpha alumina the outer peripheral surface

layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of cations within said outer peripheral surface layer, thereby improving resistance to sintering and agglomeration of the fluidized bed, said particles being produced by acid washing of the alpha alumina.

148. Beadle, S. W., W. H. Summerlin and E. T. A. Van Driessche; Airless cobalt demetalling in the cobalt flash combination catalyst cycle; U.S. Patent 5,410,090, April 25, 1995. **Claim 1:** A method for removing cobalt values from the crude product of a cobalt-catalyzed hydroformylation reaction formed from an olefinic feedstock, said crude product containing cobalt compounds in addition to an organic hydroformylation reaction product, which comprises: (a) contacting said crude product with an organic acid and water, in the absence of any oxygen-containing gases, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (b) separating said substantially cobalt-free crude product from said water soluble cobaltous salt aqueous product; (c) diverting said substantially cobalt-free organic hydroformylation reaction product for further downstream treatment such as distillation or hydrogenation; (d) concentrating said water soluble cobaltous salt aqueous product thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free water containing said organic acid, whereby said concentrated aqueous solution of cobaltous salt is separated from said substantially cobalt-free water containing said organic acid; (e) recycling said substantially cobalt-free water containing said organic acid to step (a); (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol stream and synthesis gas, and passing this mixture to a preformer reactor where said concentrated aqueous solution of cobaltous salt is converted to a cobalt carbonyl; (g) contacting said cobalt carbonyl with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas and to generate as bottoms alcohol products and dissolved cobaltous salts, whereby said entrained volatile cobalt compounds are taken out overhead and the alcohol products and dissolved cobaltous salts are taken out as bottoms; (h) separating said alcohol products of step (g) from said dissolved cobaltous salts; (i) recycling said alcohol products from step (h) to step (f); (j) recycling said dissolved cobaltous salts from step (h) to step (a); and (k) contacting said volatile cobalt compounds from step (g) with said olefinic feedstock, whereby said volatile cobalt compounds are absorbed into said olefinic feedstock.

149. Beadle, S. W. and C. A. Poulin; Use of stripper reactor reflux as an initiator for preforming reaction of cobaltous salts to cobalt carbonyls, U.S. Patent 5,457,240, October 10, 1995. **Claim 1:** A method for producing higher aldehydes and higher alcohols which comprises: (a) hydroformylating an olefinic feedstock with synthesis gas in the presence of a cobalt-containing catalyst to form a crude product containing higher aldehyde, higher alcohol, secondary products and dissolved cobalt catalysts; (b) contacting said crude product with an oxygen-containing gas, an organic acid and water, thereby producing a substantially cobalt-free organic hydroformylation reaction product and a water soluble cobaltous salt aqueous product; (c) separating said substantially cobalt-free

crude product from said water soluble cobaltous salt aqueous product; (d) concentrating said water soluble cobaltous salt aqueous product, thereby producing a concentrated aqueous solution of cobaltous salt and a substantially cobalt-free aqueous solution; (e) separating said concentrated aqueous solution of cobaltous salt from said substantially cobalt-free aqueous solution; (f) contacting said concentrated aqueous solution of cobaltous salt with an alcohol and synthesis gas, and passing this mixture to a preformer reactor where said concentrated solution of cobaltous salt is converted to a cobalt carbonyl; (g) passing said cobalt carbonyl to a stripping reactor wherein said cobalt carbonyl is contacted with a stream of stripping gas to entrain volatile cobalt compounds in said stripping gas; whereby said entrained volatile cobalt compounds are taken overhead; and (h) recycling at least a portion of said entrained volatile cobalt compounds taken overhead in step (g) to said preformer reactor.

150. Vanderspurt, T. H. and J.-L. Kao; Noble metal large pore zeolite catalyst for methanol-ethanol coupling; U.S. Patent 5,493,064, February 20, 1996. **Claim 1:** An alcohol coupling process, comprising: contacting a vaporized mixture of starting alcohols of methanol in combination with a second alcohol selected from the group consisting of ethanol, n-propanol, and mixtures thereof with a carrier gas containing CO and H_2 in the presence of an alumina-bound highly dispersed metallic Pd-loaded, alkali metal cation exchanged L zeolite wherein the zeolite and alumina have an essential absence of strongly acidic catalytic sites and wherein said contacting is carried out at a temperature and partial pressure of CO and H of from about 300 to 400^oC and from 3000 kPa to about 15,000 kPa at a sufficient pressure to minimize the decomposition of methanol to CO and H_2 and at a space velocity of from about 4000 hr^{-1} to about 10,000 hr^{-1} to produce isobutanol and n-propanol in the substantial absence of light gaseous alkanes and C_{6+} oxygenates.

151. Clavenna, L. R., S. M. Davis, R. A. Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials; U. S. Patent 5,395,813, March 7, 1995. **Claim 1:** As a composition, a fluidizable contact mass for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon contacted with a fluidized bed of said contact mass at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, which comprises: an admixture of, a particulate, fluidizable precalcined zirconia heat transfer solid which contains from 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15, and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

160. Davis, S. M., L. R. Clavenna, R. A. Fiato and G. R. Say; High performance alumina heat transfer solids for high temperature fluidized bed synthesis gas reactions; U.S. 5,360,777, Nov. 1, 1994. **Claim 1:** As a composition of matter, a heat transfer solid resistant to sintering and agglomeration for admixture with a catalyst to form a fluidized bed useful in the conversion of a low molecular weight hydrocarbon to hydrogen and carbon monoxide on contact therewith at high temperature in the presence of steam, or oxygen, or both steam and oxygen which comprises: alumina solids particles: (i) the outer peripheral surface layer of which contains no greater than about 5 atom percent silicon and boron, based on the total number of aluminum cations within said outer peripheral surface layer, while the bulk concentration of silicon in the particles does not exceed about 0.5%, based on the weight of the alumina solids, and the bulk concentration of boron in the particles does not exceed about 500 ppm, based on the weight of the alumina solids; (ii) the outer peripheral surface layer of which contains no more than 20 atom percent impurities based on the sum-total concentration of sodium, iron, calcium, and titanium as impurities; (iii) the tapped bulk density of the particles ranges from about 1.2 g/cc to about 2.5 g/cc; (iv) the Davison Attrition Index of the solids particles is no greater than about 12; and the sum total effect of these relationships between surface purity particle density, and attrition resistance is such as to provide a performance index categorized by the formula:

$$\textit{Performance Index} = \frac{1}{(i)x(ii)x(iii)x(iv)} > 20.$$

161. Vanderspurt, T H. and R. J. Koveal; Isoalcohol synthesis; U.S. Patent 5,703,133, Dec. 30, 1997. **Claim 1:** A method for producing isobutanol and methyl butanols from syngas, comprising: (a) contacting a reactant stream containing syngas with a first stage catalyst having alkali promoted La-stabilized, highly dispersed microcrystalline Cu_2O having a particle size of $\leq$ 6 nm interspersed with metallic copper crystallites having a particle size of $\leq$ 25 nm, and zinc oxide crystallites having a particle size of $\leq$ 6 nm in the presence of an alumina structural promoter, wherein on a mol % alkali free metals only basis, Cu is present in from about 45% to about 55%, Zn from about 10% to about 20%, Al from about 10% to about 25%, La from about 5% to about 15% and wherein the alkali is between about 0% to about 1% K and from about 3% to about 6.5% Cs, wherein the first stage catalyst is produced by the process of: coprecipitating at a constant pH of from 0.7 to 11.0 at a temperature of from about 30^oC to about 100^oC in the essential absence of CO_2 from a solution of soluble metal salts of copper, zinc, lanthanum and aluminum with alkali hydroxide solution selected from the group consisting of LiOH, NaOH, KOH, CsOH and RbOH and mixtures thereof; aging the washed precipitate for from about 1 to 24 hrs at from to 50 to 90^oC in the essential absence of CO_2; washing the precipitate in the essential absence of CO_2; drying the washed coprecipitate in air at up to about 120^oC; calcining the dried coprecipitate in air for greater than 3 hrs at a temperature of from about 300 to 700^oC; contacting the calcined coprecipitate with from 0.01% to 0.91% K and 3% to 6.5% Cs to form a promoted catalyst; drying the promoted catalyst at up to

120°C; recalcining the promoted catalyst at from about 300 to 700°C to produce a catalyst precursor containing highly dispersed CuO crystallites of up to about 10 nm; activating the promoted catalyst in flowing hydrogen for at least 1 hr at 175 to 185°C then for at least 1 hr at 250 to 270°C; wherein said contacting of reactant stream and first stage catalyst is carried out at a pressure of from about 850 psi (5,840 kPa) to about 1500 psi (10,310 kPa) a temperature of from about 240°C to about 340°C for a time sufficient to produce a product stream containing methanol, ethanol, propanol, and methyl butanols; (b) contacting methanol, ethanol and propanol from step (a) with a second stage catalyst having at least a first phase of mixed oxide crystallite containing from about 60 to 74 atomic % zirconium, from about 21 to 31 atomic 5 manganese and from about 5 to 9 atomic % zinc, and less than about 1 atomic % alkali, a second phase of zirconium doped hetaerolite containing from about 65 to 69 atomic % manganese, about 31 to 35 atomic % zinc, 0.5 to 5 atomic % zirconium, and optionally a trace atomic % alkali, and a third phase containing from about 20 to 55 atomic % manganese, from about 13 to 55% atomic zinc and 13 to 35 atomic % zirconium wherein the first phase mixed oxide crystallites have a zirconium oxide like structure have a particle size of at least about 40 D to about 100 D, the second phase of at least about 200 D to greater than about 2000 D and the third phase of at least about 1000 D to greater than 400 D at a pressure of from about 850 psi to about 1500 psi (10,300 kPa) a temperature of from about 340 to about 380°C to produce additional isobutanol and methyl butanols from the methanol, ethanol and propanol and trace ethylene and propylene.

162. Koveal, R. J and T. H. Vanderspurt; Isoalcohol synthesis catalyst; US Patent 5,691,268, Nov. 25, 1997. **Claim 1:** A syngas-to-alcohol catalyst, comprising: highly dispersed, alkali promoted, La stabilized, microcrystalline Cu_2O having a particle size of $\leq$ 6 nm in the presence of an alumina structural promoter, wherein on a mole % alkali free metals-only basis Cu is present in from 45% to 55%, Zn from 10% to 20%, Al from 10% to 25%, La from 5% to 15%, and wherein the alkali is from 0.01% to 0.91% K and from 3% to 6.5% Cs.

163. Apesteguia, C. R., S L Soled and S. Miseo; Catalysts for iso-alcohol synthesis from $CO+H_2$; US patent 5,508,246, Apr. 16, 1996. **Claim 1:** A syngas conversion process, having increased selectivity to methanol and isobutanol and conducted under syngas conversion conditions at pressures of about 20 to about 250 atmospheres, comprising contacting a carbon monoxide and hydrogen feedstream with a catalyst composition consisting essentially of a solid solution or a coprecipitated mixture of a first oxide and a second oxide, wherein said first oxide is selected from the group consisting of yttria, rare earth oxides and mixtures thereof and wherein said second oxide is a Group IIA oxide, and a Group IB metal.

164. Vanderspurt, T H., M A Greaney, D Pl Leta, R J Koveal, M M Disko, A V Klaus, S K Behal and R. B. Harris; Isobutanol synthesis catalyst; US patent 5,707,920, Jan 13, 1998. **Claim 1:** A catalyst composition, comprising: a noble metal supported on at least a first phase having a poorly crystalline manganese and

zinc coped zirconium oxide phase containing about 71 to about 91 atomic % zirconium, about 10 to about 16 atomic % manganese and about 4 to about 8 atomic % zinc and a second phase of irregularly shaped hetaerolite crystals containing about 65 to about 69 atomic % manganese, about 31 to about 35 atomic % zinc and 0 to about 5 atomic % zirconium embedded in the first phase.

165. Herskowitz, M.,, Method for hydrocarbon synthesis reactions; US patent 5,652,193, July 29, 1997. **Claim 1:** A method for making a CO hydrogenation catalyst wherein said catalyst includes a metal selected from the group consisting of cobalt and ruthenium deposited in a porous, inorganic, refractory oxide support, said catalyst having said metal located in a rim on the outer surface of said support, said method comprising: (a) determining the rim thickness by: (i) determining intrinsic kinetic rate data including the intrinsic rate of reaction of carbon monoxide hydrogenation and the rate of CO conversion to methane for said catalyst; (ii) determining the thickness of said rim by relating the rates of diffusion of said carbon monoxide and said hydrogen to the intrinsic rate of reaction in said rim for a support geometry selected from the group consisting of a sphere, a ring, a cylinder, and a semi-circle and combinations thereof, such that said rim thickness optimizes both the rate of carbon monoxide hydrogenation and the reduction in methane selectivity; and (b) making a catalyst having a rim thickness determined in step (a).

166. Davis, S. M. and J. W. Johnson; Process for hydroisomerization of waxy hydrocarbon feeds over a slurried catalyst; EP 0 753 563 A1; 04/07/96. **Claim 1:** A hydroisomerization process for the conversion of a C_{5+} paraffinic feedstock to middle distillates which comprises contacting and reacting at hydroisomerization reaction conditions said C_{5+} paraffinic feedstock, and hydrogen, with a catalyst comprising a Group IB metal component, or a Group VIB metal component, or a Group VII metal component or a mixture of two or more of said metal components, supported on an acidic particulate solid, of average particle diameter in a range of from about 30 microns (30 :m) to about 150 microns (150 :m), dispersed in a paraffinic liquid hydrocarbon.

167. Wittenbrink, R. J., R. F. Bauman, P. J. Berlowitz, and B. R. Cook; Synthetic diesel fuel and process for its production; WO 97/14769, 24 April 1997. **Claim 1:** A material useful as a fuel heavier than gasoline or as a blending component for a distillate fuel comprising: 1 250-700^{o}F fraction derived from a non-shifting FT catalyst process and containing at least 95 wt.% paraffins with an iso to normal ratio of about 0.3 to 3.0, $\leq$ 50 ppm (wt.) of sulfur and nitrogen less than about 2 wt.% unsaturates, and about 0.001 to less than 0.3 wt.% oxygen.

168. Wittenbrink, R. J., S. E. Silverberg and D F Ryan; High purity paraffinic solvent compositions, and process for their manufacture; WO 97/21787, 19 June 1997. **Claim 1:** A high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to about C_{20}, has a molar ratio of isoparaffins:n-paraffins ranging from about 0.5:1 to about 9:1 and the

isoparaffins of the mixture contain greater than 50% of the mono-methyl species, based on the total weight of the isoparaffins of the mixture.

169. Stark, T M; Heat removal in gas conversion process, EP appl. 0 614 864 A1, 03/03/94. **Claim 1:** A method for removing heat from a hydrocarbon synthesis process reaction zone, which comprises passing a cooling medium through the reaction zone, in indirect heat exchange therewith, thereby vaporizing the cooling medium; the cooling medium being inert, condensible, and vaporizing at a pressure which is at least as great as the pressure in the reaction zone.

171. Hershkowitz, F. and G. Kiss; Unsaturates recovery and recycle process; U.S. patent 5,516,965, May 14, 1996. **Claim 1:** A process for recovering unreacted acetylene from an effluent stream of a process for synthesizing oxygenated hydrocarbons from unsaturated hydrocarbons, said stream containing unreacted unsaturated hydrocarbons, oxygenated reaction products, and low-boiling gaseous components selected from the group including CO, H_2, CO_2, H_2O, C_1-C_5 alkanes, nitrogen, helium, and argon, comprising: (a) absorbing the unreacted acetylene and the oxygenated hydrocarbons of the synthesis process effluent stream in a solvent wherein said solvent is an acetylene-depleted stream of the oxygenated product of said synthesis process; and (b) stripping the acetylene from the solvent to produce a first stream concentrated in acetylene and a second stream of oxygenated product depleted in acetylene, wherein said acetylene-depleted stream is the absorption solvent and the synthesis process product.

172, Clavenns, L. R., R A Fiato and G. R. Say; Particulate solids for catalyst supports and heat transfer materials, U.S. patent 5,476,877, Dec. 19, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperature in the presence of steam, or oxygen, or both steam and oxygen, the improvement wherein the fluidized bed is comprised of an admixture of a particulate, fluidizable precalcined zirconia heat transfer solid which contains from abut 0% to about 1% silica, based on the weight of the zirconia, in concentration ranging from about 10% to about 99.9%, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15 and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1% to about 90%, based on the total weight of the admixture.

173. Herfbolzheimer, E., F J Kaiser, Jr and E. Iglesia; Catalyst fluidization improvements; U.S. patent 5,157,054, Oct. 20, 1992. **Claim 1:** A slurry phase hydrocarbon synthesis process for the conversion of hydrogen and carbon monoxide at reaction conditions to products which comprises: injecting a gas comprising hydrogen and carbon monoxide at or near the bottom of a bubble

column containing a slurry liquid, a catalytically active first solid and at less a second solid, dispersing the solids in the slurry liquid, all of the energy thereof being supplied by the gas, in the absence of liquid product recycle, the amount of the second solid being sufficient to increase the bed height of the first catalytic solid by at least 10%, and recovering liquid product.

174. Long, D. C.; Staged hydrocarbon synthesis process; U.S. patent 5,498,638, March 12, 1996. **Claim 1:** A once through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst containing cobalt or ruthenium, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.

175. Long, D. C.; Staged hydrocarbon synthesis process; EP appl. 0 679 620 A2, 26/04/95. **Claim 1:** A substantially once-through hydrocarbon synthesis process which comprises reacting in a first stage or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst, recovering the product therefrom, condensing liquids from the product and reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shifting activity, and recovering the products therefrom.

176. Taylor, J. H., and G. R. Say; Production of synthesis gas via fluidized bed/fixed bed process combination; U.S. patent 5,421,840, June 6, 1995. **Claim 1:** In a process for the production of hydrogen and carbon monoxide, the steps comprising: contacting, in a first reaction zone, low molecular weight hydrocarbons comprising methane, oxygen, and steam, at high temperature in a net reducing atmosphere, with a fluidized bed of catalyst, or catalyst and a solids diluent, to convert from about 85% to about 92% of the hydrocarbons to hydrogen and carbon monoxide and form a reaction mixture of hydrogen, carbon monoxide and unreacted hydrocarbons, oxygen and steam, withdrawing said reaction mixture as an effluent from said first reaction zone, and contacting said effluent, in a second reaction zone, with a fixed bed of catalytic metal solids with a void fraction of at least about 0.9 to convert, sufficient of the unreacted hydrocarbons, oxygen, and steam and increase the hydrocarbon conversion to a level ranging from about 0.5% to about 5% above that obtained in said first reaction zone.

ADDENDUM - EXXON FISCHER-TROPSCH WORK

Fischer Synthesis Process

A patent (A.1), a continuation of four prior applications with the first dated October 3, 1989, claimed a method for hydrocarbon synthesis reactions. This patent relates to the use of a catalyst of the "rim" type, as the terminology is used by Exxon. These are catalysts where the active metal(s) are deposited in the outermost layer of the support particle, and in a mannor that the interior of the support particle is essentially devoid of the metal(s). This approach is widely used in the manufacturer of auto exhaust catalysts that are shaped into spheres, cylinders, etc. The specific experiments were conducted with a 6 wt.% cobalt and 0.5 wt.% ruthenium on silica or titania support; since the surface area of the catalyst used in the example was reported to be about 20 m^2/g it is assumed that the support was titania. The description of the preferred embodiment includes a derivation of the theoretical aspects of the determination of the rim loaded thickness needed to optimize CO conversion and/or minimize methane production. This theory has been included in several of the reviews of Fischer-Tropsch synthesis that have recently been published by Exxon workers. It is surprising that the authors of these reviews are not inventors of this method for hydrocarbon synthesis reactions and that the inventor (M. Herskowitz) is not an author of the review articles.

The outer layer containing the catalytic metal has a thickness determined so as to optimize CO conversion to heavy hydrocarbons so that conversion to methane is maintained at a predetermined level. The inventor maintains that it is not possible to simultaneously maximize CO conversion and minimize methane conversion. However it is possible to define a rim thickness so as to optimize one of these products. The thickness of the rim-loaded catalyst is determined by relating the rate of diffusion of CO and H_2 to a rate of reaction in the porous inorganic oxide for a predetermined support geometry, partial pressures and temperatures.

The fluxes of the two reactants at steady state must be equal since there is no accumulation; thus,

$$\beta D_{e,CO}\ [dC_{CO}/d\chi] = D_{e,H}\ [dC_H/d\chi] \qquad [A.1]$$

where the flux is expressed as a product of the effective diffusivity, D_e, and the concentration gradient. β is the stoichiometric coefficient and is equal to 2.07 in the reported work. Since hydrogen diffuses more rapidly than CO, the relative concentration of hydrogen should increase from the surface to the center of the catalyst pellet.

The differential mass balance inside the pores of the catalyst pellet of carbon monoxide, the limiting reactant, is

$$[D_{e,CO}\ (1/\chi^s)]\ d/d\chi[\chi^s\ (dC_{CO}/d\chi)] = \rho_p r_{CO} \qquad [A.2]$$

where χ is the radial position measured from the external surface toward the center, ρ_p is the pellet density, C_{CO} is the CO concentration in the liquid-filled pores and r_{CO} is the intrinsic rate of reaction on the active sites. The shape factor, s, is equal to two for a sphere and to unity for a cylinder; the treatment can be extended to other pellet shapes.

The boundary condition on the external surface is:

$$C_{CO} = P_{CO,b}/H_{CO} \qquad [A.3]$$

where $P_{CO,b}$ is the CO partial pressure in the bulk gas phase and H_{CO} is the Henry's Law constant. The other boundary condition can be defined for two cases as:

$$\text{inert core} \quad dC_{CO}/d\chi = 0 \quad \chi = \chi_i \qquad [A.4]$$

$$\text{hollow core} \quad C_{CO} - P_{CO,b}/H_{CO} \quad \chi = \chi_i \qquad [A.5]$$

This derivation assumes that external mass transfer resistance is negligible and that the pellet is isothermal. Experimental data verified that these are valid assumptions.

The intrinsic rate expression (small particle, diffusion free case) for cobalt or ruthenium on titania or silica support is

$$r_{CO} = k_1\exp(-E_1/RT)[\,P_{CO}{}^{a}P_H{}^{b}/(1 + k_2P_{CO} + k_3P_H)_c] \qquad [A.6]$$

where k_1, k_2, k_3, E_1, a, b, and c are calculated from experimental rate data. [In this and other Exxon patents there are many typos that are usually obvious but sometimes cause concern. Thus, in the above equation we have modified the equation given in the patent by replacing 1 in the original with a and 2 with c to produce equation [A.6].] The inventor indicates that the kinetic parameter, k_1, usually depends only on the metal concentration on the support; presumably the dispersion must also be included. The inventor indicates that in certain cases such as cobalt on titania, it is also a function of water partial pressure:

$$k_1 = A[(1 + k_4P_{H_2O})/(1 + (k_5P_{H_2O})^2)] \qquad [A.7]$$

where A is the activity of the catalyst.

Henry's Law can be used to express equation [A6] in concentrations of CO and H_2:

$$C_{CO} = P_{CO}/H_{CO}\ ;\ \ C_H = P_H/H_H \qquad [A.8]$$

Integrating equation [A1] allows the expression of the hydrogen concentration in terms of the carbon monoxide concentration:

$$C_H = [P_{H,b}/H_H] - [\beta D_{e,CO}/D_{e,H}][(P_{CO,b}/H_{CO}) - C_{CO}\,] \qquad [A.9]$$

or

$$H_HC_H/P_{H,b} = 1 - \gamma[1 - (H_{CO}C_{CO}/P_{CO,b})\,] \qquad [A.10]$$

where

$$\gamma \;=\; (\beta D_{e,CO}/D_{e,H})(H_H/H_{CO})(P_{CO,b}/P_{H,b}) \qquad \text{[A.11]}$$

Substituting equations [A6] and [A7] into equation [A8] and expressing in dimensionless form yields

$$\phi = (\chi_s - \chi_C)[\rho k_1 \exp(-E_1/RT)[\, P_{CO}{}^{a} P_H{}^{b} \,/\, D_{e,CO}(k_2 P_{CO,b})^{c}\,]^{1.2} \qquad \text{[A.12]}$$

The Thiele modulus, ϕ, is the ratio between the maximum rate of reaction and the maximum rate of diffusion. Likewise, γ expresses the ratio between the maximum rate of diffusion of the two reactants; when $\gamma = 1$ the ratio C_{CO}/C_H remains constant and when it is less than one the ratio decreases.

Equation [A.2] is solved to yield the concentration profiles in the pores of the catalyst pellet. This concentration profile is then integrated over the volume of the pellet and this is used to calculate the effectiveness factor which is the ratio of the actual reaction rate (global rate) averaged over the pellet and the maximum reaction rate calculated for the surface conditions:

$$\eta_{CO} \;=\; [1/V \int_{VP} r_{CO} dV]/[R_{CO}(P_{HP_{CO}} P_{H_2O}) \qquad \text{[A.13]}$$

The effectiveness factor for methane can also be obtained in a similar manner using the rate of methane production, r_{CH_4}:

$$\eta_{CH_4} \;=\; [1/V \int_{VP} r_{CH_4} dV]/[R_{CH_4}(P_{HP_{CO}} P_{H_2O}) \qquad \text{[A.14]}$$

and r_{CH_4} is obtained from kinetic measurements:

$$r_{CH_4} \;=\; k_4 \exp(-(E_2 - E_1)/RT)\; [P_H/(1 \;+\; k_2 P_{CO} \;+\; k_3 P_H)] r_{CO} \qquad \text{[A.15]}$$

Assuming an isothermal reactor for simplicity, η_{CO} and η_{CH4} are used in a reactor mass balance to calculate the carbon monoxide conversion and methane selectivity:

$$y_{CO,i}(G_f/M_i)(dX_{CO}/dZ) = \eta_{CO}\,\rho_B\,r_{CO} \qquad [A.16]$$

$$y_{CO,i}(G_f/M_i)(dX_{CH_4}/dZ) = \eta_{CH_4}\,\rho_B\,r_{CH_4} \qquad [A.17]$$

where $Y_{CO,i}$ is the carbon monoxide mole fraction in the feed, G_f is the mass velocity, M_i is the molecular weight of the feed, ρ_B is the bed density and X_{CO} and X_{CH_4} are the carbon monoxide and methane conversion, respectively.

Using a 6% Co/0.5% Re catalyst of different pellet sizes and a feed with H_2/CO = 2, the CO conversion and CH_4 selectivity were measured. These conversion data were used to estimate the CO and H_2 diffusivities using the following procedure:

a. values of $D_{e,CO}$ and $D_{e,H}$ were assumed;

b. effectiveness factors η_{CO} and η_{CH_4} were calculated from equations [A.9] and [A.10] and the solution of equation [A.2] given the inlet conditions of the reactor;

c. the CO conversion and conversion to methane were calculated by integrating equations [A.16] and [A.17]; since the effectiveness factors are functions of the partial pressures of CO, CH_4 and H_2O they must be recalculated along the length of the reactor taking into account of the changes in the partial pressures;

d. methane selectivity was calculated from the ratio of conversion to methane, X_{CH_4} and carbon monoxide conversion, X_{CO};

e. the calculated carbon monoxide conversion and the methane selectivity were compared with the experimental values for the various pellet sizes; and

f. the effective diffusivities are adjusted to give the best fit of the experimental data.

An example of the agreement between the calculated and the experimental data for catalysts with a range of diameters is shown in figure A.1.

In one example the experiments were performed in a 3'x0.5" reactor that was packed with 1 mm diameter spherical particles uniformly loaded with 6%Co-0.5%Re. Data were obtained as the reaction temperature and the H_2/CO ratio were varied and the CO conversion and CH_4 selectivity obtained as described above. When the initial H_2/CO ratio is less than 2, the ratio will decrease along the catalyst bed and, since methane selectivity depends upon this ratio, it will decrease down the bed.

Simulations of carbon monoxide conversion and methane selectivity were made for various thickness of the rim loaded metals. As shown in figure A.2, both conversion and methane selectivity increase with increasing rim thickness. However, the important point is that these two factors increase rapidly from a low to high value and that the rim thickness where this increase occurs is different for the two factors.

In another simulation, the carbon monoxide conversion and methane selectivity were determined for two pellet shapes: ring and cylinder. As shown in figure A.3, the rim thickness needed to obtain the maximum CO conversion and a low methane selectivity depends upon the pellet shape. Thus, the cylindrical shape provides a much greater difference between the rapid increase in the two factors than the ring shape does.

The inventor claims a method for making a catalyst by determining the rim thickness which optimizes both the rate of carbon monoxide hydrogenation and the reduction of methane selectivity.

Long (A.2,A.3) claims a substantially once-through hydrocarbon synthesis process which comprises reacting in a first reactor or stages, a feed comprising hydrogen and carbon monoxide, and optionally CO_2, in the presence of a non-shifting hydrocarbon synthesis catalyst. The effluent is treated to recover the product from the first reactor by condensing the liquids and then reacting the remaining gases in a subsequent stage or stages in the presence of a hydrocarbon synthesis catalyst having shift activity, producing and recovering additional products.

A basis for this invention is that "The shift reaction can, however, be suppressed if the feed contains higher amounts of CO_2 relative to CO, and CO_2 is known to be added to H_2 + CO synthesis gas feeds for hydrocarbon synthesis. Synthesis gas feeds can contain up to 10% CO_2, that is, about 0.1-10% CO_2." The feed to the first stage(s) has H_2/CO in a 1.5:1 to 1.5:1 mole ratio, preferably 1.9: to 2.3:1, and CO_2 in the range 1.0-10 mole%, preferably 5-10 mole%. This mixture is subjected to synthesis with a non-shifting catalyst, preferably cobalt on alumina, silica or titania (preferred), and preferably promoted by metals as Ru, Rh, Ce or Hf, most particularly Rh (A.4). Conversion of CO in the first stage(s) are preferably at least 90%. Following conversion by the non-shifting catalyst, the liquid products, containing C_5+ hydrocarbons, water, oxygenated compounds and small amounts of dissolved gases.

The feed for the stage 2 reactor(s) with shift catalyst is illustrated in Table A.1. Based on our calculations, the mole fraction of water in the feed is 0.0024 (1.83 mm if operating at 20 atm). For a water-vapor saturated stream, we estimate the temperature of the separation to be -10 to -15°C, a surprisingly low temperature. The gas shown in Table A.1 is fed to a stage 2 reactor(s) where subsequent hydrocarbon synthesis produces a product with an olefin:paraffin ratio of 1.5:1 to 4:1, the lower ratios being favored for higher hydrocarbons and the higher ratios favored for the lower carbon number hydrocarbons. The H_2/CO ratio entering the stage 2 reactor(s) will be essentially the same as the stage 1 reactor(s) because of the non-shifting character in the stage 1 operations. However, because of the conversion in stage 1 reactor(s), less gas will enter stage 2 reactor(s) with the result that the relative concentration of CO_2 will be higher in stage 2 than in stage 1 reactors. Sufficient hydrogen must be present in the feed to stage 2 reactor(s) to react with both CO and CO_2. Reaction conditions in stage 2 reactor(s) will be similar to those in stage 1 reactor(s); e.g., 10-35 bar, 220-340^o, SHSV 200-2000 dry feed (water less than 5 vol% of feed).

Slurry Reactor

Herbolzheimer et al. (A.5) claim the use of a second solid in a slurry phase hydrocarbon synthesis process. A gas is injected at or near the bottom of the bubble column containing a slurry liquid, a catalytically active first solid and at least a second solid. The energy to maintain the dispersion of the solids is supplied by the gas in the absence of liquid recycle. The second solid is added in sufficient quantity to increase the bed height by at least 10%.

The authors state that slurry phase reaction, particularly those occurring in bubble columns, are well-known and do not need to be discussed. In column 6, line 23, the authors state that, "Slurry reactors are well known..." This is surprising since it would appear to imply that at the time of filing this patent [February 25, 1991] the use of slurry reactions are well known and, since bubble column reactors are also well known, only specific improvements to the operation of slurry bubble column reactors should be patentable inventions. Catalyst settling is a problem that can be encountered in bubble column reactors. Particles tend to settle to the bottom because of the influence of gravity. Opposing the settling tendency is the dispersion forces created by the rising bubbles of gas injected at or near the bottom of the reactor. The balancing effect of these two forces results in an exponential distribution of catalyst solids concentration.

The authors utilize the data employing a dispersion coefficient and the settling velocity. D, the dispersion coefficient, depends on the superficial gas velocity through the system and on the effective diameter of the reactor column. The authors do not define this term in more detail, and presumably are considering the dispersion coefficient for the solids. The settling velocity of the catalyst particles, U_s, is given as

$$U_s = U_o(1 - c)^n \qquad [A.18]$$

where

$$U_o = dp^2(\rho_s - \rho)g/18\mu \text{ [}\rho_s\text{ is given as }\rho s\text{ in the patent]} \qquad [A.19]$$

where c is the volume fraction of solids in the slurry, d_p is the particle diameter, ρ_s is the density of the solids, g is the gravitational constant, μ is the viscosity of the suspending liquid, and n is a constant ranging from 4 to 8.

In the description, they indicate that most reactors operate in a regime somewhere between plug-flow and fully-backmixed (or CSTR) conditions. A plug-flow condition can be attained by using fixed-bed catalyst or a very large L/d (where L and d are the length and effective diameter of the reactor, respectively). In the plug-flow reactor the concentration (or partial pressure) of hydrogen and carbon monoxide, the reactants for Fischer-Tropsch Synthesis, decrease along the path of reactor flow due to reaction, and this decreases the driving force of the reaction. On the contrary, complete backmixing results in the same concentration of reactants along the entire length of the reactor resulting in a constant driving force and reflects the relatively low driving force at exit conditions.

Productivity is generally favored in plug-flow systems and selectivity is favored in backmixed systems. Later Exxon patents pertain to the operating conditions for plug-flow bubble column slurry reactors .

In the preferred mode for this patent, there ia an absence of liquid throughput; thus, in the preferred mode, all of the energy from maintaining solids as a dispersion in the liquid is provided by the injection of gas at or near the bottom of the slurry reactor.

The catalysts utiliized in the examples are typical of those described in many Exxon, and other, patents. The preferred catalyst is cobalt supported on titania and promoted with rhenium. The preferred catalyst particle size is in the range of 20 to 100 microns.

The data described in the examples were obtained in a 5 meter tall, non-reactive bubble column with 15 cm internal diameter (i.e., the L/d ratio was greater than 20, corresponding to nearly plug-flow conditions). Nitrogen gas was injected vertically into the column through a half inch hole at the bottom of a conical insert. This cone was used to insure fluidization of all the particles charged to the system. Pressure and temperature were monitored at 1 meter intervals along the column length, and slurry samples were withdrawn at these locations. The slurry liquid was C_{20}-C_{40} paraffinic wax produced by Fischer-Tropsch synthesis using a cobalt catalyst. The solid was either TiO_2 or glass beads. No liquid was added during the measurements.

The solids distribution of 80 micron glass beads in FT product was determined at a temperature of 400^{o}F (204^{o}C) and 280 psig (for gas velocities below 8 cm/sec) or 150 psig (for gas velocities above 8 cm/sec). The decay length of the particle concentration profile was obtained by taking the slope of a line segment joining the data points when plotted as the logarithm of the solids concentration versus height. In figure A.4, the decay length in each zone is plotted versus the average concentration in the zone for superficial gas velocities of 2-16 cm/sec.

They correlated the data by

$$D/U_s(\text{feet}) = 0.2(1 + 20c^2 + 3000c^4)/U_o(\text{cm/sec}) \qquad [A.20]$$

for $U_g < 4$ cm/sec and

$$D/U_s(\text{feet}) = 1.2(1 + 3c^2 + 500c^4)/U_o(\text{cm/sec}) \qquad [A.21]$$

for $U_g < 4$ cm/sec.

U_o is Stokes settling velocity and c is the volume fraction of solids in the slurry.

The results of the above experiment with glass beads was then used in models to predict solids distribution for several examples of various solids combinations. For catalyst and inert solids of the same density (2.7 g/cm^3) and diameter (50 microns) that are (1) dispersed in a solvent with a liquid viscosity of 0.9 cp and density of 0.7 g/cm$_3$, (2) with an average catalyst loading of 0.05 by volume (gas-free basis), (3) an expand bed height of 30 feet, (4)a gas inlet velocity of 8 cm/sec, and (5) an overall conversion of 0.8, they obtained catalyst distributions with 0, 0.05, 0.1, 0.2 and 0.3 volume fraction of inert solids added.

The data in figure 5.A show that with only catalyst the effective bed height is about 13 feet, and with the catalyst more heavily concentrated at the bottom of the reactor. The addition of even a small amount of inerts increase the bed height. As the inert solids content is increased the bed expands further in height and the catalyst concentration profile becomes flatter.

In another example, they use the same catalyst and inert solid except the inerts are 1 micron in size. This example would be approximated by the use of 80 micron iron catalyst spheres made up of 1 micron particles that, because of attrition, produce individual 1 micron fines. Effects similar to those of equal sized particles are obtained. A similar calculation was made using an active catalyst of density 2.7 g/cm^3 and lower activity catalyst with a density of 1.0 g/cm^3. They also made calculations for the case when the original activity is decreased by factors of 2, 4, and 6. The use of the less active component also causes the bed to expand.

In the examples provided, the authors do not provide an identification of the meaning of the curves for volume fraction of catalyst vs. height in figures A.2-A.5 of the patent or in the figure legend. Thus, the reader must assume the identity of the curves.

It appears that this patent is the basis for the several patents that pertain to inert solids. For example, a structurally modified alumina prepared by incorporating a Group IIA metal or metals, particularly Mg or Ba, is claimed to have increased resistance to sintering and agglomeration (A.6). These materials are considered as aiding catalyst fluidization, as a catalyst support, and as heat transfer agents in syngas production or utilization in the slurry phase (A.7-A.12).

Stark (A.13,A.14) was issued a patent to cover the use of pentane (or similar light hydrocarbon) to remove the exothermic heat of reaction of the Fischer-Tropsch process and to expand the pentane to recover the energy to drive air plant compressors. Steam/water is the usual material for heat removal, and is utilized in the commercial reactors at Sasol. However, Stark indicates that it is desirable to have a coolant that has a boiling point and vaporizes at a pressure higher than the reaction pressure; this will ensure that no problem will arise if a leak allows coolant to enter the reaction zone. In order for vaporization to occur with pentane, it is necessary that the coolant side be below the critical conditions (197^{o}C; 44.1 atm. (679 psi)).

Stark (A.13,A.14) claims a method for removing heat from a hydrocarbon synthesis process reaction zone. A cooling medium is passed through the reactor zone in an indirect heat exchange, thereby vaporizing the cooling medium. The cooling medium is chosen so that it possesses the properties of inertness, condensable and vaporizes at a pressure which is at least as great as the pressure in the reaction zone.

Water/steam is frequently employed as the heat transfer medium. However, the authors claim that there is a reasonable expectation of leaks in a F.T. reactor because of the presence of numerous tubes and welds. In the case of water/steam, the reactor pressure is higher than the water/steam side so that F.T. products will leak into the cooling section whenever a leak occurs. The accumulation of products in the cooling side will eventually require the unit to be shut down for cleaning and/or repairs. In this instance, the cooling medium is chosen to have a higher vapor pressure than inside the reactor so that any leakage will be from cooling side to reactor. An appropriate cooling medium is n-pentane, a product of the F.T. synthesis.

The high pressure energy is recovered from the cooling medium through an expander. Preferably a substantial portion of the energy recovered from the expander is used to drive compressors for an air plant which separates oxygen from nitrogen.

The U.S. patent, but not the European patent application, indicates that the F.T. synthesis is carried out in a slurry phase system.

Hydrocracking and Hydroisomerization

Davis et al. (A.15) claim a hydroisomerization process for the conversion of a C_{5+} paraffinic feedstock to middle distillates. This involves contacting and reacting the feedstock and hydrogen at hydroisomerization reaction conditions with a catalyst comprising a Group IB, VIB or Group VIII metal component, or two or more metals, supported on an acidic particulate solid with an average particle diameter of the size range 30 to 150 µm which is dispersed in a paraffinic liquid hydrocarbon.

Davis et al. (A.15) report that in normal hydrocracking with large catalyst particles, secondary reactions, arising from diffusional limitations, produce large amounts of gas and naphtha, and decrease the yield of the desirable middle distillate fractions. To overcome this limitation, staged fixed-bed reactors are operated at relatively low space velocities. They cite an earlier process [U.S. Patent 5,378,348] utilizing a separation into two boiling range fractions (500^{o}F^{-} and 500^{o}F^{+}) and separately hydroisomerizing to make middle distillates.

The hydroisomerization of the present invention is conducted in a slurry phase, preferably with greater than 25% catalyst slurry of particles in the micron size range (preferably 40-60 micron). The catalyst is bifunctional, possessing metallic hydrogenation and acidic functions. The metal oxide support, preferably a silica-alumina material, is prepared as described in reference -[U.S. Patent 3,843,509].

It is reported that one slurry reactor can be used to obtain approximately as much conversion as in three packed bed reactors in series under similar reaction conditions. An additional advantage of the slurry reactor is that a water-steam cooling coil can be used to remove the exothermic heat of reaction and to control the temperature. Using a packed fixed-bed reactor, a complex system of traps and quenching techniques are required to control the heat that is released during the reaction.

Data for the conversion of n-hexane show that the conversion decreases with increasing hydrogen pressure. At a given temperature, the fraction of single methyl branches decreases with increasing feedstock conversion; significant amounts of multi-methyl branched compounds appear at higher feedstock conversion. In contrast, in a fixed bed reactor undesirable cracked products result at higher conversion levels. Even with the slurry technology, the fraction of cracking increases with feedstock conversion at levels above about 80%.

The kinetics of the Fischer-Tropsch wax cracking with a Pd/silica-alumina catalyst was obtained to design a reactor for a commercial scale process. They report that conversion followed zero order kinetics with an apparent activation energy of 30-35 kcal/mole for the conversion range of 30-70%.

Davis and Ryan (A.16) claim a process for producing middle distillate transportation fuels from a waxy product of a hydrocarbon synthesis process. The process consists of:

1. separating the product into a heavier (500^oF^+) and at least one lower (500^oF^-),
2. catalytically isomerize the heavier products in the presence of hydrogen,
3. catalytic hydrotreat the lighter fraction to remove heteroatoms (primarily O), and,
4. catalytically isomerize the product from step (3) to a product with a freeze point of -30^oF or lower.

The authors indicate that a cobalt catalyst tends to produce heavier products, e.g., containing C_{20+}, whereas ruthenium tends to produce more distillate type products, e.g., C_5-C_{20}. A typical product slate for a cobalt catalyst is given as (the values may vary by ±10% for each fraction) is given in Table A.2.

Surprisingly, they found that hydrotreatment of the heavier fraction (containing about 0.45 wt% oxygen) prevents the production of a product with the excellent cold flow properties that was formed by hydroisomerization of the untreated material. They indicate the need to limit the conversion for the 700^oF+ to the 700^oF- products to the 35-

80% range as a measure to limit cracking to produce gases and thereby a lower yield of distillates.

The lighter fraction can be the 320-500°F or, preferably, the entire liquid fraction boiling below 500°F. Following a conventional hydrotreatment, the naphtha is flashed off and the remaining material is hydroisomerized using a catalyst appropriate for light fractions, such as the ones described in reference A.17.

The most active catalysts were those materials containing a surface silica additive. However, it is stated that selectivity is more important than activity. Activity was improved when a 4% surface SiO_2/CoNiMo/10%SiO_2-Al_2O_3 catalyst was used at 700 psig rather than 1,000 psig. Increasing the LHSV to 3.0 and increasing the temperature to provide activity similar to that of LHSV = 0.5 to 1.0 dramatically effected the products; the yield of jet fuel was decreased in favor of gas and naphtha production and the jet fuel had an increased freeze point. The cause for this was not understood but it was speculated that diffusional problems were the major factor.

An international patent application (A.18) claims the production of a high purity solvent composition which comprises a mixture of paraffins of carbon number ranging from about C_8 to C_{20}. The solvent has a molar ratio of iso-/n-paraffins ranging from about 0.5:1 to 9:1 and the isoparaffins of the mixture contain greater than 50% of the mono-methyl species. This patent application employees catalysts and processing schemes that are included in reference (A.19).

The Fischer-Tropsch product was obtained from the conversion of a synthesis gas (H_2:CO = 2.11-2.16) with a titania supported cobalt-rhenium catalyst. The reaction conditions were in the range of 422-428°F, 287-289 psig and feed linear velocity of 12 to 17.5. The alpha of the Fischer-Tropsch synthesis was 0.92.

The 700°F+ boiling fraction was hydroconverted over a Pd-silica-alumina catalyst (0.5 wt.% Pd, 38 wt.% Al_2O_3) to produce 39.4 wt.% conversion of the 700°F+ to 700°F- materials (Table A.3).

Wittenbrink et al. (A.20) describe a processing scheme whereby some oxygenates (primary alcohols) remain in the finished fuel. These oxygenates function to improve the lubricity of the diesel fuel.

The process scheme illustrated in their figure A.6 leads to some confusion. Shown leaving the Fischer-Tropsch reactor (vessel 2) are two streams: 3 (700°F+; 370°C) and 4 (700°F-). It is reported that the reactor is operated in the range 422-428°F (217-220°C) and 287-289 psig using a titania supported cobalt/rhenium catalyst (A22). The syngas had a composition of H_2/CO = 2.11-2.16. The alpha for FTS was 0.92. The FTS products were separated into three fractions having approximate boiling ranges: (1) C_5-500°F (designated F-T cold separator liquids); (2) 500-700°F (F.T. hot separator liquids) and 700°F+ (F.T. reactor wax). It appears that streams 3 and 4 in figure A.6 must be sent to a fractionator (not shown in the figure) to generate three streams.

The hydroisomerization and recombining of fractions are the same, or essentially the same, as described by Davis et al. (A.15) above.

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A.4. See, for example, U.S. 4,637,993; U.S. 4,717,702; U.S. 4,477,595; U.S. U.S. 4,663,305; U.S. 4,822,824; U.S. 5,036,032; U.S. 5,140,050; U.S. 5,292,705.

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A16. S. M. Davis and D. F. Ryan, U.S. Patent 5,378,348, January 3, 1995.

A.17. U.S. Patent 5,187,138]

A.18. WO 97/21787

A.19. U.S. Patent 5,378,348

A.20. R. J. Wittenbrink, R. F. Bauman, P. J. Berlowitz and B. R. Cook, International Publication No. WO 97/14769, April 24, 1997.

A.21. U.S. Patent 4,568,663.

Table A.1

Reactor Simulation Results

		Stage 2 Product	
	Stage 2 Feed	Shifting Catalyst	Non-shifting
Component Rates, Moles/Hr			
H_2	11584	3021	6781
CO	2823	564	524
CO_2	16324	15065	16326
H_2O	113	4887	2400
Hydrocarbon + Alcohol	13701	14045	13924
Inert	2434	2434	2434
Moles Converted			
CO		2259	2299
CO_2		1259	-2
Total		3518	2297
% ($CO+CO_2$) Converted		18.4	12.0
Hydrocarbon + alcohol		344	223
Yield, Moles/Hr			

Table A.2

Typical Product Slate from FT Process Liquids Produced with a Cobalt Catalyst (from ref. A.17)

Fraction	Wt.%
IBP-320°F	13
320-500°F	23
500-700°F	19
700-1050°F	34
1050°F+	11
TOTAL	100

Table A.3 Fischer-Tropsch Synthesis conditions	
Operating Conditions	
Temperature, ^{o}F	638
LHSV, v/v/h	1.2
Psig	711
H_2 treat rate, SCF/B	2,100
Yields, Wt.%	
C_1-C_4	0.97
C_5-320^{o}F	10.27
320-500^{o}F	14.91
500-700^{o}F	29.99
700^{o}F+	43.86
TOTAL	100
700^{o}F Conversion, Wt.%	39.4
15/5 Distillation Yields, Wt.%	
IBP-650^{o}F	50.76
650^{o}F+	49.24

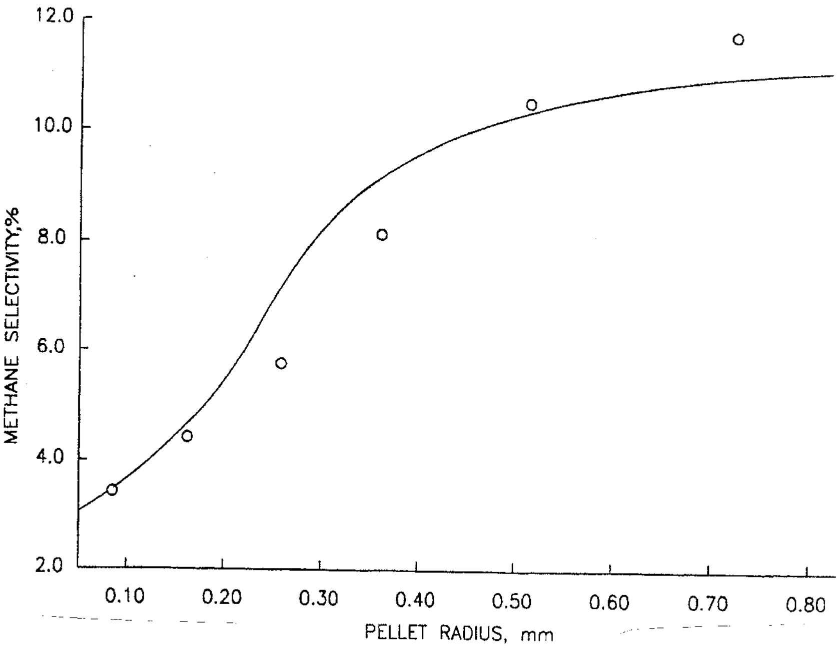

Figure A.1. Model predictions for methane selectivity as a function of pellet radius compared to experimental data (6% CO-0.5% Re catalyst; T = 200°C; $(P_{H_2}/P_{CO})_{feed}$= 2.0; P_t = 19 atm) (from ref. A.????).

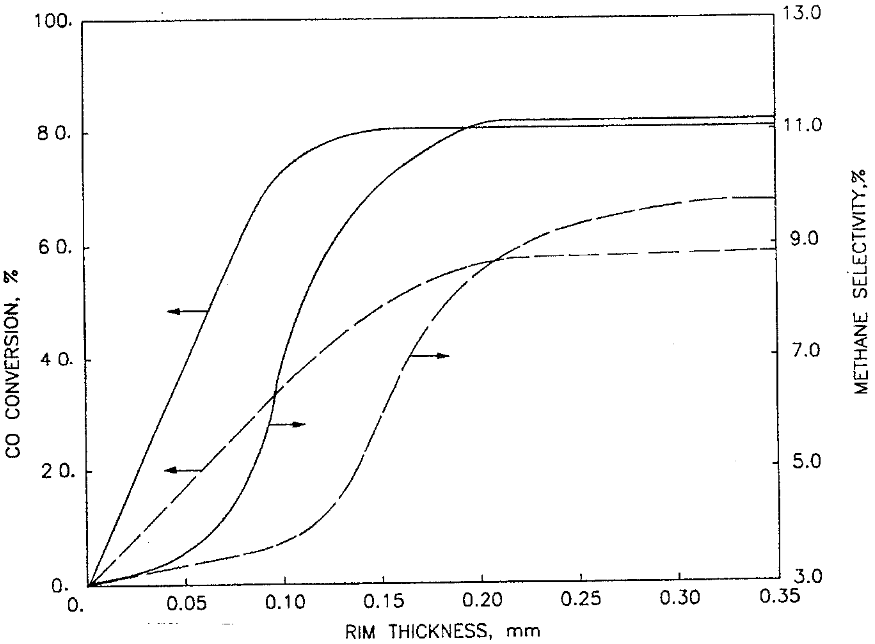

Figure A.2. CO conversion and methane selectivity as a function of rim thickness for spherical particles (d_p = 1.0 mm; T = 200°C; GHSV = 770 v/v/hr; --- A = .6 x 10^{+5} mole/s/s•g•atm^2;))) A = 1.2 x 10^{+5} mole/mole/s/s•g•atm^2) (from ref. A.1).

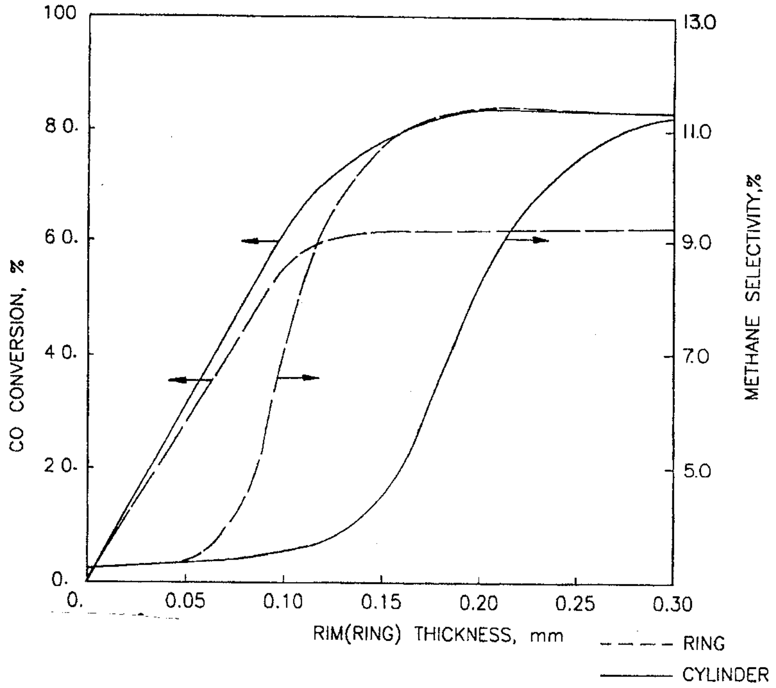

Figure A.3. CO conversion and methane selectivity as a function of rim thickness for ring (---) and cylinder ( ))))) pellets (d_p = 1.0 mm; T = 200°C; GHSV = 770; A = 1.2 x 10^5 mole/s•g•atm^2 (from ref. A.1).

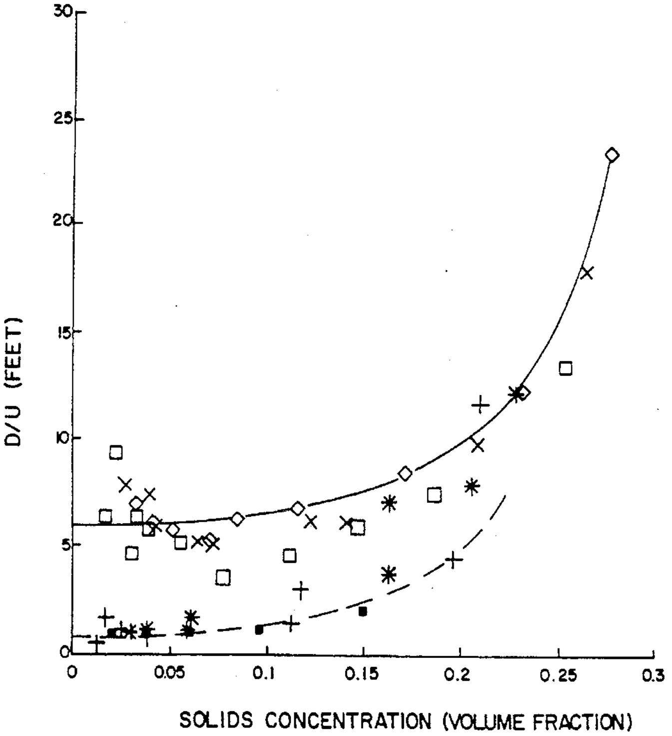

Figure A.4. Plot of decay length versus volume fraction solids concentration (#, 2 cm/sec; G, 8 cm/sec; +, 4 cm/sec; X, 12 cm/sec; *, 6 cm/sec; ◇, 16-18 cm/sec).

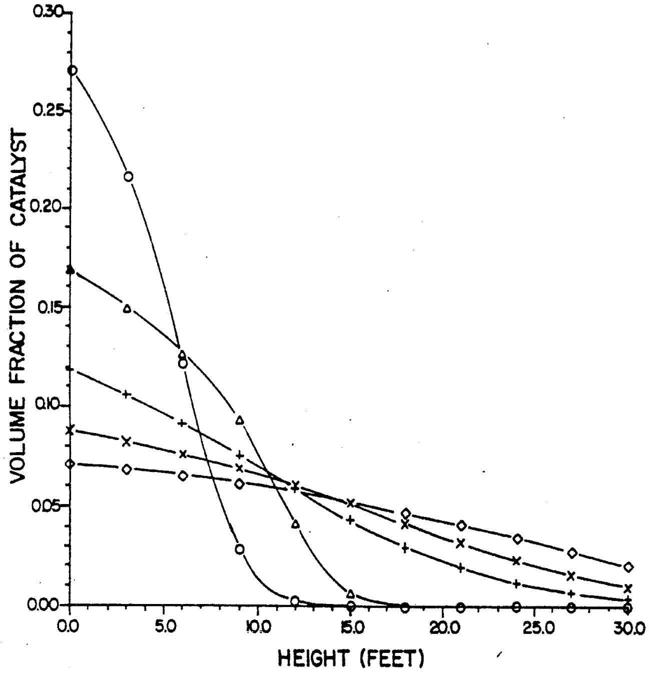

Figure A.5. A plot of volume fraction versus bed height when a second inert solid to a first catalytically active solid in a bubble column, the inerts being of the same density and diameter as the catalytic solid.

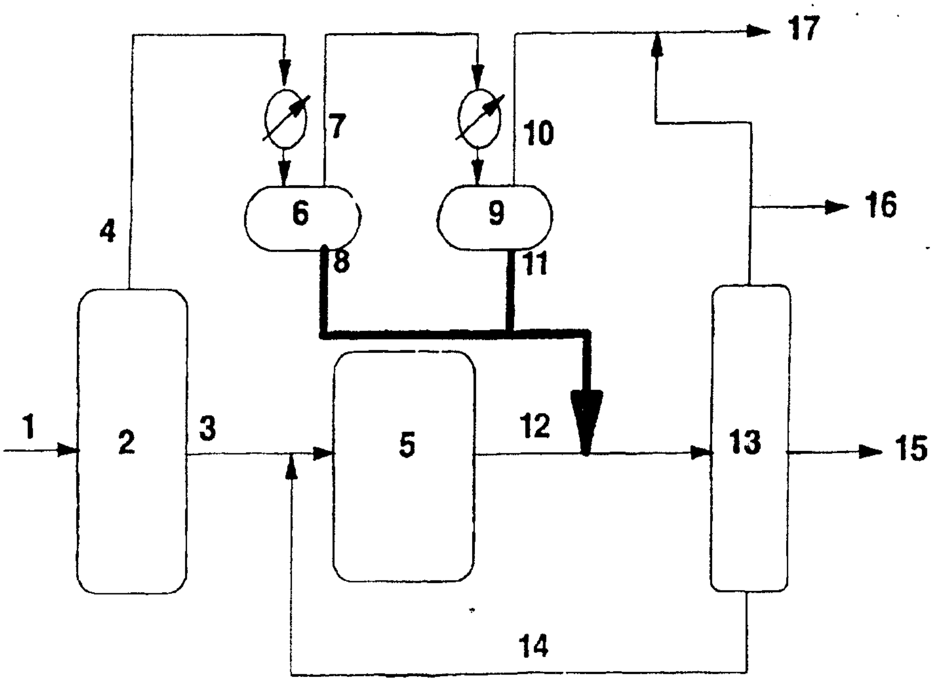

Figure A.6. Schematic of the process (from ref. A.21).

ATTACHMENT XI

Listing of Open Literature Description of Exxon FT Work

A listing of papers by Exxon personnel, and including two by E. Iglesia identified by * that were published after he left Exxon but covering work that was conducted at Exxon. The synopsis will be brief since the results and conclusions in these papers are reviewed in papers XI.1, XI.12, XI.15 and XI.26.

The polymerization of the C_1 monomer produces a distribution described by the Anderson-Schulz-Flory (ASF) distribution. Thus, each carbon number surface species has a probability of continuing the chain growth or terminating the polymerization to produce a product. The ASF mechanism assumes that the ratio of chain propagation r_p, and termination, r_t, are independent of they hydrocarbon chain length. The resulting hydrocarbon selectivity predicted is described as:

$$m_i = \alpha\ m_{i-1} = (1 - \alpha)\ \alpha^{i-1} \qquad [1]$$

where m_i is the mole fraction of hydrocarbon containing i carbon atoms and α is the probability for chain growth and is related to the probability for chain growth and termination as

$$\alpha = r_p / (r_p + r_t). \qquad [2]$$

According to the ASF mechanism, a plot of the logarithm of the mole fractions of the hydrocarbons produced versus the number of carbon atoms in the hydrocarbon should result in a straight line with a single slope given by the chain growth probability, α. Much of the data generated, both in small and large reactor systems, exhibit two values of α. Recently an explanation has been given for this deviation of the hydrocarbon selectivity from that predicted by the ASF reaction mechanism has been offered by workers at Exxon (XI.1,XI.15,XI.18,XI.26). The explanation termed as the Transport-Enhanced Olefin Re-adsorption (TEOR) model is briefly outlined below.

The normal ASF chain growth scheme is outlined in Figure 1. This mechanism for hydrocarbon production has been modified by the Exxon workers first as shown in figure 2 and later as shown in figure 3. The modified mechanism is claimed to be applicable for iron, cobalt and ruthenium catalysts, although date for iron has not been included.

This mechanism distinguishes between paraffins and olefins formed by termination of the hydrocarbon chain on the catalyst surface. Further, the olefins formed can re-adsorb back onto the catalyst surface and re-enter the chain growth process. This process of re-adsorption is quantified by a re-adsorption rate (r_R). Finally, the olefins formed can be hydrogenated, at least partially on other catalytic sites (rate given by r_S) to paraffins. The effective rate of chain termination is then

$$r_t = r_o + r_H - r_R \tag{3}$$

where r_o is the rate of termination to olefins and r_H is the rate of termination to paraffins. Thus olefin re-adsorption serves to decrease the effective rate of termination.

The rates of chain growth, olefin termination, paraffin termination, hydrogenation and olefin re-adsorption are assumed to be independent of chain length, i.e., the number of carbon atoms in the hydrocarbon. The value of the chain growth parameter, α, is then

$$\alpha = r_p/(r_p + r_o + r_H - r_R) \tag{4}$$

Note that due to the independence of the rates with chain length, this modified mechanism by itself cannot predict two or more values of the chain growth probability with increasing number of carbon atoms in the hydrocarbon.

The pores inside a catalyst particle are filled with the heavier hydrocarbon products (presumably liquid under reaction conditions) from the FTS. In the TEOR model it is assumed that this limits or exerts a strong influence on the diffusion of the FTS hydrocarbon products (both olefins and paraffins) out of the pores. The effect of diffusion resistance is to increase the time spent in a catalyst pore by the FTS hydrocarbon products. The diffusivity of individual hydrocarbons is dependent on their molecular weight or chain length or the number of carbon atoms. In the TEOR model, the dependence of diffusivity is assumed to be an exponential function of the number of carbon atoms:

$$D = D_o e^{-0.3i} \qquad [5]$$

where D_o is a constant.

As the diffusivity increases with chain length, the time spent inside a catalyst pore is longer for a hydrocarbon containing, for instance, 20 carbon atoms than for a hydrocarbon containing 10 carbon atoms. Thus the olefins containing 20 carbon atoms have a greater chance to re-adsorb on to the catalyst surface and re-enter the chain growth process than olefins containing 10 carbon atoms. Hence, the rate of re-adsorption for a C_{20} olefin is greater than the rate of re-adsorption of a C_{10} olefin, i.e., the re-adsorption rate for heavier olefins is enhanced by transport limitations. Then, according to equation [4], the probability for chain growth, α, should increase with the number of carbon atoms in the hydrocarbon.

The diffusivity of light olefins (C_2-C_{10}) in the liquid-filled catalyst pores is fairly high so that the re-adsorption rate of these olefins is relatively unaffected. Thus, a single value of the chain growth probability, α, is obtained for these hydrocarbons. For hydrocarbons containing higher than 10 carbon atoms, the rate of diffusion becomes increasingly significant. Hence, the rate of re-adsorption, and thus the chain growth probability (α), increases with the hydrocarbon chain length. The increasing rate of olefin re-adsorption with hydrocarbon chain length finally reaches the rate of olefin termination, i.e.,

$$r_R = r_o \tag{6}$$

at a sufficiently high value of the number of carbon atoms (C_{25} or greater) in the olefin. At this point no more olefins are desorbed from the catalyst surface and the resulting probability for chain growth becomes

$$\alpha = r_p/r_p + r_H \text{ for } C_{25}\text{+ olefins} \tag{7}$$

Thus, for C_{25}+ hydrocarbons, the chain growth probability does not depend on the hydrocarbon length and once again approaches a constant value.

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ATTACHMENT XII

Review of Fischer-Tropsch Work by Gulf Oil

The Gulf-Badger process leads from the catalysis research work on Fischer-Tropsch synthesis work and the reaction engineering analysis conducted by Gulf Oil, and later the process and engineering design provided by Badger (XII.1). A simplified process scheme is shown in Figure XII.1 (XII.2). The process was first discovered from exploratory work conducted by Gulf in the early 1970s. As Gulf continued to discover large reserves of natural gas, the need to convert remote natural gas to transportation fuels became important (XII.1). Since the exploratory research was successful, fundamental engineering and development work were undertaken, in the early 1980s. Because of its experience with others in the Fischer-Tropsch Synthesis, the Badger Company was invited to participate in some of the experimental work on reactor development and later provided the process engineering as well as the basis for the process economics (XII.2).

The initial involvement by Badger was because they had experience with fluid bed reactors and already had two of them set up in their lab. Gulf management wanted rapid development and did not want to delay to build their own reactors. Gulf researchers apparently advised against using the cobalt catalyst in a fluidized bed reactor but the work progressed to the point where 100 g batches of catalysts were prepared. The catalyst proved to be so active they had to strip insulation off the reactors when the reaction started to go out of control.

More money was spent on the fluid bed work in six months than Gulf had spent in the previous six years. With the result, of course, that the catalyst behaved just as Gulf researchers had predicted. The unit ran fine for half a day or so but then it began to be difficult to keep the catalyst suspended. The catalyst had to be hydrogen-stripped once or twice a day, and the methane make was so high during those stripping periods that the overall selectivity to liquids was rather poor.

At the same time, the go-ahead for fixed bed development was given, and Gulf continued with Badger because they were already familiar with the catalyst and process. The scale-up of the fixed bed process of the catalyst manufacture by Davison were successfully accomplished.

Two types of reactors - two fluid-phase fixed bed and fluidized bed - were seriously considered. Because of the high molecular weight products that are produced by Gulf's most promising catalysts and thermal instability of the reactor, the fluidized bed reactor design concept presented real problems. Therefore, the Gulf Oil reaction engineering staff selected a fixed bed reactor. Its design and operation were critical, but success was quickly achieved.

The proprietary catalyst (in 1983) was inherently stable when combined with the proper reactor design and operation. Catalyst activity decay was avoided when stable, parametrically insensitive conditions and operation were achieved. The catalyst could be regenerated to the original activity by controlled oxidation and reduction.

The catalyst activity is an important property. It has a direct impact on the reactor design and operation as well as on capital and operating costs. The catalysts activity and selectivity in the developed reactor determine the reactor size that is required to produce a given quantity of desirable product, and to convert a given volume of synthesis gas, per day.

Operating conditions also influence the catalytic conversion and selectivity, and thereby the product distribution. An increase in temperature increases the reaction rate whereas decreasing the H_2/CO ratio at constant temperature and pressure decreases the rate with the Gulf catalyst (XII.2). It was found that a 10°C increase in temperature would just about compensate the rate loss for a decrease in H_2/CO ratio from 2 to 1.5. A substantial increase in reaction rate results from increasing the total pressure. The results for increasing pressure and temperature are illustrated in Figures XII.2 and XII.3 (XII.2). Representative data are summarized in Table XII.1 (XII.2). The Gulf-Badger reactor design has a constrained range of performance and acceptable operation.

Production of C_5+ products depends upon both the activity and selectivity of the catalyst, and is a product of these two factors. Thus, some of the effects that increase activity may decrease productivity.

Pilot plant data for a reactor, consisting of a single, commercial-size reactor (1" x 40') tube show that reasonable temperature control can be achieved. Conditions that are representative of those used at Gulf are (XII.2):

Temperature	200-225°C
Pressure	250 psig
H_2/CO feed ratio	1.5-2
Feed space velocity	500-1,000/hr.
CO conversion	40-60% per pass
Selectivity to C_5+	ca. 70-75% of carbon converted

A typical product make from a reactor operating under such conditions are illustrated in Table XII.2.

Two reactor concepts were tested during the pilot plant work - a tubular fixed bed and a fluidized bed at Badger. The latter was not satisfactory. Details on only the fixed bed reactor were given in reference XII.2. Gulf's pilot plant consisted of two reactor sections in series (Figure XII.4, ref. XII.2). After initial operation, temperature of the hot spot in the Gulf Oil reactor did not exceed that of the average temperature by more than 5^{o}C. The illustrated CO conversions depended linearly upon temperature, as did the relative rate (Figures XII.5 and XII.6; ref. XII.2). The productivity of C_5+ hydrocarbons did not increase linearly with temperature due to the relative increased production of light (C_1 - C_4) gaseous products (Figure XII.7; ref. XII.2).

A demonstration unit was designed (in 1983) that would produce approximately 15 b/d of naphtha, 15 b/d of diesel fuel and 7 b/d of wax from 350,000 scf of natural gas (Figure XII.7; ref. XII.2). Natural gas was compressed to the reformer pressure and mixed with recycle CO_2, heated and passed through a zinc oxide bed to remove sulfur compounds. The natural gas was obtained by drilling a well at the laboratory site. It then entered a steam-methane reformer and was converted to synthesis gas. Carbon dioxide was removed in an amine scrubber after the gas was cooled and compressed. The gas then passed through a membrane separation system to adjust the H_2/CO ratio. Hydrogen would be used as fuel in the demo plant but could be utilized for upgrading in a commercial operation.

Gulf-Badger Process - Patent Literature

A series of catalysts was prepared that demonstrated a beneficial effect of a minor amount of ruthenium on a catalyst containing a major amount of cobalt for the low pressure synthesis of higher hydrocarbons from synthesis gas (XII.3).

A standard reference cobalt catalyst was prepared according to a published procedure (XII.4) whereby solution I (49.4 g. $Co(NO_3)_2 \cdot 6H_2O$; 11.0 g. $Mg(NO_3)_2 \cdot 6H_2O$ and 1.5 g. $Th(NO_3)_4 \cdot 4H_2O$ dissolved in 250 ml water) and solution II (35 g. K_2CO_3 in 250 ml water) were heated to boiling. Solution I was added rapidly with vigorous stirring to solution II, and immediately thereafter, 20 grams of dry powdered kieselguhr was admixed with stirring which continued for 10 minutes. The mixture was filtered and washed with distilled water until no evidence for nitrate ion was observed in the wash water. The solid was dried at 120°C for 16 hours, calcined in air at 350°C for 16 hours, then reduced in flowing hydrogen at 350°C for 3 hours. A second catalyst was prepared following the same procedure except that 0.35 g. of $RuCl_3$ was added to solution; this catalyst had the following composition: Co (31.6 wt.%); Mg (3.25 wt.%); ThO_2 (1.98 wt.%); Ru (0.53 wt.%); and kieselguhr (62.64 wt.%).

These two catalysts were subjected to synthesis runs using the same experimental conditions ($H_2/CO = 2$; upflow reactor with preheater for feed gas; atmospheric pressure; gas hourly space velocity based on the total amount of charge gas was 250; g.c. analysis). A series of experiments were conducted at various reaction temperatures with the CO conversion levels shown in Figure XII.9. It is seen that a measurable conversion is obtained only at a temperature of about 125°C or higher. On the other hand, the same catalyst except that it contains Ru, exhibits appreciable conversion at 50°C and maintains this superiority with increasing reaction temperature. The products from the runs at 220°C with the standard Co catalyst and the Ru containing catalyst were analyzed. The products from the standard catalyst exhibited an ASF distribution, with an alpha value of 0.85 (Figure XII.10). The products from the Ru containing catalyst exhibited a product distribution that contained significantly heavier hydrocarbons; the alpha value, based on the curve in Figure XII.10, was 0.98. Thus, the addition of Ru to the standard catalyst resulted in a significant increase in the catalytic activity as well as producing a significantly heavier products. The data indicated that the presence of Ru essentially eliminated the production of methane and ethane (however, this conclusion is on a relative basis). In addition, the C_{9+} product from the standard catalyst contained 29% of olefinic product compared to 4% with the Ru containing catalyst. The gaseous products were found to contain about 15 volume percent CO_2 for the standard cobalt catalyst but only traces of this gas were obtained with the Ru containing catalyst. While it is not stated how the samples were collected, the low value for the C_{9-11} product fraction, relative to lower and higher carbon number products (Figure XII.10), suggests that the products consisted of gaseous and liquid fractions that were subsequently analyzed separately, resulting in loss of some C_{9-11} hydrocarbons.

Similar catalysts were prepared. For catalyst 3, about equal amounts of alumina and magnesia were added to replace kieselguhr in the above Ru containing catalyst (31.6 wt.% Co, 2.0 wt.% thoria, 0.5 wt.% Ru, 32.9 wt.% alumina and 32.9 wt.% magnesia). The other catalyst (4) contained a lower amount of Co and no thoria; at the same time alumina was substituted for the kieselguhr and the amount of magnesium oxide was increased. This catalyst (XII.4) contained 17.77 wt.% Co; 0.70 wt.% Ru, 40.77 wt. % alumina and 40.77 wt.% MgO.

The three catalysts were compared for methane production at various reaction temperatures; these results are compiled in Table XII.3. Referring to Table XII.3, it is apparent that the presence of Ru significantly decreased the amount of methane produced at all reaction temperatures. All Ru containing catalysts produced only traces of CO_2. Substituting gamma-alumina for kieselguhr had little, if any, effect on methane production; likewise, the removal of thoria and an increase in magnesia had little effect on methane production.

As shown in Table XII.4, it is noted that the "% selectivity for C_{9+} fraction" increased, and the % olefin in the fraction decreased, when Ru was present in the catalyst.

It appears that another Gulf worker later repeated Kobylinski's work with precipitated Co and CoRu catalysts, as well as one with the $20Co-0.5Ru-1La_2O_3$ composition. Ru was found to confer better dispersion and activity, just as it did for the impregnated catalysts, but that there was no appreciable change in product distribution in standard week-long tests. Apparently a problem with the GC analysis, such as getting drops of liquid product in with the vapor phase products impacted the reported data. The precipitated catalysts were found to have activities per unit weight of metal that were intermediate between those of catalysts made by aqueous impregnation and those made by nonaqueous impregnation.

High octane gasoline and diesel fuel are produced from synthesis in a two stage process (XII.5). In the first stage, synthesis gas is converted to straight chain paraffins that have a boiling range that falls mainly in the diesel fuel range. A cobalt catalyst, preferably containing a Group IIIB or IVB metal oxide, is supported on gamma- or eta-alumina, or a mixture of these two aluminas. The C_5-C_9 straight chain portion of the product from the first stage is converted in the second stage to highly aromatic plus branched chain paraffinic gasoline using a platinum group metal catalyst. The most preferred metal oxide for use in the catalyst for the first stage is thoria. The support should have low acidity, meaning a Brønsted acidity with $H_o \leq 1.5$, which is less than 5 micromole per gram (about 10^{16} acid sites per m^2 of surface area). The deleterious effect of acidity is the isomerization and cracking of intermediate alkenes, removing them from chain growth and producing a low molecular weight product. **This latter**

statement implies that higher molecular weight alkenes readsorb on the catalyst to react with synthesis gas (or other alkenes) to produce higher alkenes. In addition, the production of low molecular weight products requires either that low molecular weight alkenes do not readsorb to undergo subsequent chain growth or that the low molecular weight products produced by cracking are alkanes, and not alkenes.

The catalyst for the first stage was defined by hydrogen chemisorption and should adsorb at 25^{o}C from 125 to 300 micromole per gram of total catalyst. The chemisorption of hydrogen is illustrated in Figure XII.11 and shows a maximum for a catalyst that is receded in flowing hydrogen at 350^{o}C. The maximum hydrogen adsorption corresponds to a dispersion, d, of cobalt of 0.066; that is, 6.6% of the Co atoms are located on the surface of cobalt metal crystallites.

The support must be of high purity and have a surface area in excess of 50 m^2/g, and preferably in the range of 150 to 225 m^2/g. High purity means that the support will contain negligible amounts of sodium, sulphate, silicon, phosphates or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbons.

The preparation of the catalyst was accomplished using a nonaqueous, organic impregnation solution containing the soluble cobalt and Group IIIB or IVB salts in order to achieve the necessary metal loading and distribution. The alumina was calcined in air prior to impregnation, preferably in 5h 400 to 600^{o}C range. Suitable solvents include ketones, such as acetone or methyl ethyl ketone; the lower alcohols; amides, amines, ethers, hydrocarbons or mixtures thereof. A mixture of ethanol and acetone (4 parts acetone; 1 part ethanol) is preferred and is used in an amount that will fill the pore volume; a maximum amount would be equivalent to five times the total pore volume.

The impregnated material is dried (25 to 45°C) to remove solvent to "dryness" and the material is then calcined in air, preferably 225 to 275°C. The impregnation, drying and calcination steps are repeated until the desired metal loading is obtained. The catalyst is slowly reduced in hydrogen. In the first reduction step, the catalyst is heated slowly (0.5 to 5°C/min) to a maximum temperature of 180 to 220°C and held at this temperature for about 24 hours. The second reduction step is accomplished by heating at a rate of 5 to 20°C per minute to the optimum temperature. Initially the reduction step is accomplished in a diluted hydrogen stream (e.g., 5% hydrogen in nitrogen); gradually the hydrogen concentration is increased to provide pure hydrogen.

While it is stated that the reactor type utilized is not critical, a fixed bed, with gas downflow, was preferred.

The catalyst for the second stage could be a typical naphtha reforming catalyst; that is, a platinum group metal supported on alumina using halogen to impart acidity.

The catalyst which gave the hydrogen adsorption data that is shown in Figure XII.11 contained the following composition by weight: $100Co/18ThO_2/200Al_2O_3$. This catalyst was evaluated for activity using a flow of 240 $cm^2/g/hr$ of CO and the same flow of H_2. Data were obtained for the above catalyst and are summarized in Tables XII.5 and XII.6.

The conversion depends upon temperature as is shown in Figure XII.12 (the numbers in parentheses are the total gas flow rate ($cm^2/g/hr$)). Thus, at a flow rate of 1:1 synthesis gas of 1.22 NL/g/hr; the conversion of CO was 6.5%. The activation energy was calculated using the data in Figure XII.12 to be 15 kcal/mole. The product distribution changed slightly to favor lower weight products as the temperature increased (Figure XII.13). The product distribution did not adhere to the ASF plot except perhaps for the lowest temperature run; in all instances the C_2-C_4 products were much too low to approach fitting an ASF plot. It was not possible to fit the data in Table XII.2 with an ASF distribution.

This patent covers the activation of a promoted or unpromoted supported cobalt catalyst (XII.6). The catalyst is prepared using cobalt carbonyl and the support is either silica or alumina. The activation procedure comprises three steps: (1) reduction in hydrogen, (2) oxidation in an oxygen-containing gas, and (3) reduction in hydrogen, all three steps conducted at temperatures less than 500°C. This activation comprising reduction, oxidation and reduction has been called "ROR". It has been found that the addition of promoter, such as lanthanum or manganese (and oxides of the lanthanides and actinides), reduces the activity of the unpromoted catalyst. However, if in addition to the above promoters, ruthenium is also incorporated the ROR activation results in an increase in activity above that of the unpromoted cobalt catalyst.

The cobalt carbonyl is added by an impregnation technique using a non-aqueous solvent. If desired, the addition of promoter can be accomplished by co-impregnation along with cobalt. In the preferred procedure, the promoters (metal oxide and/or ruthenium) are added prior to the cobalt carbonyl.

Thus, the promoter is added to the calcined support as described in ref. XII.5. The impregnated catalyst, preferably using the incipient wetness technique, is dried slowly in air. The slow drying procedure is used so as to spread the metals over the entire support. After drying in air, the catalyst is calcined by heating slowly in flowing air to, preferably, 250 to 300°C. The drying and first calcination can be accomplished separately, or done in a combined step. The calcination step is accomplished at a slow heating rate, preferably 0.5 to 1.0°C/min., and held at the final temperature for up to 20 hours (2 h. is preferred). If necessary, the impregnation, drying and calcination steps are repeated to provide the optimum metals loading.

Following the calcination, the catalyst is impregnated with an organic solution containing cobalt carbonyl. Prior to impregnation, the catalyst is not exposed to the atmosphere sufficiently for the support to be rehydrated. If more than one impregnation is required, the catalyst must be subjected to a reduction-reoxidation treatment, the first two steps of the ROR procedure.

The preferred procedure for the ROR process is:

(1) Slowly heat to about 200°C and hold at this temperature for about 20 hours (starting with about 5% H_2 in nitrogen and increase gradually to pure H_2), then heat to the optimum reduction temperature (about 350°C) and hold for about 24 h. Reduction should be slow enough to prevent the volatilization of cobalt carbonyl and to prevent the water vapor from exceeding 1% in the exit gas. Passivation is effected at room temperature using diluted air.

(2) The oxidation step is conducted as described in ref. XII.5.

(3) The oxidized catalyst is reduced as described in step (1) above.

The advantage of the ROR technique was illustrated by the preparation of three catalysts: (A) cobalt carbonyl was impregnated onto Ketjen gamma-alumina; (B) impregnating gamma alumina with cobalt and ruthenium nitrates (20 wt.% Co and 0.5 wt.% Ru); and (C) impregnating gamma-alumina with nitrate salts to give a material containing 25 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% lanthanum oxide. The three catalysts were tested at 185^{o}C; H_2/CO = 1.85 (atmospheric pressure), producing the results shown in Table XII.7.

The ROR treatment of the cobalt carbonyl catalyst provided a more active catalyst than the other two preparations and the selectivity of the cobalt carbonyl catalyst for C_5+ hydrocarbon is comparable to the ruthenium-promoted cobalt catalyst.

Hydrogen adsorption studies showed that the ROR treatment produced lower dispersions of Co than just hydrogen reduction. Thus, catalyst A had a metal dispersion of 0.29 following a reduction in hydrogen, but only 0.13 following the ROR treatment. Thus, the activity per metal site increased rather than the number of sites.

The activity of a silica-supported catalyst prepared using cobalt carbonyl is higher than that of an alumina-supported catalyst; however, the selectivity for C_5+ hydrocarbons is lower. The ROR treatment of the silica-supported material improves the C_5+ hydrocarbon selectivity.

This patent provides additional data to support the view that the reduction-oxidation-reduction, "ROR", technique provides superior activity over the same catalyst when it is just treated with hydrogen (XII.7). Data is also presented to show the improvement in activity when ruthenium is incorporated into the cobalt catalyst. The data shown in Table XII.8 was obtained at 1 atm pressure with [the patent gives the gas composition as weight percent but it surely is molar percent] a 35% CO and 65% H_2 synthesis gas mixture.

As shown in Table XII.8, the use or ruthenium significantly improved the catalyst activity as compared to the test of a catalyst that did not contain ruthenium. Even when the Co/Ru molar ratio exceeded 200/1, the catalyst activity increased in excess of 100 percent over that in which ruthenium was absent. Likewise, the ROR activation led to a catalyst that exceeded the activity of a hydrogen treated material by 24-34 percent.

Data were also presented to show the benefit of Ru for a catalyst prepared by precipitation of cobalt, ruthenium and lanthanum oxide onto an alumina support by the addition of potassium carbonate. In this case the use of the ROR treatment improved the catalyst activity. However, when the amount of ruthenium exceeded 0.5 wt.%, the activity showed a decline of 4%.

A method of catalyst preparation is given which consists of an aqueous impregnation using a solution of a cobalt salt, drying the impregnated material and then employing a nonaqueous, organic impregnation solution of salts of ruthenium and a Group IIIB or IVB metal (XII.8).

A supported catalyst was prepared using a microspheroidal gamma-alumina commercially available from Harshaw; this alumina had an average particle diameter of about 60 microns. After calcination at 600°C, the alumina was impregnated with a cobalt nitrate solution. The material was dried at 120°C and then impregnated with thorium nitrate and ruthenium acetylacetonate dissolved in an acetone-ethanol (=2:1 ratio) solution. Excess solvent was removed at reduced pressure at room temperature in a rotary evaporator. The catalyst was then dried by heating to 90°C with the nitrate salt melting with evolution of water in the temperature range of 50-60°C. Prereduction and passivation was conducted using a hydrogen flow of 720 ml/g/hr. The catalyst was heated to 100°C at 1°C/min and maintained at this temperature for 1 hr and then heated at the same rate to 200°C. After holding at the latter temperature for 2 hr., the catalyst was heated at 10°C/min to 360°C and held at this temperature 16 hrs. After cooling below 200°C, the catalyst was flushed with nitrogen and the temperature lowered to room temperature. Air was then bled into the nitrogen (1:50 air:nitrogen with flow of 50 mL per minute per 5 g catalyst for 16 hr). The final reduced catalyst contained 21.9 wt.% Co, 0.5 wt.% Ru, 2.2 wt.% Tho_2 and 75.4 wt.% alumina.

The activity of the catalyst was obtained using a 1/2" fluid bed reactor where 50 grams of catalyst was heated to a temperature of 350°C in a flow of hydrogen (N L/g/hr) and held at this temperature overnight. The hydrogen flow was reduced to 0.3-0.4 L/g/hr and an equal flow of CO was introduced (if $H_2/CO = 2$, the hydrogen flow was doubled). The results of runs are summarized in Table XII.9.

The results show that, for similar conditions, an increase in the H_2/CO ratio from 1 to 2 caused a decrease in the C_5+ hydrocarbon yield and an increase in the amount of methane. An increase in pressure from 15 to 30 psia caused an even greater decrease in the C_5+ hydrocarbons and increase in methane; an increase in temperature had a similar effect.

A recent paper by Haddad and Goodwin (XII.16) on the CoRu catalyst claimed to obtain no change in activity from a ROR treatment. Looking at their catalyst preparation, they claimed to add 20% Co as the nitrate apparently in one step. This would appear to require the use of a supersaturated cobalt solution. In most catalysts, the alumina does not have enough pore volume to accommodate that much cobalt nitrate. The fact that they saw no ROR effect could be taken to mean that they had not produced an alloy catalyst whereas measurements of Curie point changes showed that the Gulf workers had done so. Goodwin reports TGA studies after a wide range of precalcination and reduction temperature, but none for an RO-treated catalyst. Gulf workers usually found a 100°C lowering in the reduction temperature for an RO-treated catalyst, compared to a fresh one - more evidence of a drastic change in properties.

The best proof of the advantage of ROR was obtained ona large scale - after one year of operation and several hydrogen strippings, the catalyst in the demo plant was regenerated (mainly for experience with recalcination). It was then 50% more active than it had been after initial startup and this made operation with the regenerated catalyst even more difficult. After the plant was shut down Gulf workers tested catalysts from about 20% of the reactor tubes and the catalysts, except for one tube, had the expected catalytic properties.

This patent relates to the use of a mixture of a catalyst active for the Fischer-Tropsch synthesis and one that effects alkene isomerization and/or cracking to produce gasoline from synthesis gas (XII.9). The Fischer-Tropsch synthesis catalyst is any one of the many examples that are comprised of cobalt alone or promoted by ruthenium and/or Group IIIB or IVB metal oxides. The acid cracking/isomerization catalyst is a silicalite-1 type (see XII.10 - XII.12).

An example utilized a catalyst containing 50 wt.% silicalite and 50 wt.% of a catalyst with the composition $100Co/18ThO_2/200Al_2O_3$ (example of conversion data given above). The particles were separately ground to give a particle size 100 mesh, mixed and then wetted, and then comminuting and sieving the resultant mixture to provide uniform 30-40 mesh particle size. Tests were conducted using 0.5 g samples of the prereduced catalyst by reducing in hydrogen at 360^oC in hydrogen 2.4 L/g/hr at one atmosphere. The hydrogen flow was then reduced to 0.48 L/g/hr and an equal flow of CO ($H_2/CO = 1:1$). The tests were effected at 185^oC and one atmosphere pressure to provide the data in Table XII.10.

The impact of the addition of silicalite to the Fischer-Tropsch catalyst is apparent (Figure XII.14). The ASF plot shows that alpha = ~1 for the C_3+ hydrocarbons; however the amount of methane is much above and the C_2 products much below the values expected for conformity to the ASF plot. When silicalite is added to the Fischer-Tropsch catalyst, the data do not fit the ASF distribution. Methane and the C_2-products are slightly higher than was obtained with the Fischer-Tropsch catalyst alone. More importantly, the C_3-C_{10} hydrocarbon products significantly deviate from the ASF distribution. Thus, it is apparent that the acid catalyst has effected a significant amount of isomerization and cracking of heavier hydrocarbons to lighter, gasoline range hydrocarbons.

The fraction of n-alkane in each carbon number hydrocarbon fraction provides a surprising distribution (Figure XII.15). When the catalyst contains only the Fischer-Tropsch component, the amount of n-alkane drops from about 75% for C_2 to about 20% for C_3 and then slowly increases with increasing carbon number to approach 60% for the C_{10} carbon number fraction. In this respect, the cobalt catalyst, when operated at 1 atmosphere, exhibits a distribution that is very similar to the one obtained for an iron catalyst at 1 atmosphere or at intermediate pressure levels (XII.13). However, when the silicalite catalyst is present, the alkane fraction deviates from the one obtained for Fischer-Tropsch synthesis. Up to carbon number 6, a similar trend is obtained for both catalysts; however, above carbon number 6 there is significantly less n-alkane when the silicalite is present. The apparent explanation for this is that the products have increasing fractions of isoalkanes, isoolefins and internal olefins as the carbon number increases above C_4, thus lower fractions of n-alkanes and 1-olefins. Isomerization to iso or internal olefins is not possible with C_2 and C_3. The degree of olefin reincorporation may be strongly influenced by the degree of substitution at the double bond. Ethylene readsorbs the most readily because it has two free CH_2 groups. Among the 1-olefins, readsorption and chain initiation declines slowly with carbon number. Internal olefins readsorb poorly because they have no free CH_2 group, but they can isomerize back to 1-olefins and that gives them a small path towards readsorption. Isoolefins are also relatively unreactive. Although some have a free CH_2, if they have two substituents on the adjacent carbon that appears to be enough to make readsorption difficult.

All that is needed then to lower the effective chain growth probability among C4+ chains is for the 1-olefins, produced as primary products, to be isomerized to internal olefins or isoolefins. That removes them from the F-T reaction. With a catalyst that does this (almost any acidic catalyst), one can observe a large drop in chain growth probability between C_3 and C_4.

The isomerization to isoolefins requires a strong acid site and it was found that this reaction declined fairly quickly with time over silicalite or ZSM-5. However, the isomerization to internal olefins, which requires only moderate acidity, persisted for as long as any of the composites were run, and it was sufficient to alter the ASF distribution.

A layered aluminosilicate (montmorillonite-type structure) containing cobalt substituted into the crystal lattice was activated for the Fischer-Tropsch reaction using a sequential reduction-oxidation-reduction (ROR) technique (XII.14). A Group VIII noble metal, such as ruthenium, is also added by impregnation prior to the final reduction step.

The hydrothermally produced cobalt aluminosilicate has the following general formula prior to its activation:

$$Al_{4-n-x3}Co_{3/1n}O_8(OH,F)_4Si_{8-y}Al_yO(3x-y)NH_4^{+}zH_2O$$

[it is 3x-+y in the patent]

where n is between 0.02 and 4 (prefer 2 to 3); x is up to about 1 (prefer 0.1 to 0.1); n+x between 0.02 and 4 (prefer 2 to 3); y is between 0.05 and 2 (prefer 0.5 to 2); and z is up to about 10. In the above the predominant amount of Al, Co, OH, and F are in the octahedral layers, and the Si and minor amounts of Al are in the tetrahedral layers. Ammonia and water are located between the layers. Water and ammonia are lost in the pre-activation calcination. The reduction is carried out in hydrogen (or other reducing gas) and the oxidation process is preferable accomplished in air or diluted air. The activation is accomplished in three steps - the ROR process described earlier.

A catalyst is prepared using a saturated aqueous solution of 161 g of $AlCl_3$•$6H_2O$ in two liters of water that is slurried with 1.84 g of a silicic acid solution providing a Si/Al=4.7 ratio. The silica-alumina gel was precipitated by adding the slurry to 1 L of ammonium hydroxide with a pH of 8. The gel was washed with distilled water to remove chloride. A 50 g sample of the washed gel was slurried with 225 ml of water containing 60 g of cobalt acetate, 0.78 g of ammonium fluoride, and 0.42 g of HF while stirring and maintaining the pH at 8.-0 by adding ammonium hydroxide as needed. The mixture was heated at 300^{o}C in an autoclave (1,240 psig) for four hours. After drying at 120^{o}C, the gel was calcined at 500^{o}C for 4 hrs and produced a hard, wine-red solid with SiO_2/Al_2O_3 = 0.30. The catalyst was reduced at 400^{o}C for 2 hr in hydrogen and then reoxidized at 500^{o}C. A hydrogen reduction at 600^{o}C (16 hr.; 8.5% wt. loss) then reoxidized in air at 500^{o}C (8.1% wt. gain). A final reduction was effected at 400^{o}C for 16 hours.

This catalyst was utilized at 1 atm. in a 0.5 g. catalyst bed using a hydrogen:carbon monoxide = 1:1 with a feed of 0.48 l/g/hr. Three temperatures were utilized following activity stabilization to produce the results shown in Table XII.11.

The major products in the C_5+ hydrocarbons were found to be isoalkanes and isoalkenes. The alkenes contained a high fraction of internal alkenes.

The catalyst is a rare earth promoted layered complex metal silicate composition characterized as having repeating units with a structural formula

$$[(1\text{-}x)Ni^{a} + xRu^{b}]_{n}(OH)_{4}Si_{2}O_{5}\bullet wH_{2}O$$

where x is a number from 0 to 1 (fraction of Ru in Ru+Ni); a is the valence of nickel, b is the valence of ruthenium; n is a number defined by

$$6/[a(1-x) + bx]$$

and w is a number ranging from 0 to 4 (XII.15). The preferred catalyst is a rare earth promoted nickel chrysotile.

These catalysts produce much methane in addition to higher carbon number hydrocarbons. Typical examples, using H_2/CO = 2.5; 350 GHSV; 210°C; and atmospheric pressure, are shown in Table XII.12.

Low concentrations of thoria are needed but higher (30% or more) are not beneficial, and may have a slight detrimental effect. The inclusion of low concentrations of thoria greatly increase the amount of C_2+.

Typical examples, using H_2/CO = 2.3; 400 GHSV; 204°C; and atmospheric pressure, to define the differences in rare earth promoters, if any, are shown in Table XII.13.

The results show that there is a synergistic benefit in conversion when a mixture of two rare earth promoters are used. Thus, thoria incorporation provides a CO conversion of 31.5% and lanthana 25%; rather than the expected intermediate value for CO conversion when a mixture of thoria and lanthana are incorporated, the CO conversion is 71.5%. A similar result is obtained when thoria and praseodymium is utilized.

Slurry Phase Synthesis

A patent (XII.17) claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support. In subsequent claims the support was identified as alumina or silica. Another subclaim indicated that the fluid is a liquid medium which could be a synthetic hydrocarbon liquid or a hydrocarbon conversion product. The activation known as ROR (reduction in hydrogen, oxidation, reduction in hydrogen) was claimed. A promoter could be selected from the group consisting of Rh, Pt, Pd, Ir, Os, Ag and Au. The use of these catalysts produced a product with less than 16 wt.% methane. The catalyst cobalt concentration covered was from about 5 to about 25 wt.% and the promoter in an amount from about 0.01 to 0.5 wt.% based upon the total catalyst weight.

The patent contains examples of conversions in fixed-bed reactors with a catalyst prepared to have various particle sizes. A catalyst was prepared that had a particle size that one normally encounters in fixed-bed operations (1/16th inch (0.16 cm) extrudate) and then this catalyst was ground to produce average particle sizes of 0.28 and 0.54 mm. The found that both catalyst activity and product selectivity changed with particle size. In particular, the fraction of methane decreased and the amount of C_5+ increased with decreasing particle size of the catalyst (Figures XII.16 and XII.17); over the particle sizes tested it appears that both selectivities change linearly with particle size. It appears that the methane production of the three catalyst sizes extrapolates to a common value of about 4 wt% at very small particle size (Figure XII.16). Likewise, the C_5+ selectivity appears to approach about 87 wt.% at very small particle size. This means that the C_2-C_4 yield is about 9 wt.% for the very small particle size catalyst. As expected, the rate of reaction increased as the particle size was decreased (Figure XII.18). For the smallest particle size (0.24 mm) the reaction rate increased by a factor of 1.94 for an increase in temperature of 10.5°C, a factor close to the rule of thumb of a doubling in reaction rate for every 10°C increase in temperature. At 195°C, the rate decreased by 27% when the H_2/CO ratio was decreased from 2.0 to 1.5.

The authors indicate that the catalyst prepared using an organic solvent has higher activity than one prepared in the same manner but using an aqueous solution. The authors indicate that the catalyst may contain Group IIIB or IVB metal oxide as a promoter, with oxides of the actinide and lanthanide series being preferred. Especially preferred metal oxides are La_2O_3, CeO_2, ZrO_2, TiO_2, HfO_2, or ThO_2. MnO_2 and MgO are also listed as preferred promoters. The amounts of these promoters can be from about 0.05 to 100 parts by weight to 100 parts by weight of cobalt. It appears that the patent covers only catalysts using these oxides as promoters, and not as the support material.

The support should have low acidity. Its surface area should be at least about 40 to 50 m^2/g but not so high that "permit reactant materials to enter the interstices of the catalyst." A preferred surface area is in the range of 150 to 225 m^2/g. The support should be high purity, meaning having low concentrations of components having deleterious effects on the cobalt catalyst.

The process is outlined in figure XII.19 and does not differ significantly from one used by Kölbel and coworkers (XII.18). In the reactor, the catalyst particles are suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present from about 2 to 40 wt.%. The catalyst density can be in the range of 0.25 to 0.90. The gas flow enters at a rate sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Figure XII.19. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone (54) before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. The catalyst for the fixed bed reactor was supported on 1/16 inch extrudate alumina which contained about 20 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides. The synthesis gas ($H_2/CO = 2.03:1$ with methane diluent of 19.1 mole %) passed through the 1" i.d. reactor at a maximum stable temperature of 215°C with a pressure of 275 psi (18.7 atm., 1895 kPa). For the slurry reactor, alumina which contained about 12 wt.% Co, 0.3 wt.% Ru and 0.6 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides was in the form of 20-105 microns (less than 140 mesh; average particle size 52 microns). A liquid with a viscosity of 8 centistokes (8×10^{-6} m^2/s) was composed mainly of C_{40}-C_{50} isoparaffins. Gas entered at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (10.7 atm) and the gas flow with $H_2/CO = 1.95$ was 1826 cm/s. Initially the temperature was 225^oC but was increased and held at several higher temperatures to obtain additional conversion data.

The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol) (Figure XII.20). This value of the activation energy is surprisingly close to that reported for a fused iron catalyst (20.0 kcal/mol; 83.6 kJ/mol) and a precipitated iron catalyst (20.9 kcal/mol;87.4 kJ/mol) (XII.19). At 225^oC, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240^oC. As the temperature increases, the C_5+ fraction gradually decreases (Figure XII.21) and the C_5-C_{20} fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table XII.14).

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XII.4. "Catalysis," (P. H. Emmett, Ed.), Reinhold Pub. Corp., 1956, pp. 409 [presumably the reference should be F. G. C. Apetta and C. J. Plank in, "Catalysis" (P. H. Emmet, Ed.) Reinhold Pub. Corp., Vol 1, 1954, pp. 315-352.].

XII.5. U.S. Patent 4,605,680; August 12, 1986; H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell.

XII.6. U.S. Patent 4,605,679; August 12, 1986; T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy.

XII.7. U. S. Patent 4,605,676; August 12, 1986; T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy.

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XII.9. U. S. Patent 4,399,234; August 16, 1983; H. Beuther, C. L. Kibby, T. P. Kobylinski and R. B. Pannell.

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XII.17. H. Beuther, T. P. Kobylinski, C. E. Kibby and R. B. Pannell, "Conversion of synthesis gas to diesel fuel in controlled particle size fluid system," South Africa Application No. 85/5317, July 15, 1985.

XII.18. H. Kolbel and M. Ralek, *Catal. Rev. Sci. Eng.*, **21**, 225 (1980).

XII.19. H. H. Storch, N. Golumbic and r. A. Anderson, "The Fischer-Tropsch and Related Synthesis," John Wiley & Sons, Inc., New York, NY, 1951, p. 541.

Table XII.1

Evaluation of G-B Catalyst in Pilot Fluid Bed Reactor
Data Taken at 25 Hours on Stream (from XII.2)

Run	Temp., °C	Pressure, (psig)	H_2/CO	Syngas Space Velocity, $cm^3/g/h$	Per Pass CO Conversion, %	Selectivity to C_5+[a]
First	195	15	2.0	600	25	74
Second	195	30	2.0	1200	22	82
Third	195	30	2.0	1200	16	74
	215	30	2.0	1200	44	71
Fourth	215	60	2.0	1950	41	72
Fifth	205	30	1.5	1200	17	72
Sixth	215	30	3.0	1200	76	55
Seventh	205	30	2.0	1200	23	67
Eighth	205	30	2.0	1800	25	73
Ninth	215	40	1.5	1600	25	72

a. C_5+ expressed as percent of carbon selectivity basis.
b. At some point, every run had one or more reactor "run aways." They all failed.

Table XII.2

Typical Data from Fixed Bed Pilot Plant (XII.2)

Temperature, °C	210
Yields, Wt.% of Hydrocarbon Product	
CH_4	13.7
C_2H_4 to C_4H_{10}	11.6
C_5-C_8 (naphtha)	25.4
C_9-C_{20} (distillate)	33.4
$C_{21}+$ (wax)	14.2
Oxygenates	1.7

Table XII.3

Influence of Ru on Catalyst Performance (from ref. XII.3)

Experimental Conditions: H_2:CO = 2:1,
GHSV = 380

		% Selectivity to CH_4 Catalyst from Example			
Ex. No.	Temp., °C	1 (Co)	2 (Co + Ru)	3 (Co + Ru)	4 (Co + Ru)
18	200	9.8	0[a]	0	0
19	300	27.5	0	0	0
20	400	48.0	0	1.2	0.5
21	450	87.0	10.1	21.0	25.0

a. The low selectivities (zero) are most likely not real.

Table XII.4

Influence of Ru on the Production of C_9^+ (from ref. XII.3)

		% Selectivity to C_9+ Fraction Catalyst from Example Number in Table XII.3				% Olefins in C_9+ Fraction Catalyst from Example Number in Table XII.3			
No.	Temp., °C	1	2	3	4	1	2	3	4
22	200	41	88	87	--	29	4	5	3
23	300	30	75	71	73	32	10	9	7
24	400	18	41	38	34	48	30	26	21

Table XII.5

Products Using a Prereduced Co-Th-Alumina Catalyst (from ref. XII.5)

Example No.	2	3	4	5[2]	6[3]
Temp., °C	175	185	195	205	194
H_2/CO	1:1	1:1	1:1	1:1	2:1
CO Flowrate (cm^3/gram/hour)	155	155	270	610	270
CO Conversion Rate (cm^3/gram/hour)					
To CO_2	0.2	1.1	1.6	2.9	(1.3)
To Hydrocarbons	19	41	61	79	(120)
CO Conversion (Percent)	13	27	23	13	44
Product Distribution (Carbon Atom %)					
CH_4	4	5	6	8	9
C_2-C_4	6	7	8	10	9
C_5-C_8	23	25	29	34	24
C_9-C_{20}	62	59	50	44	49
C_{21}+	5	4	7	4	9

2. Separate run.
3. Not aged at 205°C.

Table XII.6

Alpha Values for Runs Shown in Table XII.5 (From ref. XII.5)

Run Number	Alpha, Based on C_5-C_8/C_9-C_{20}
2	0.89
3	0.82
4	0.83
5	0.79
6	0.74

Table XII.7

Impact of ROR (reduction-oxidation-rereduction) of a Co Catalyst (from ref. XII.6)

	CO Conversion Rate (cc/gram Co/hour)		C_5+ Liquid (Wt.%)	
Catalyst	R350	ROR	R350	ROR
A	1230	1485	73	81
B	790	1190	80	79
C	690	960	81	--

Table XII.8

Influence of Ru on Activity of a Co Catalyst (from ref. XII.7)

		Co/Ru Ratio		195°C CO Conversion Rate (cc/gram metal/hour)	
Test No.	Ru (Wt.%)	(Wt.)	(Molar)	R350 (F)	ROR (G)
1	0.0	---	---	382	476
2	0.05	400	693	780	968
3	0.10	200	346	879	1093
4	0.50	40	69	1034	1415
5	1.00	20	35	930	1286

Table XII.9
Influence of Temperature on a Co-Th-Alumina Catalyst (from ref. XII.8)

Example No.	2	3	4	5	6
Temp., ^oC	195	195	195	205	215
Pressure, psia	15	15	30	30	30
H_2/CO	1:1	2:1	2:1	2:1	2:1
CO Flowrate (cm^3/gram/hour)	310	310	735	735	735
CO Specific Rate (cm^3/gram/hour)	70	95	102	200	257
C_5+ Synthesis Rate (mg/gram/hour)	38	48	47	83	97
Product Distribution Carbon (Atom %)					
CH_4	6	10	15	19	22
C_5+	88	79	73	64	58
C_9-C_{20}	57	45	41	32	25
C_{21}+	9	5	6	4	1
CO_2	2	2	1	2	2

Table XII.10
Influence of Silicalite on the Product Distribution (from ref. XII.9)

	$Co/ThO_2/Al_2O_3$		$Co/ThO_2/Al_2O_3$ + Silicalite	
Carbon No.	Carbon Atom %	Wt.% n-Paraffin in Fraction	Carbon Atom %	Wt.% n-Paraffin in Fraction
1	4.7	(100)	11.3	(100)
2	0.7	50	1.8	75
3	2.5	15	8.4	24
4	3.5	20	23.2	25
5	5.0	25	23.1	35
6	6.1	33	14.9	45
7	6.8	46	9.0	38
8	7.5	56	4.8	22
9	8.5	58	2.3	13
10	9.4	62	0.9	5
11+	45		1	

Table XII.11

Products from the Conversion of Syngas with a Co-Silica-Alumina Catalyst (from ref. XII.14)

	Temperature, ^oC		
	175	185	195
Yield, Wt.%			
C_1-C_4	22	25	34
C_5-C_{11}	54	60	57
C_{12}+	24	15	9
Relative Rate, mg/g/hr[a]			
C_1-C_4	0.3	0.5	1.1
C_5-C_{11}	0.7	1.2	1.8
C_{12}+	0.3	0.3	0.3

[a] The units or the numerical values are probably in error. They may be specific rates (mg/g cat/hr) but if this is the case, the magnitude of the values are questionable. In any event, it appears that the rates are only about one-tenth that of a good Co-Al_2O_3 catalyst. The low activity may be due to the difficulty of reducing Co in the above catalysts.

Table XII.12

Effect of Thoria Concentration on Product Composition (from ref. XII.15)

			Mol % Selectivity to	
Example No.	Wt.% ThO_2	% CO Conversion	CH_4	C_{2+}
30	0.5	31.1	92.0	8.0
31	1.5	29.0	55.0	45.0
32	2.0	30.5	57.0	43.0
33	3.0	33.2	57.5	42.5
34	5.0	31.0	54.3	45.7
35	10.0	28.6	55.5	44.5
36	20.0	21.4	58.2	41.8
37	30.0	11.2	50.3	49.7

Table XII.13

Relation of Catalyst Composition to Conversion and Product Selectivity (from ref. XII.15)

Example No.	Catalyst	Wt.% Rare Earth	% CO Conversion	% Selectivity to C_{2+}
11	Ni-Chrysotile	0	17.0	0
38	Th-Ni Chrysotile	2	31.5	43.0
39	La-Ni Chrysotile	2	25.0	39.0
40	Ce-Ni Chrysotile	2.5	32.5	32.1
41	Pr-Ni Chrysotile	2	35.3	35.0
42	Th + La-Ni Chrysotile	2 + 2	71.5	49.0
43	Th + Pr-Ni Chrysotile	2 + 2	69.1	48.0

Table XII.14

Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. XII.17)

Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, ^{o}C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C_5-C_{20} (mg/g/h)	67	325	400	478	560
C_5+, wt.%	60.0	79.0	78.0	76.0	73.0

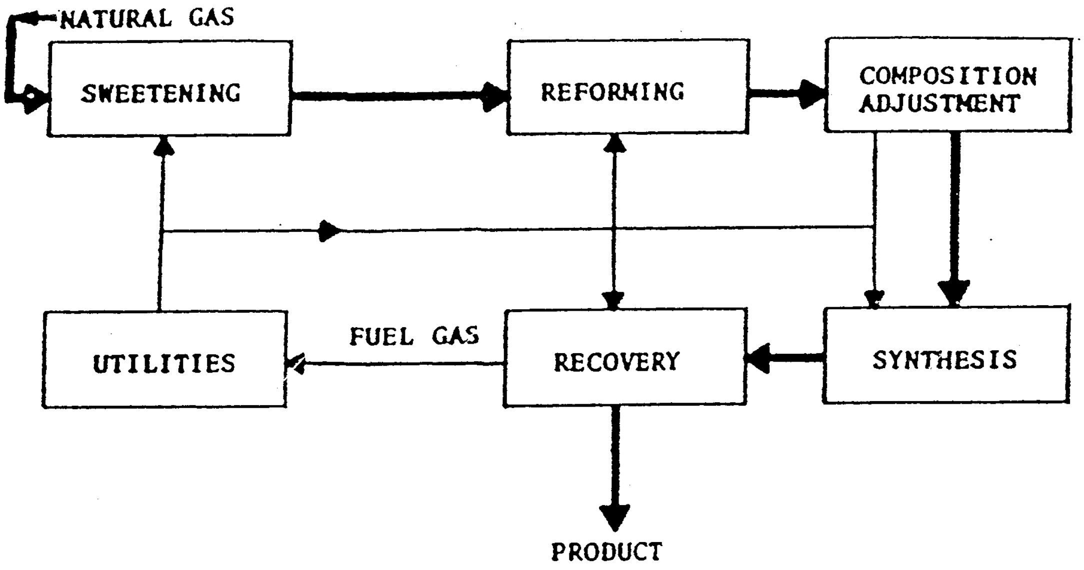


Figure XII.1. G.B. process, remote natural-gas conversion (from ref. XII.2).

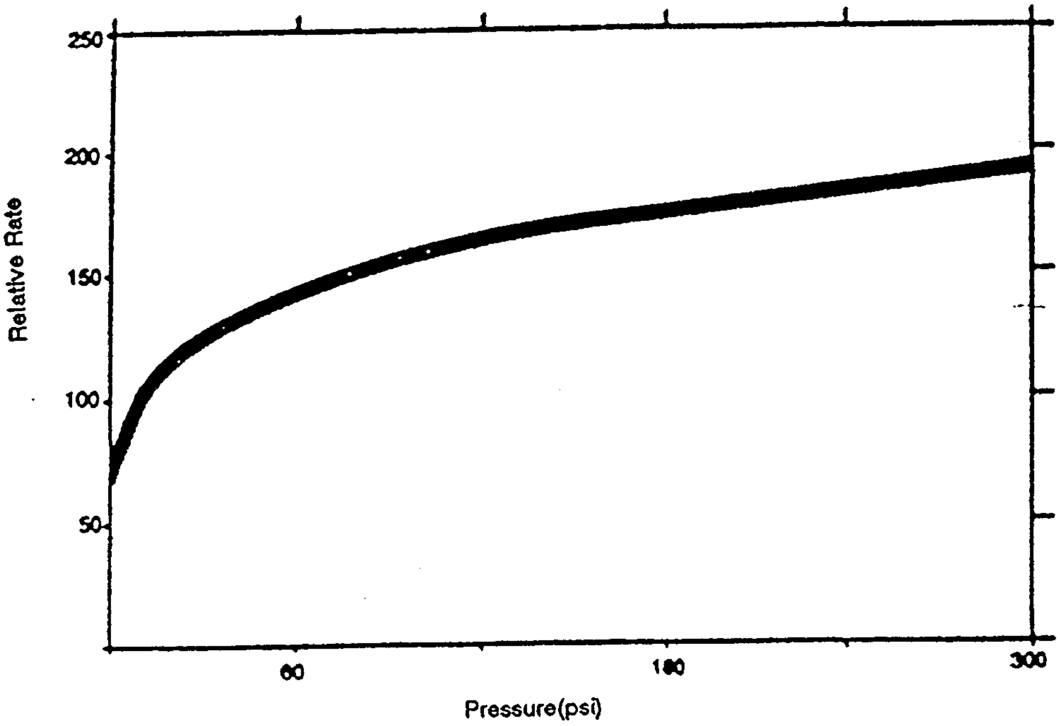


Figure XII.2. Effect of pressure on catalyst activity (relative rate based on data as given in Table XII.1) (from ref. XII.2).

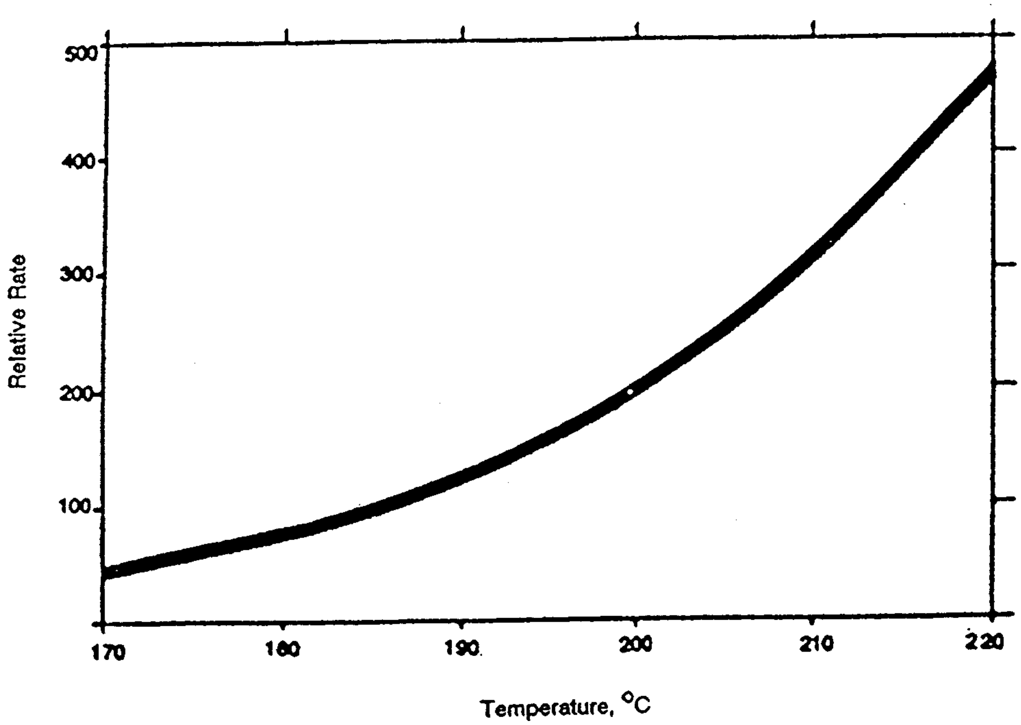


Figure XII.3. Effect of temperature on catalyst activity (relative rate) (from ref. XII.2).

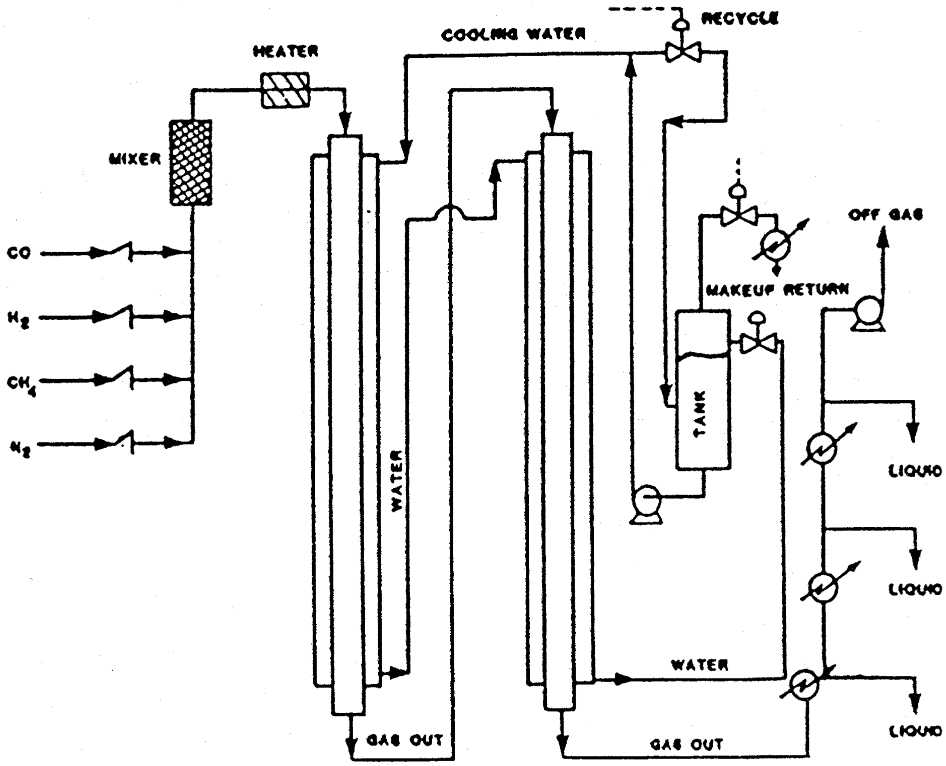


Figure XII.4. Schematic diagram of the pilot plant remote-gas-to-diesel fixed-bed process (from ref. XII.2).

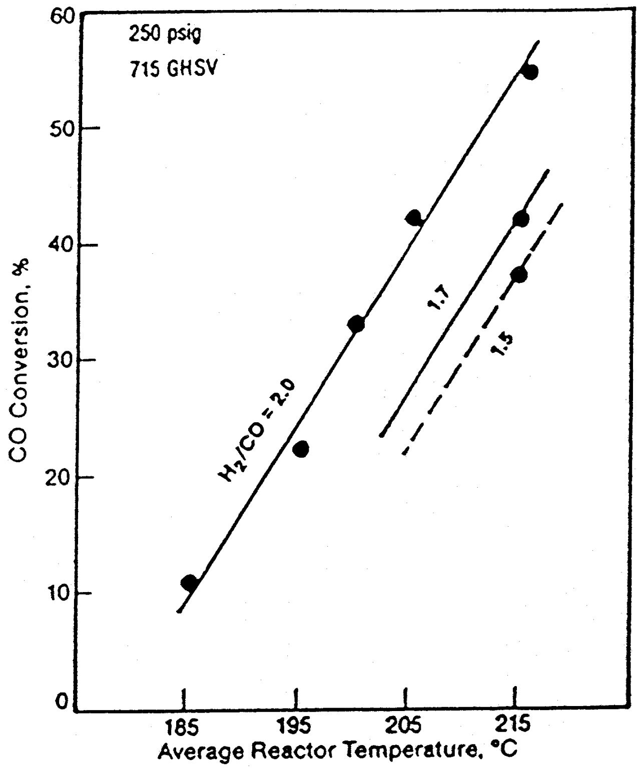


Figure XII.5. Effect of temperature and H_2/CO on carbon monoxide conversion (from ref. XII.2).

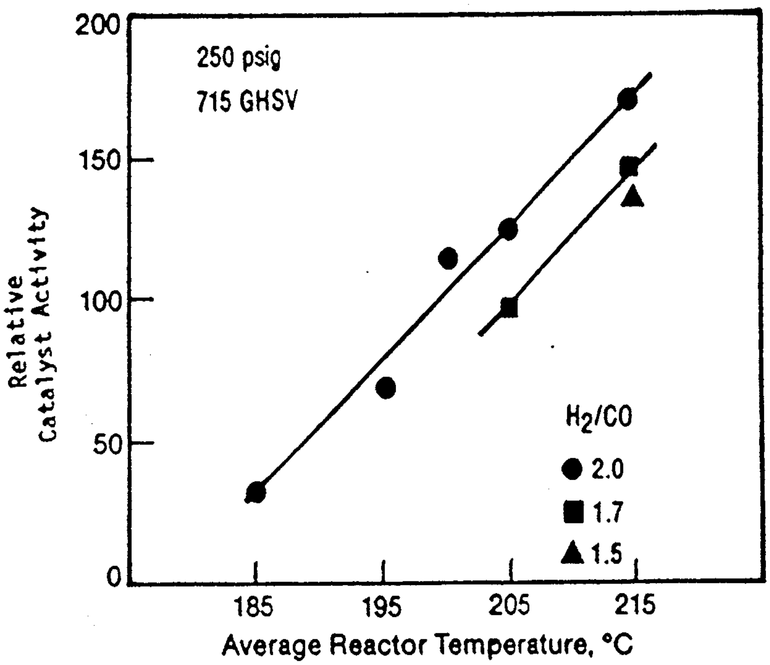


Figure XII.6. Catalyst activity (from ref. XII.2).

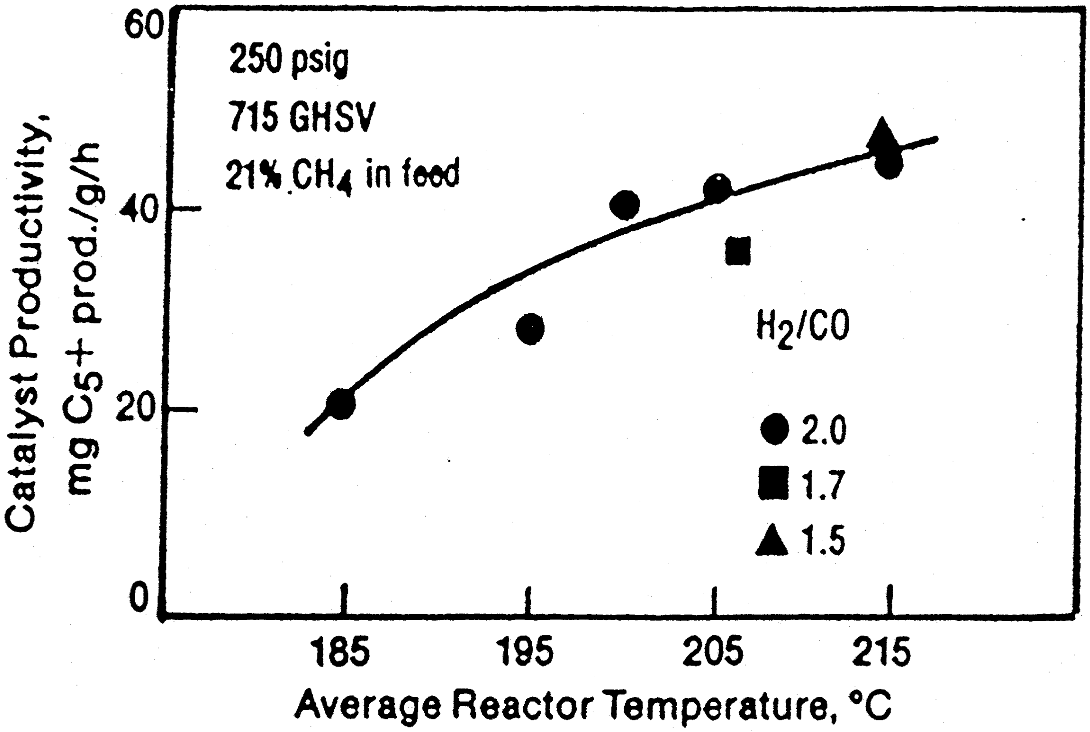
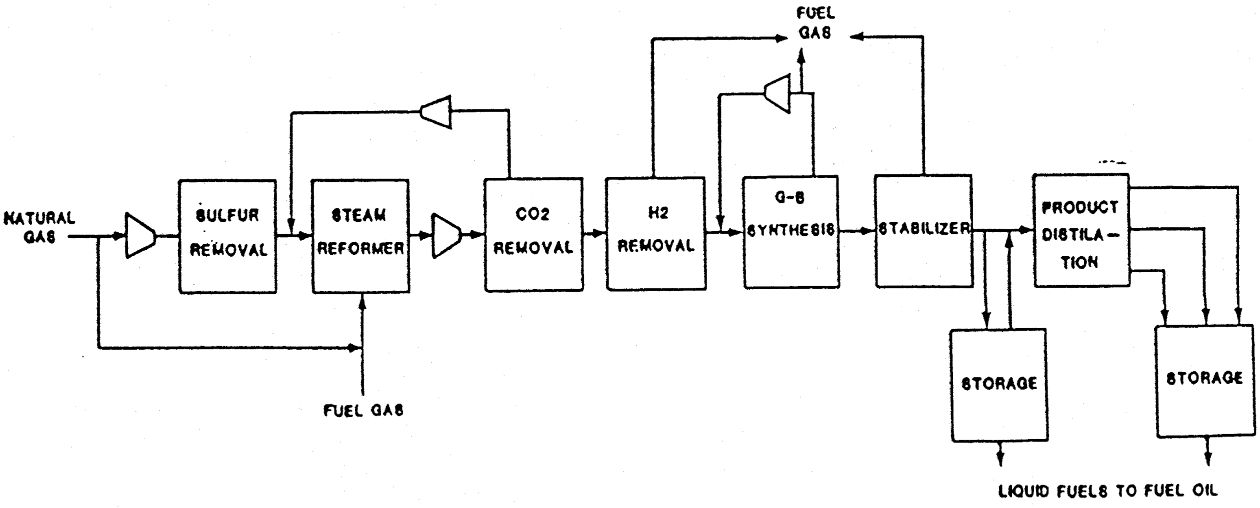


Figure XII.7. Catalyst productivity (specific rate) (from ref. XII.2).
Figure XII.8. G.B. demonstration plant, block-flow diagram (from ref. XII.2).



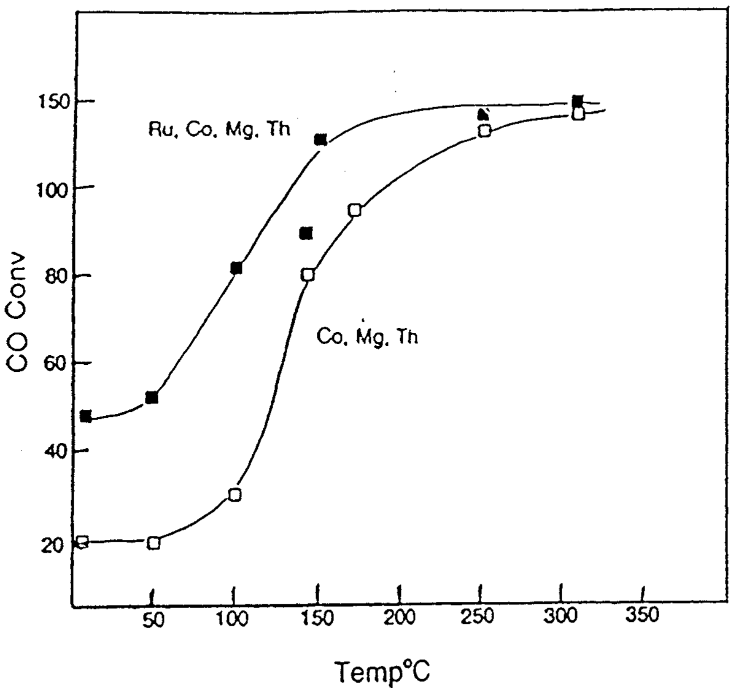


Figure XII.9. The impact of Ru (# data points) on a Co ($MgThO_x$) catalytic conversion as a function of temperature (data from XII.3).

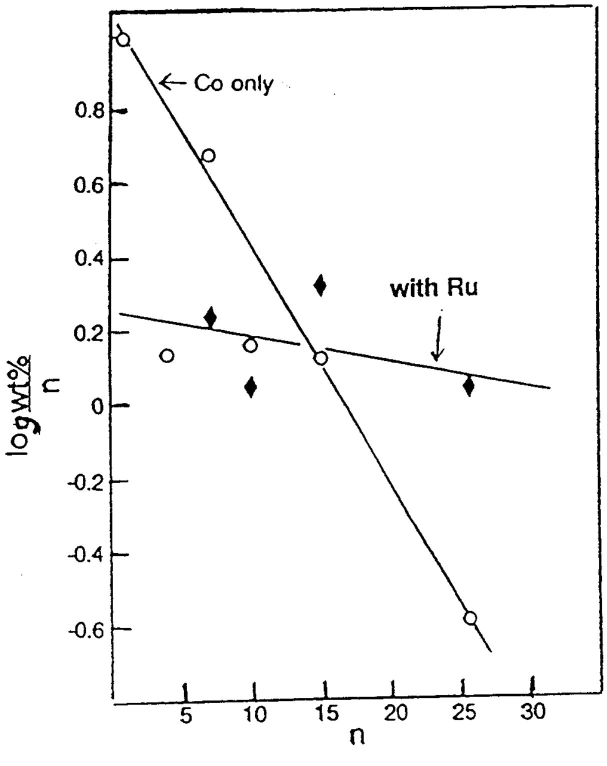


Figure XII.10. Anderson-Schulz-Flory plot of the products from the synthesis using a Co catalyst and one also containing Ru, Mg and Th) (data from XII.3).

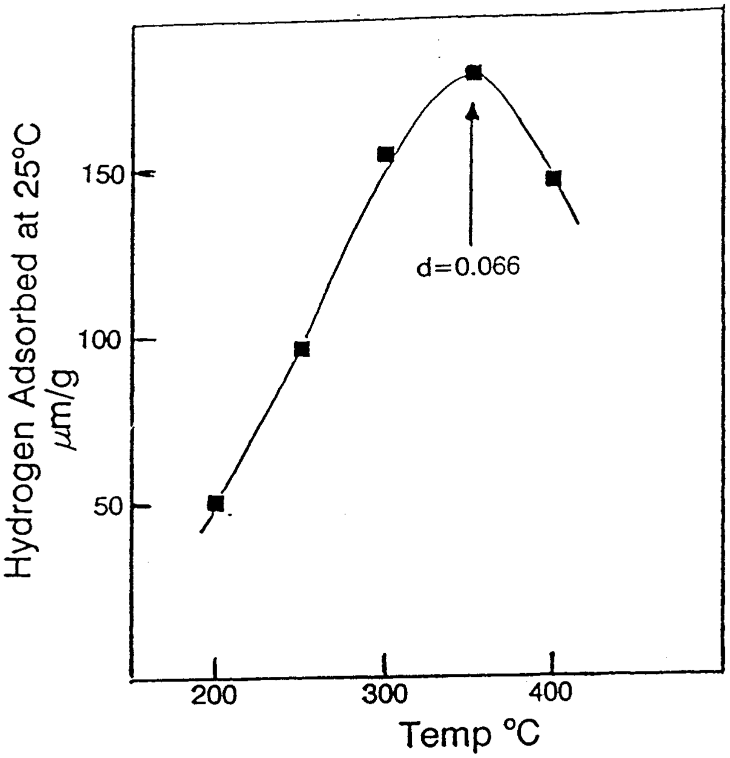
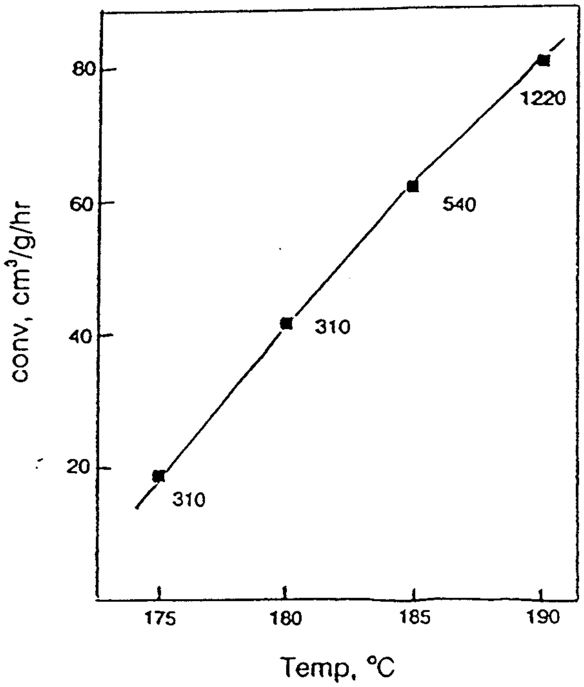


Figure XII.11. Co dispersion measurements as a function of temperature (data from XII.5).



igure XII.12. Dependence of CO conversion on the temperature (numbers in figure are the GHSV) (data from ref. XII.5).

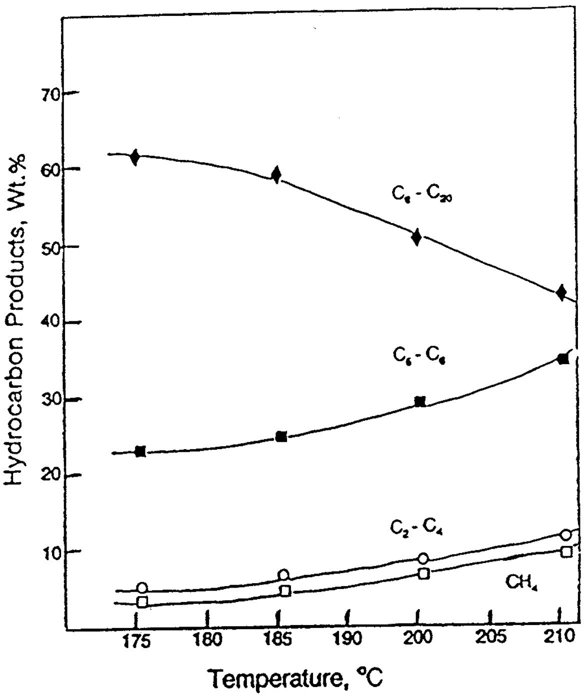


Figure XII.13. Hydrocarbon product distribution for a cobalt catalyst as a function of temperature (data from XII.5).

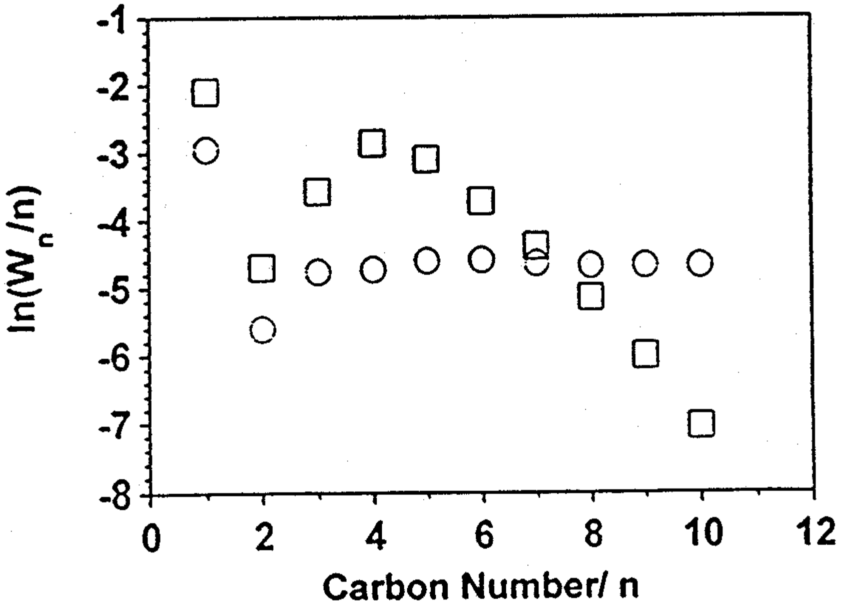


Figure XII.14. Anderson-Schulz-Flory plot of the products from the Fischer-Tropsch synthesis with a cobalt (Th, Al_2O_3) catalyst alone (F) and physically admixed with a silicate zeolite catalyst (G) (data from XII.9).

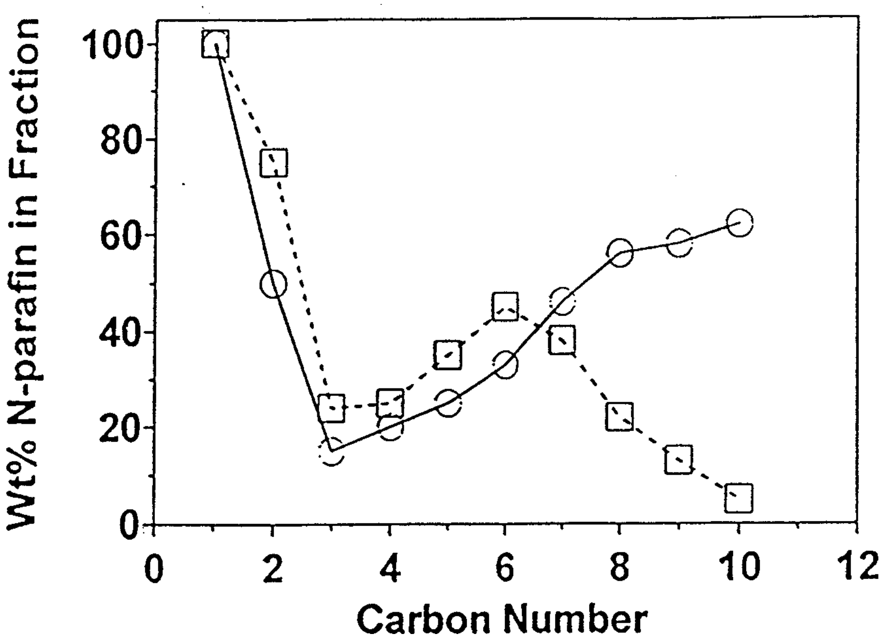


Figure XII.15. Wt% N-alkane in the carbon fractions of the products from Fischer-Tropsch synthesis with cobalt (Th, Al_2O_3) catalyst (F) and physically admixed with silicate zeolite (G) (data from XII.9).

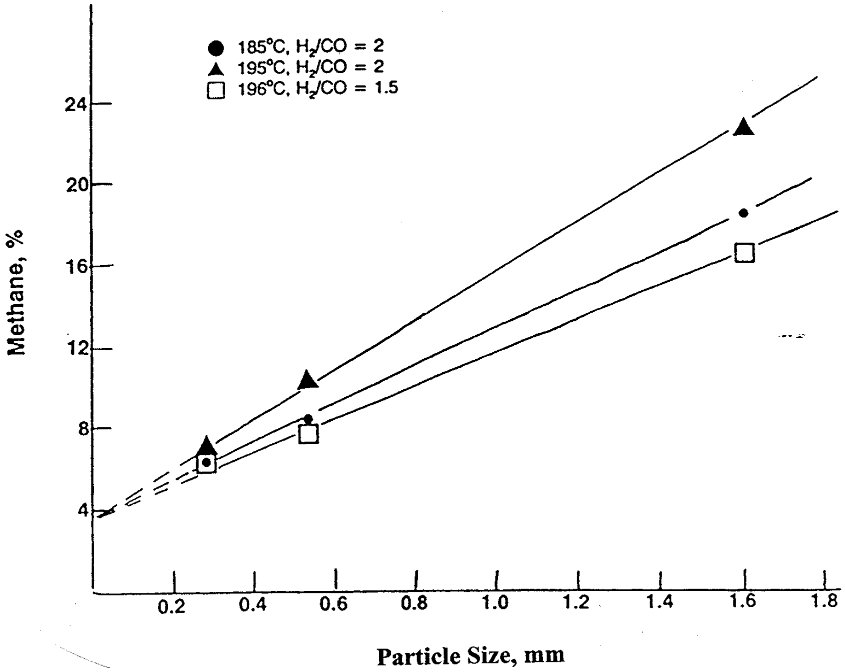


Figure XII.16. Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).

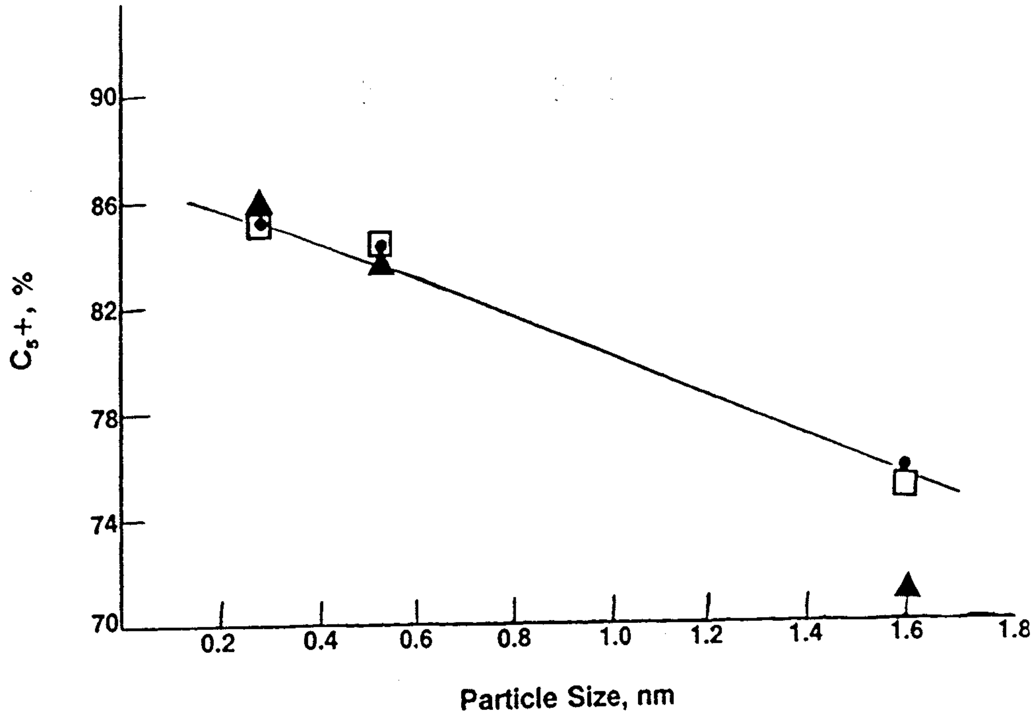


Figure XII.17. C_5+ product selectivity for three particle size catalysts in fixed-bed reactor (! , 185°C, $H_2/CO = 2$; ▲, 195°C, $H_2/CO = 2$; G, 195°C, $H_2/CO = 1.5$) (from XII.17).

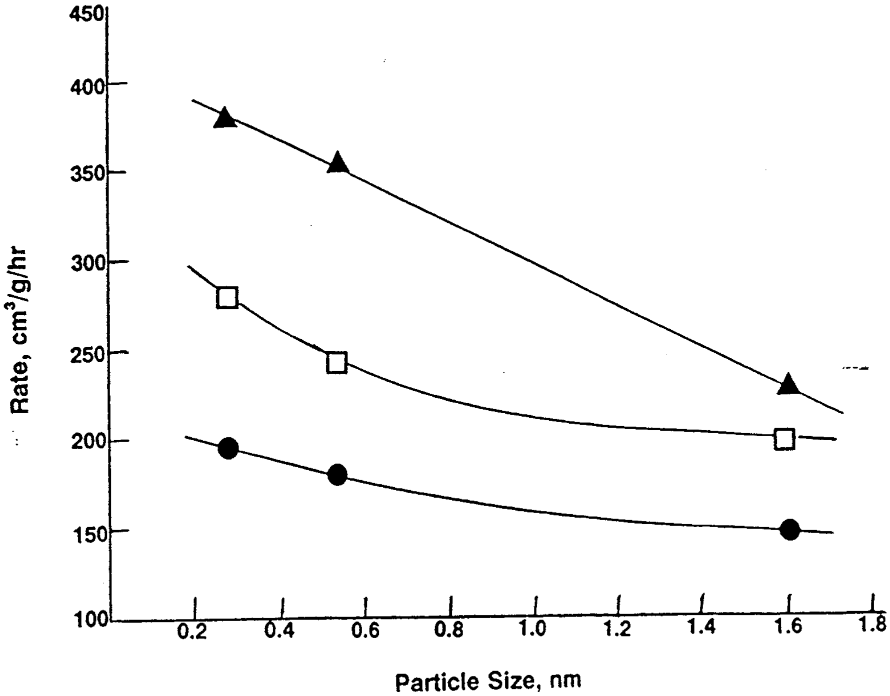


Figure XII.18. Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (! , 185°C, $H_2/CO = 2$; ▲, 195°C, $H_2/CO = 2$; G, 195°C, $H_2/CO = 1.5$) (from XII.17).

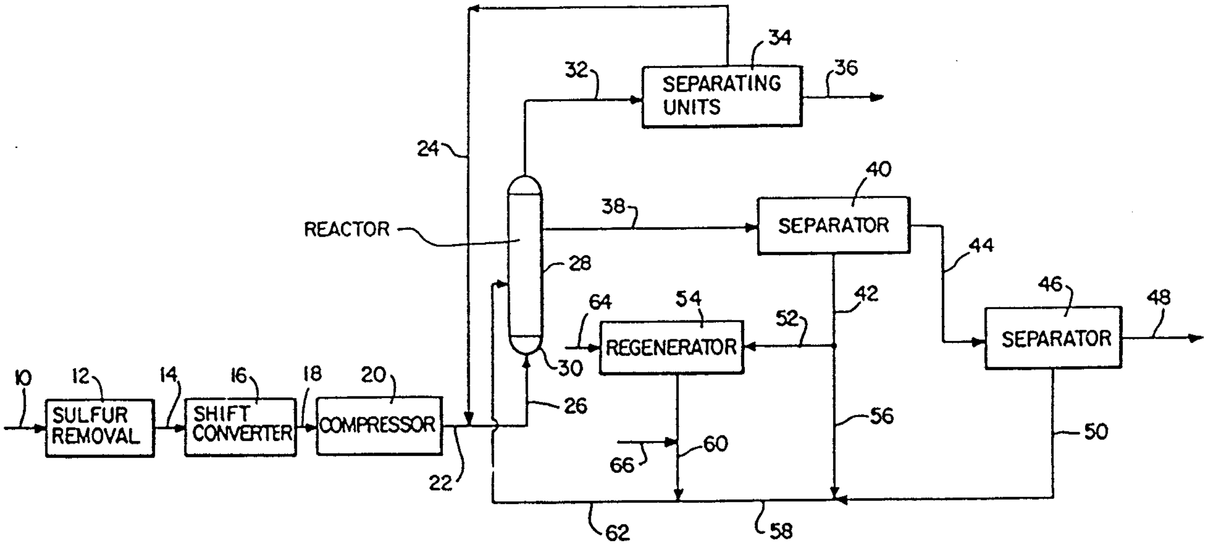


Figure XII.19. Process schematic for slurry reactor system using cobalt catalyst (from XII.17).

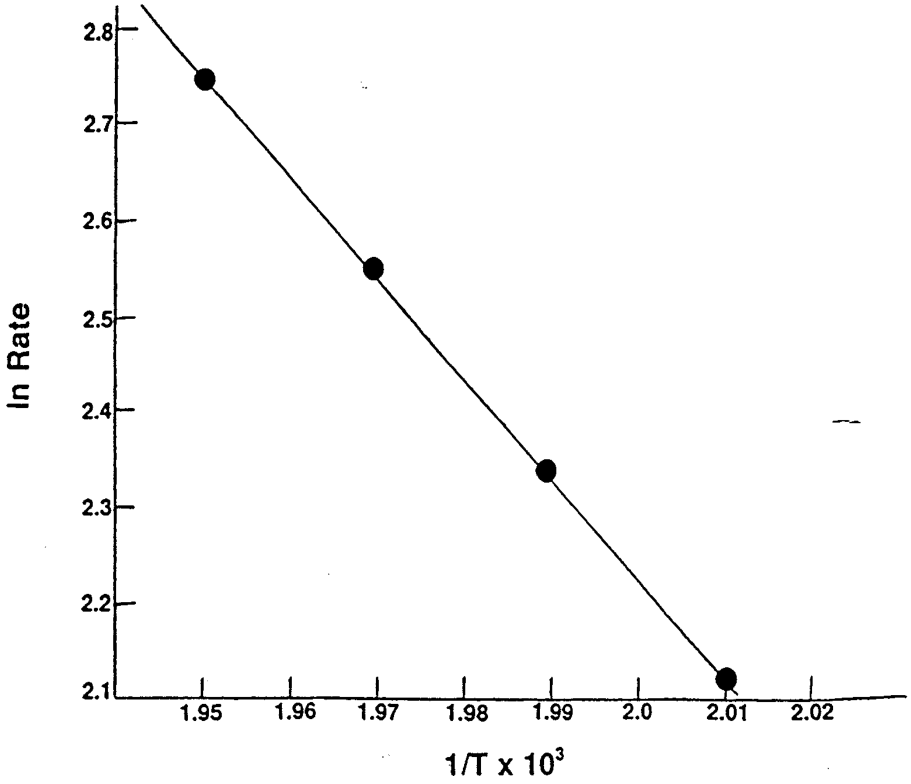


Figure XII.20. Arrhenius plot for CO conversion in slurry reactor with Co catalyst (data from XII.17).

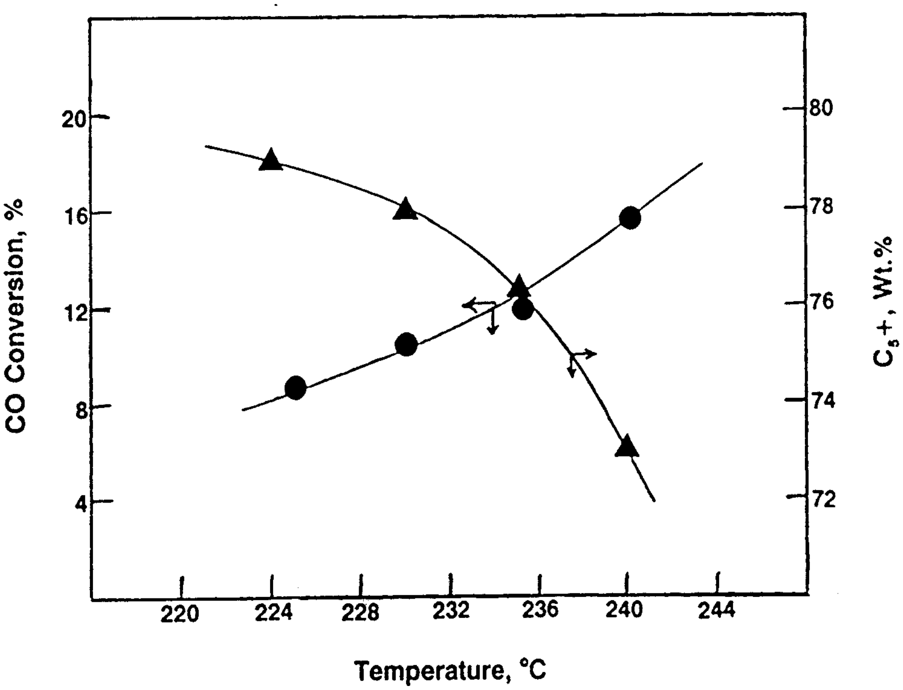


Figure XII.21. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).

ATTACHMENT XIII

Review of Fischer-Tropsch Work by Statoil

Three patents on Fischer-Tropsch synthesis catalysts assigned Den Norske Stats Olijeselskap A.S., Norway by Norwegian and U.S. investigators are summarized below (XIII.1-XIII.3). These individuals summarize the background for their invention. Anderson's book (XIII.4) is taken as the main background for the inventions and consider this book to indicate that the common Fischer-Tropsch (FT) catalysts are nickel, cobalt and iron. Nickel is considered to be active but it produces mainly methane. Among the Group VIII metals (old U.S. Periodic Table nomenclature), ruthenium is a very active catalyst and produces mainly hydrocarbons. Ruthenium is considered to have higher activity than Fe, Co or Ni at low temperatures. Other metals which possess high activity are considered to produce oxygenates and the patentees cite rhodium as an example (XIII.5). Osmium is considered to have moderate activity and Pt, Pd and Ir to have low activity (XIII.4,XIII.6,XIII.7).

These investigators recognize that others have used various combinations of metals for Fischer-Tropsch Synthesis (FTS). For example, nickel-doped cobalt has a higher productivity of methane that cobalt alone (XIII.8). On the other hand, Kobylinski taught that the addition of small amounts of ruthenium to a cobalt catalyst provided a material with a higher activity and with lower methane production than a similar catalyst comprised of cobalt without the ruthenium (XIII.9). Other work has documented that the activity is higher when ruthenium is added to the catalyst but the lower methane make is not as well documented.

These investigators indicate that, "In general, the catalysts [of combinations of metals] of these [prior] teachings have activities and selectivities which are within the ranges of the individual components." They also note that the combination of a metal with certain oxide supports may lead to higher productivity of products, presumably due to the increase in surface area of the active metal component. The authors cite the case of using titania to support cobalt or cobalt-thoria (XIII.10) with a resulting increase in activity for the production of hydrocarbons and, by implication, attribute this beneficial effect to strong-metal-support-interactions (SMSI) (XIII.11).

Statoil investigators also indicate that a patent (XIII.12) teaches that combinations of cobalt, rhenium and thoria or cobalt and rhenium supported on titania are useful for hydrocarbon production. The patent indicates that similar improvements in activity can be obtained when using other inorganic oxide supports; however, the inventors indicate that titania is the only support specifically discussed in reference 12. These workers indicate that, "The typical improvement [reported in reference 12] in activity gained by promotion of cobalt metal supported on titania with rhenium is less than a factor of 2."

The major teaching of the Statoil patent is that the choice of support for Co is critical, "and the addition of a small amount of rhenium to an alumina—supported cobalt catalyst gives a much greater improvement in activity than the addition of rhenium to cobalt supported on any other inorganic oxide. To be effective as a support for cobalt, the alumina should possess low acidity, high surface area and high porosity. The method of adding the active metals to the alumina support is, according to the inventors, not critical.

Included in inventions by the Statoil investigators is the finding that it is beneficial to include a small amount (0.1 - 5%, preferably 0.1 to 2 wt.%) of a metal oxide promoter in addition to cobalt and rhenium. The inventors conclude that the most preferable metal oxide is La_2O_3 or a mixture of lanthanides rich in La.

After preparation, the catalyst is calcined in a specified manner ultimately to attain a preferred temperature between 250 and 350°C for 2-5 hours. To activate the catalyst, it is reduced in hydrogen, again using a specified heating ramp to attain a preferred temperature of 300-400°C and holding at this temperature for 6-24 hours. Catalyst passivation and rereduction cycles may be carried out.

Catalyst testing was accomplished with a H_2/CO = 2 synthesis gas. A fixed-bed reactor (0.5 g catalyst) was utilized at atmospheric pressure and temperatures of 185, 195 and 205°C [a standard testing procedure involved 9.82 hr at 195°C, 4.3 hr at 205°C, 4.5 hr at 185°C and 9.5 hr at 195°C]. The flow rate of synthesis gas was 1.68 L/g catalyst/hr. Catalysts were compared using results obtained during the period of 10 and 30 hours-on-stream.

A series of identical catalysts (12 wt.% Co, 1 wt.% rare earth oxide), except for the content of rhenium, were prepared. For the alumina supported catalyst, there was a greater than 3-fold increase in CO conversion as Re content increases to about 1 wt.% and then a gradual decline in CO conversion was noted for further increases in Re content Figure XIII.1). The incorporation of these amounts of Re did not substantially increase the production of either methane (10-14%) or CO_2 (0.6-1.3%).

Two series of catalysts were prepared in which the Co loading was increased, one series with and one without rhenium. Re was added so as to keep the wt.% Co/wt.% Re constant at 12 for 3, 6 and 9 wt.% Co; for the 20 and 40 wt.% Co formulations, the ratios were 0, 4, 20 and 0, 8, 20 and 40, respectively. The impact of Re is evident in Figure XIII.2 (apparently the data for the 20 and 40% Co are for Co/Re ratio of 20 samples in Table V of reference XIII.1). This patent indicates that the improvement in activity due to the addition of rhenium increases as the cobalt content increases.

The Statoil investigators report that,

> "The catalysts in Table VII (Table XIII.1 of this report) were prepared to test the teaching that various inorganic supports are acceptable for preparing cobalt plus rhenium F-T catalysts. An examination of the data in Table VIII (Table XIII.2 of this report) leads to the surprising conclusion that the type of support is extremely important and that vast differences in activity exist between catalysts prepared on one support and catalysts of the same catalytic metals content on another support. More surprisingly, only cobalt plus rhenium on alumina showed a commercially attractive activity level and selectivity."

Some may question the conclusion that a selectivity that includes 13-18 wt.% methane is a commercially attractive catalyst.

The MgO and Cr_2O_3 supports provide catalysts with very low activity. The zirconia and silica-alumina supported catalysts showed improved but low activity and poor selectivity for C_2^+. For silica and titania supports, the cobalt only catalysts exhibited activities similar to an alumina supported cobalt catalyst. However, for the addition of rhenium to the alumina, titania and silica cobalt catalysts, a significant improvement was observed **only** for the material employing alumina as a support. The authors report that, "This [latter] result is surprising and would not have been predicted based on teachings in the prior art." [This does not appear to be in complete agreement with some Exxon patents.]

The "Weisz Window" provides a rule-of-thumb estimation of the productivity needed for commercial operation as 10^{-5} - 10^{-6} mole sec^{-1} (cm^3 reactor)$^{-1}$ (XIII.13). In the following we assume: (1) a fixed-bed reactor, (2) the density of the alumina supported catalyst as 2 g/cm^3, (3) the flow of syngas as 1.88 NL/hr/g and (4) H_2/CO = 2. From Table XIII.2 for the Re containing catalyst (example 8), the CO conversion is 33%. Thus we calculate that the conversion of CO is 0.209 NL/hr/cm^3. Using this value, we calculate that the conversion of CO is 0.52 x 10^{-5} mole/cm^3/sec; this is close to the value of the Weisz Window. If the rate increases directly with pressure, then the conversion is in the Weisz Window at 10 atm.

The incorporation of alkali in the cobalt catalyst impacts both the activity and hydrocarbon product distribution. For a catalyst containing Co, Re and rare earth oxide, the incorporation of alkali caused (1) a decrease in CO conversion and (2) an increase in the alpha value of the products (Tables XIII.3 and XIII.4; Figures XIII.3 and XIII.4). However, the conclusion that the alpha value depends upon the K/Co ratio depends entirely upon the two data points obtained for the lowest to K/Co ratios. If these two points are not reliable (or are not considered), the K/Co ratio has no impact upon the value of alpha. The question of promotion changing activity and selectivity is complicated for a cobalt catalyst. Anderson pointed out that selectivity changes can be effected by changing reactor pressure (XIII.14).

van Berge and Everson (XIII.15) point out that the data in reference 1 were obtained at different conversion levels, and thus different reactor partial pressures, and that the chain of chemical promotion by K, Na, Cs and Rb could not be regarded as conclusive. Studies performed at Sastech (XIII.16) are reported to confirm the ineffectiveness of chemical promotion of cobalt Fischer-Tropsch catalysts.

The loss of activity with increasing alkali content allows one to calculate, assuming one K eliminates 1 site, that only 4.5 atomic % of the Co is catalytically active. At first glance, it appears that the data are consistent with each potassium eliminating one catalytic site, or some constant fraction of a site (Figure XIII.4). However, it must be realized that the addition of alkali causes an increase in $\ell n\ \alpha$, and a corresponding increase in the average molecular weight of the products. The average number of growing chains, and the average number of catalytic sites, is directly proportional to the average molecular weight of the growing chains (e.g., the average molecular weight of the products). Hence,

$$\overline{No.\ of\ Sites}\ \alpha\ \overline{M.W.} = 1/(1-\alpha).$$

When this is taken into account, the catalytic sites decrease more rapidly than the increase in K, or at least those catalytic sites that initiate chain growth must do so (Figure XIII.5).

During the past few years, Statoil has obtained patents related to a catalytic multi-phase reactor, and specifically to catalyst wax separation (XIII.17-XIII.21). An example of such a reactor is illustrated in Figure XIII.6 (XIII.17). "This is a solid/liquid slurry reaction apparatus which comprises: a reaction vessel **(11)**, a filter member **(13)** in contact with the slurry **(16)** defining a filtrate zone which is separated from the slurry and having an outlet **(23)** for filtrate product **(32)**; means for establishing a mean pressure differential across the filter member; means for causing fluctuations or oscillations about the mean pressure differential; and means for introducing gaseous reactants or other components in the form of gas bubbles into the slurry (XIII.17)."

One of the claims is for a filter element **(22)** which comprises a fine meshed screen, helically wound threads, fine vertical threads or sintered metal particles (XIII.17). The hydrostatic pressure preferably results from the filter member being submerged in the slurry.

The pulsating pressure can be applied directly to the filtrate or to the gas space above the filtrate, preferably by the action of a reciprocating piston in a cylinder. The pressure fluctuation may be of the order of 10 to 200% differential (preferably 2 to 5 mbar).

The filter element material and catalyst are preferably selected so that the maximum hole or pore size of the filter element is of the same order of the catalyst particle size. It might be expected that catalyst would plug the filter but this is found not to be the case. Of course, the particle size of the catalyst may be much larger than the maximum hole or pore size of the filter.

In operation, products pass through the filter element **(12)** to form a product filtrate **(32)** which is free of catalyst. Any gaseous products and unconverted reactants that pass through the filter element can be vented through outlet **(31)** and subsequently through **(17)**. The product filtrate **(32)** leaves through level device **(23)** and outlet **(24)** to collect in **(25)** for regulated continuous or periodic removal.

In an example, a reactor of 4.8 cm x 2 m dimensions was filled with approximately 10 wt.% of a Co on alumina catalyst (30 to 150 µm). The gas (H_2, CO and N_2) was fed at a superficial gas velocity of 4 cm/s. The temperature was 230^oC and pressure was 30 bar.

The filter unit was located in the upper part of the reactor and comprised of Sika stainless steel sintered metal cylinder Type R20 produced by Pressmetall Krebsöge

Gmbh. The filter had an outer diameter of 2.5 cm, a height of 25 cm and an average pore diameter of 20 µm.

The slurry was effected using a poly-α-olefin liquid. Fischer-Tropsch product **and a poly-α-olefin that was fed to the reactor** were both withdrawn through the filter unit (ratio of Fischer-Tropsch and poly-α-olefin not specified). Liquid withdrawal rate varied from 2.5 to 320 g/hr, depending on Fischer-Tropsch synthesis rate and feed rate of poly-α-olefin. The experiment lasted for about 400 hrs and approximately 30 liters was withdrawn through the filter unit. Most would therefore conclude that the test was of a short duration compared to the length of time that a commercial unit must operate. Furthermore, the product was diluted with start-up solvent that was added during the run. Thus, it appears that this example is applicable to a limited process scheme, and not for all process schemes.

A solid/liquid slurry reaction apparatus with a filtration section has been submitted for patent coverage (XIII.22) and is illustrated in figure XIII.7. The teachings of this patent application is based upon a recent report identified only as "a report issued by the United States Department of Energy." The DOE report addressed the question of catalyst/wax separation in Fischer-Tropsch slurry reactor systems and concludes:

> "Internal filters immersed in the reactor slurry, as used in some bench-scale or pilot-scale units, do not work successfully due to operational difficulties. A reactor with a section of its wall as a filter may be operable for a pilot plant but is not practicable for commercial reactors. Internal filters are subject to plugging risks, which may cause premature

termination of the run, and commercial plants are not allowed to take chances."

The patent applicants have discovered that, contrary to the teachings of the DOE report, "...it is possible to provide a continuous reaction system for a Fischer-Tropsch synthesis in which it is not necessary to perform the solid/liquid separation in an external filter unit. Furthermore, a sufficiently high flow rate of filtrate for commercial operation can be achieved."

The description in the patent application indicates that the filter screen and the catalyst are similar, or identical, to those described in the previous patent application (XIII.17). In this instance, however, the filter screen has been made a part of the slurry reactor wall or, as shown in figures XIII.8 and XIII.9, it may be incorporated in multiple locations of the slurry reactor wall. In the example shown in figure XIII.7, a conical section **(15)** is included as an expansion chamber to prevent the slurry from foaming over and to define a gas space **(16)** above the reaction zone. The cone-shaped portion **(15)** may contain additional means (that are not shown nor specified) for breaking up or reducing foam formation.

The invention was described and was then further illustrated with the following example. Experiments in a laboratory using an apparatus similar to that shown in figure XIII.7 were carried out. The length and diameter of the unit were 1250 mm and 55 mm, respectively. The filter member had a mean pore size of 30 µm and a length of 200 mm. A heat transfer oil (diethyl benzene (95%) and minor amounts of other alkyl benzenes) and 20 wt.% alumina were used as the slurry phase. The alumina particles initially had a cut-off at 53 µm. The experimental conditions in the example were: 1 bar pressure, 20-25^{o}C and 6 cm/s superficial gas velocity. After an initial start-up period, the separation capacity became approximately constant at a level of 750-800 kg/m^2h. The calculated pressure differential was approximately 5 mbar. After 40 days of operation, there was only a slight decrease in separation capacity.

The section of the DOE report that was quoted above was concerned with an operating slurry bubble column reactor for Fischer-Tropsch synthesis at a commercial scale operation. The example provided by the patent applicants was for a cold model with only an alumina solid and without Fischer-Tropsch synthesis. It would appear that the patent applicants have not shown by their example anything that would be contrary to the teachings of the DOE report since the patent applicants did not operate at any of the conditions necessary for a commercial Fischer-Tropsch plant that is currently being operated successfully.

Another patent application (XIII.19) relates to a vessel that contains a number of vertical reaction tubes, each suitable for multi-phase catalytic conversions (figure XIII.10). In this application, the above DOE report is quoted and the teaching that the applicants have provided a means of accomplishing this. Each reactor tube has essentially the features of the reactor described in the previous reference XIII.ref. 18). In operation, the gas is preferentially fed to each multi-phase catalytic reactor. These reactors are held in place by plates **(18)** and **(14)**; in effect these two plates and the vessel wall **(12)** provide the vessel to hold the heat transfer liquid/vapor.

The filter section of each reactor tube is located above the top plate **(14)**, which serves to hold a level of the wax following separation from the catalyst slurry. In another version, a sieve **(34)** surrounds each filter and is utilized to maintain a minimum wax level for each reactor tube so that the tube does not lose liquid level so that the reactor tube is depleted of liquid. Thus, the sieve extends above the level of the wax filtrate that is maintained on plate **(14)**.

The heat exchange medium is preferably a liquid at its boiling point; water is the preferred medium since the heat of reaction can be recovered as steam to be used to generate electricity or provide heat for plant operations.

In the only example of the patent application, a slurry bubble column Fischer-Tropsch reactor **is simulated** using a two phase quasihomogeneous one dimensional model. They use typical catalyst performance data contained in US 4,801,573. The simulations are utilized to **calculate** optimum values for the reactor and its operation. **Experimental data of an operating Fischer-Tropsch reactor are not provided in the application**. Since the DOE report was for an operating reactor that actually effects a separation of wax and catalyst, it is difficult to understand how the applicants can show that they have provided a solution to the problems enumerated in the DOE report.

A patent application (XIII.20) describes a separation device that has as its main object the prevention of gas from being entrained in the liquid phase in cases where it is desirable to separate gas and liquid or immiscible liquids.

A recent patent application describes a method of regenerating a catalyst in a Fischer-Tropsch synthesis reaction (XIII.21). Examples of regeneration procedures are reviewed and the conclusion is that "These arrangements all suffer the drawback that a separate source of H_2 gas must be provided to achieve regeneration." The present invention (XIII.21) is to overcome this drawback. While the use of hydrogen could be a drawback, it would appear to be so only from an operational viewpoint. For example, Sasol produces a nearly pure hydrogen stream by a pressure swing adsorption process.

It would be a disadvantage to utilize a stream of pure CO since this stream is not available in a normally operating Fischer-Tropsch plant.

Schematic sections through a slurry reactor (figure XIII.12) and a slurry reactor with a separate regeneration vessel (figure XIII.13) are shown. Details of the slurry reactor (figures XIII.12 and XIII.13) are not provided in this patent. To effect regeneration, the feed parameters of the synthesis gas are adjusted to increase the conversion of CO in the synthesis gas until the H_2/CO ratio of the gas leaving the reaction zone exceeds 10:1 and then maintaining this conversion level during the regeneration mode for some period of time to effect regeneration to a desired level. Preferable, the CO conversion is between 95 and 100%, most preferable 100%. Thus, the preferred H_2/CO ratio is 20/1, and most preferably, greater than 30/1. To achieve this high hydrogen/CO ratio, the flow is decreased, preferably slowly, so that the conversion increases to attain the desired level. Alternatively, hydrogen could be increased in the synthesis gas by modification of the generation step of the synthesis gas.

At the high conversion level, the reaction changes from synthesis to a regeneration mode. The regeneration mode is characterized by: high H_2/CO ratio, low C_{5+} selectivity and high CO_2 selectivity. This is taken to indicate a high water gas shift rate due to the high hydrogen partial pressure. Experimentally, it has been found that a few hours of regeneration is normally sufficient; however, it may take longer for more severely deactivated catalysts.

When a separate regeneration vessel is used, "normal" conditions for synthesis are maintained on the synthesis side and the high hydrogen (100% CO conversion) condition is maintained on the regeneration side. Preferably, there is a flow of deactivated and regenerated catalyst between the two sides.

Two examples are given for the regeneration. In the first example, a catalyst containing 12% Co and 0.5% Re on alumina are used at 220^{o}C and 20 bar (2 MPa) total pressure in a continuous slurry stirred tank reactor (CSTR). The reactor volume is 2 L and is half-filled with slurry. The H_2/CO inlet synthesis gas ratio was 2; the exit gas was also close to this value. The initial stable hydrocarbon activity is set relative to 1; note that this is based on hydrocarbon production. The CO conversion was 63% at this hydrocarbon production level of 1.

After the catalyst had operated for a few days, the catalytic activity had declined so that the relative hydrocarbon productivity activity number had declined to 0.69. At the relative activity number of 0.69, the CO conversion was 68% at a flow rate of 2100 NL/kg cat./hr. It is not clear whether this flow rate is for synthesis gas or for CO only; in the following we shall **assume that the flow is for CO only**. The C_{5+} selectivity was 89.4%. At this stage of catalyst deactivation, a decrease of the flow rate to 1050 NL/kg cat/hr resulted in an increase in CO conversion to 88% with a C_{5+} selectivity of 89.9%.

To establish a regeneration mode at this point (0.69 relative activity), the flow rate was reduced to 750 NL/kg cat/hr and the CO conversion was 99%. The exit H_2/CO ratio was 14/1. This regeneration mode was maintained for 10 hours and was then brought back to the Fischer-Tropsch mode by increasing the flow rate to 2100 NL/kg cat/hr. The reaction continued to produce a C_{5+} selectivity of over 88%. The relative activity at these final Fischer-Tropsch conditions was 0.77. This value is above the value of 0.69 for the deactivated catalyst but still considerably below the value of 1.0 for the fresh catalyst.

Example 2 is for a catalyst that contains 20% Co and 1% Re on alumina; however, the data are less extensive than for example 1. They report that the 20 wt.% Co catalyst was brought back to the initial level following 24 hours of the regeneration mode whereas 10 hours for the 12 wt.% Co catalyst only restored the activity to 77% of the initial activity.

The hydrocarbon production of the deactivated catalyst (relative activity of 0.69) in Example 1 corresponds to 0.983 g hydrocarbon/g cat/hr. For the fresh catalyst (relative activity of 1.0) the hydrocarbon productivity is calculated by us to be 1.29 g hydrocarbon/g cat/hr. For the reactivated catalyst (relative activity 0.77) the productivity is 1.16 g hydrocarbon/g cat/hr.

If it is assume that the catalyst productivity is linear in Co content, the productivity of the deactivated 20 wt% Co catalyst would be 1.49 g hydrocarbon/g cat/hr and that of the fresh and regenerated catalyst would be 2.15 g hydrocarbon/g cat/hr.

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Table XIII.1 (from ref. XIII.1)

			Weight of Materials in Impregnating Solution, g		Composition of Finished Catalyst, Wt.%	
Example No.	Support	Weight of Support, g	$Co(NO_3)_2$	$HReO_4$*	Co	Re
28	Silica	20	13.47	---	12	---
29	Silica	20	13.62	0.38	12	1.0
30	Titania**	25	16.84	---	12	---
31	Titania**	24.64	16.78	0.46	12	1.0
32	Titania***	25	16.84	---	12	---
33	Titania***	24.64	16.78	0.46	12	1.0
34	Chromia	20	13.47	---	12	---
35	Chromia	21.3	14.51	0.40	12	1.0
36	Magnesia	21.59	14.54	---	12	---
37	Magnesia	14.54	10.67	0.29	12	1.0
38	Silica-alumina	20	13.47	---	12	---
39	Silica-alumina	20	13.62	0.38	12	1.0
40	Zirconia	20	13.47	---	12	---
41	Zirconia	20	13.62	0.38	12	1.0

* Weight of 82.5% perrhenic acid solution.
** Calcined at 500°C.
*** Calcined at 600°C.

Table XIII.2 (from ref. XIII.1)

Example No.	Co %	Re %	Support	CO Conversion %	C_2^+ Selectivity %	CH_4 Selectivity %	CO_2 Selectivity %
1	12	---	Al_2O_3	12	90.0	8.9	1.1
8	12	1	Al_2O_3	33	87.7	11.4	0.9
28	12	---	SiO_2	11	90.1	8.7	1.2
29	12	1	SiO_2	12	88.1	10.7	1.2
30	12	---	TiO_2*	11	87.6	11.8	0.6
31	12	1	TiO_2*	17	86.5	12.8	0.7
32	12	---	TiO_2**	11	87.6	11.7	0.7
33	12	1	TiO_2**	17	85.8	13.5	0.7
34	12	---	Cr_2O_3	1	83.5	15.5	1.0
35	12	1	Cr_2O_3	2	80.8	12.3	6.9
36	12	---	MgO	0.3	20.0	30.0	50.0
37	12	1	MgO	0.3	19.1	30.9	50.0
38	12	---	SiO_2/Al_2O_3	5	76.3	22.2	1.5
39	12	1	SiO_2/Al_2O_3	6	78.6	19.8	1.6
40	12	---	ZrO_2	4	80.9	16.3	2.8
41	12	1	ZrO_2	7	78.8	18.7	2.5

* Support calcined at 500°C.
** Support calcined at 600°C.

Table XIII.3 (from ref. XIII.1)

			Weight of Material in Impregnation Solution, g				Composition of Finished Catalyst, Wt.%			
Example No.	Wt. of Al_2O_3, g	Type of Alkali	(a)	(b)	(c)	(d)	Co	Re	RE	Alkali
42	300.0	---	1039.65	17.21	13.99	---	40	2.0	1.0	0.0
43	75.0	K	260.46	4.31	3.50	0.34	40	2.0	1.0	0.1
44	75.0	K	256.36	4.25	---	0.67	40	2.0	---	0.2
45	175.0	K	609.03	10.08	8.20	1.59	40	2.0	1.0	0.2
46	100.0	K	349.50	5.79	4.70	1.83	40	2.0	1.0	0.4
47	100.0	K	354.03	5.86	4.76	4.64	40	2.0	1.0	1.0
48	60.0	Na	205.49	3.40	---	0.93	40	2.0	---	0.24
49	60.0	Cs	209.55	3.47	---	2.12	40	2.0	---	1.36
50	65.0	Rb	225.38	4.23	---	1.71	40	2.0	---	0.87
51	20.0	---	13.78	0.38	0.62	---	12	1.0	1.0	---
52	20.0	K	13.80	0.38	0.62	0.06	12	1.0	1.0	0.1
53	20.0	Li	13.64	0.38	---	0.11	12	1.0	---	0.05
54	20.0	Li	13.80	0.38	0.62	0.12	12	1.0	1.0	0.05
55	20.0	Cs	13.67	0.38	---	0.10	12	1.0	---	0.3
56	20.0	Cs	13.83	0.38	0.62	0.10	12	1.0	1.0	0.3

(a) $Co(NO_3)_2$! $6H_2O$
(b) 82.5% $HReO_4$ solution, except for example 50 which was 72.9% $HReO_4$
(c) Rare earth nitrates (RE) (see example 1)
(d) $LiNO_3$, $NaNO_3$, KNO_3, $RbNO_3$ or $CsNO_3$

Table XIII.4 (from ref. XIII.1)

	Alkali				
Example No.	Type	Content Wt.%	CO Conversion %	CH_4 Selectivity %	Product Alpha*
42	---	---	52.5**	14.2**	0.75**
43	K	0.1	52 50	8.6 11.1	0.86 0.79
44	K	0.2	43	9.3	0.83
45	K	0.2	51 44 41	9.5 11.6 9.4	0.84 0.84 0.81
46	K	0.4	30 35	7.3 7.8	0.87 0.85
47	K	1.0	12 9 6	7.0 7.9 6.2	0.88 0.85 0.87
48	Na	0.24	21	8.3	0.82
49	Cs	1.36	14	8.5	0.86
50	Rb	0.87	11	7.3	0.86
51	---	---	31.7***	10.9***	0.77***
52	K	0.1	19 22	7.6 9.8	0.78 0.84
53	Li	0.05	31	11.7	0.78
54	Li	0.05	27	12.0	0.78
55	Cs	0.3	21	11.1	0.83
56	Cs	0.3	21	10.3	0.84

* Calculated by plotting $\ln(W_n/n)$ vs. n, where n is carbon number and W_n is the weight fraction of the product having a carbon number n, and determining the slope of the line.

** Average of 21 tests.

*** Average of 6 tests.

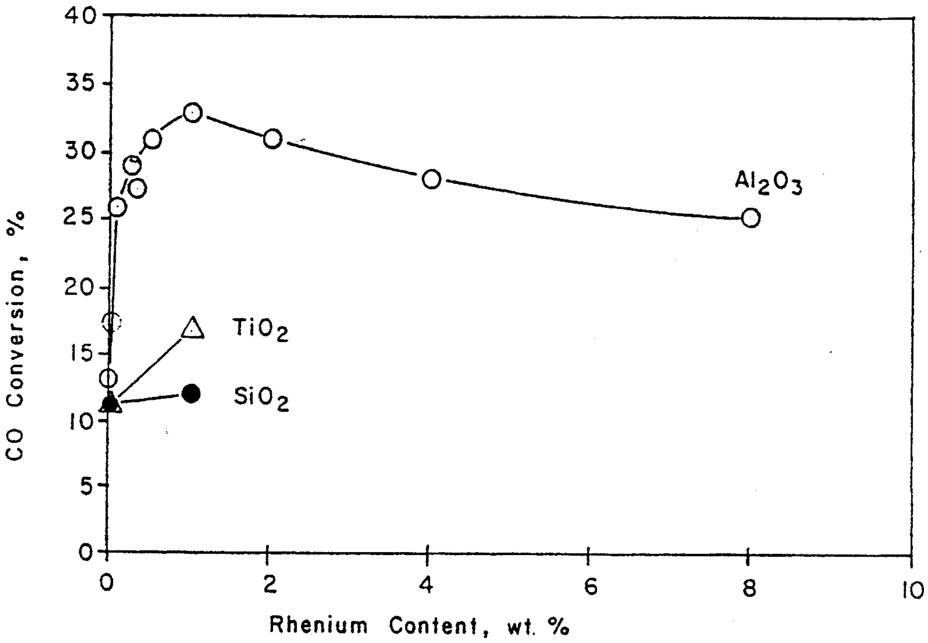

Figure XIII.1. Effect of rhenium on CO conversion catalysts containing 12% cobalt (from ref. XIII.1).

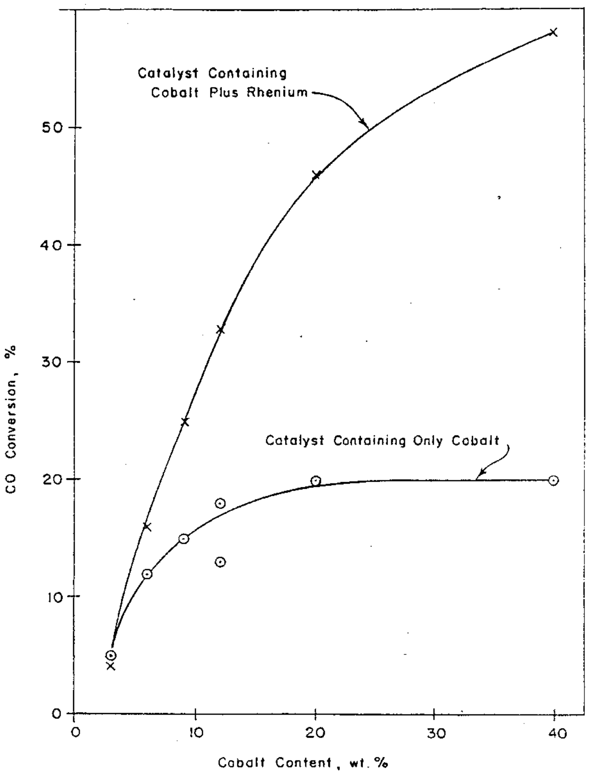

Figure XIII.2. Effect on conversion of adding rhenium to cobalt on alumina catalyst (from ref. XIII.1).

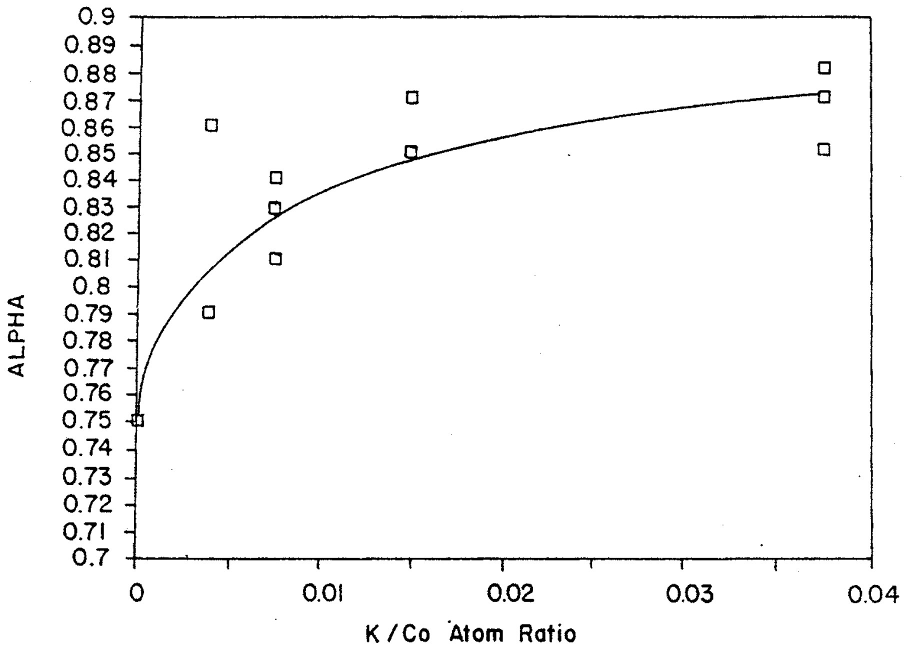

Figure XIII.3. Alpha versus K/Co (from ref. XIII.1).

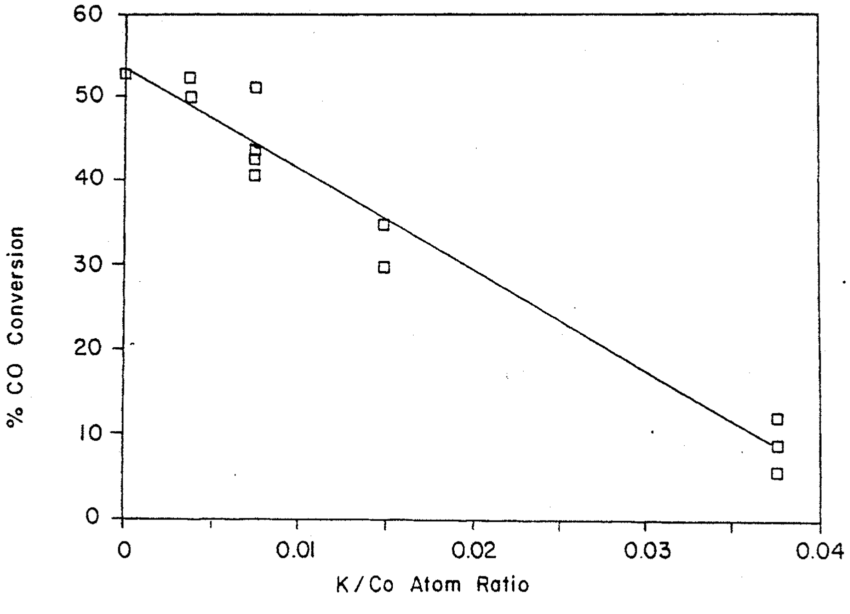

Figure XIII.4. Percent CO conversion versus K/Co (from ref. XIII.1).

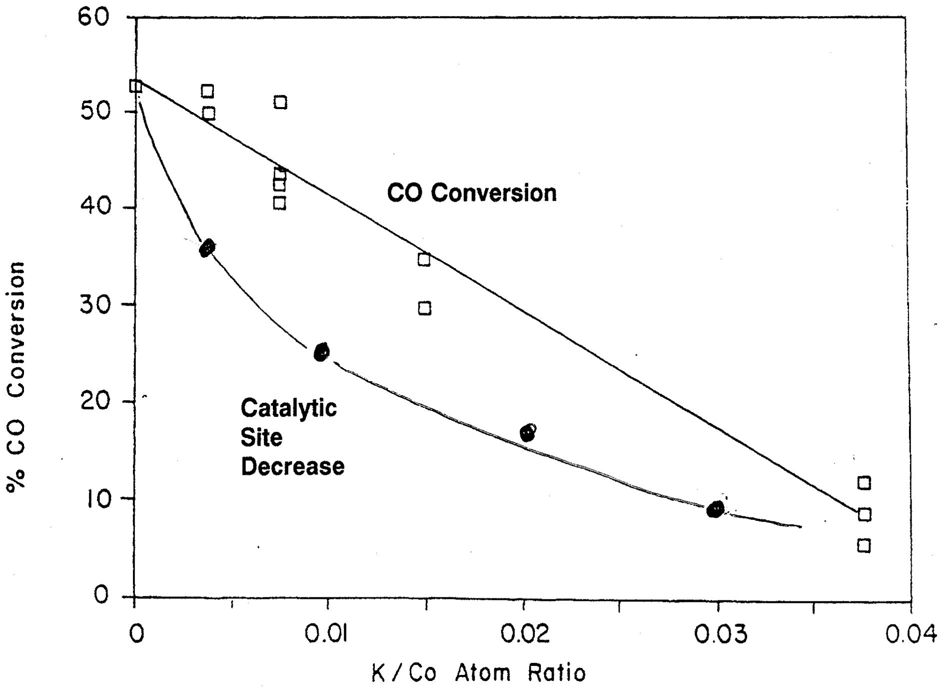

Figure XIII.5. Percent CO conversion versus K/Co (from ref. XIII.1) and our decrease calculated assuming α is related directly to the site density.

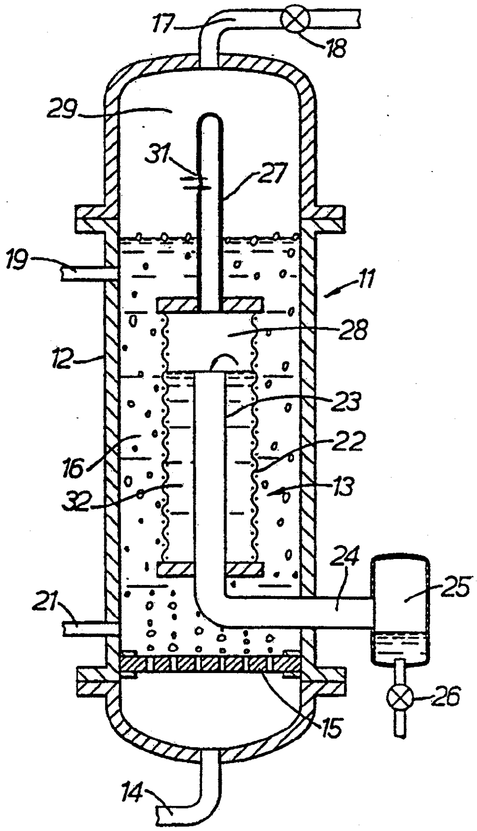

Figure XIII.6. Slurry reactor with internal filter for wax/solids separation from ref. XIII.17).

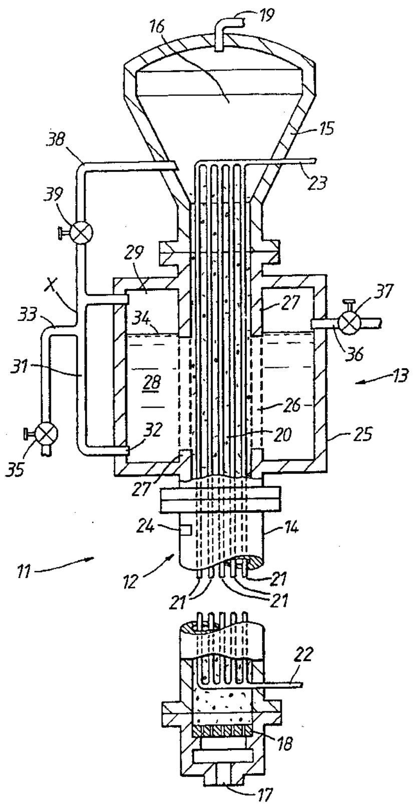

Figure XIII.7. Slurry reactor incorporating a filtration system into the reactor wall (from ref. XIII.22).

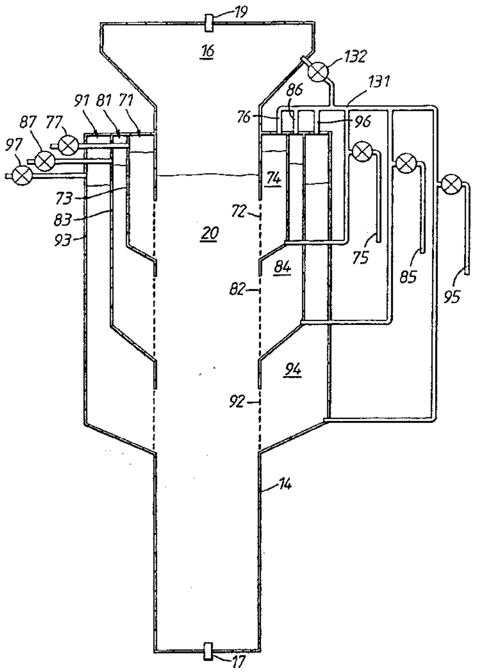

Figure XIII.8. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

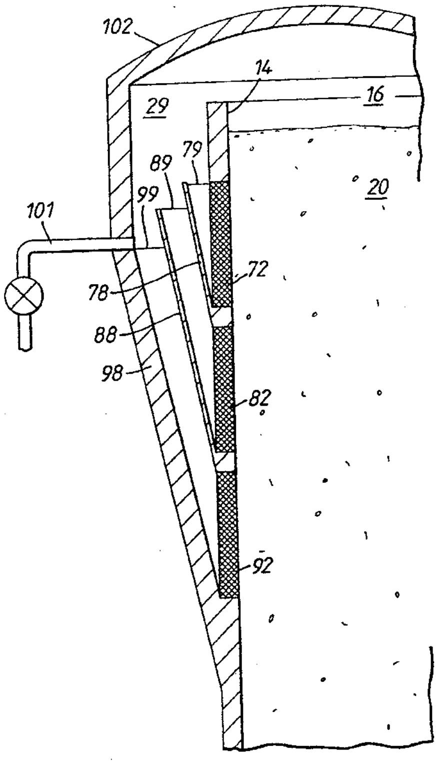

Figure XIII.9. Slurry reactor incorporating multiple filtration systems into the reactor wall (from ref. XIII.22).

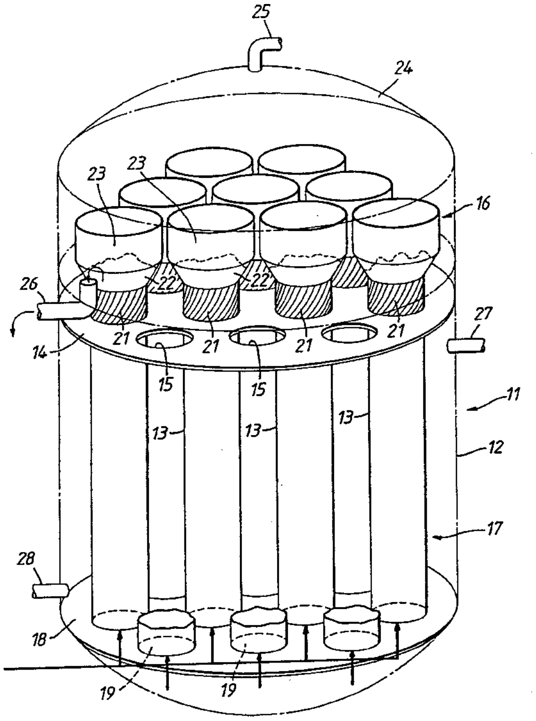

Figure XIII.10. A multi-phase catalytic reactor with multiple tubes for slurry phase reactor systems (from ref. XIII.19).

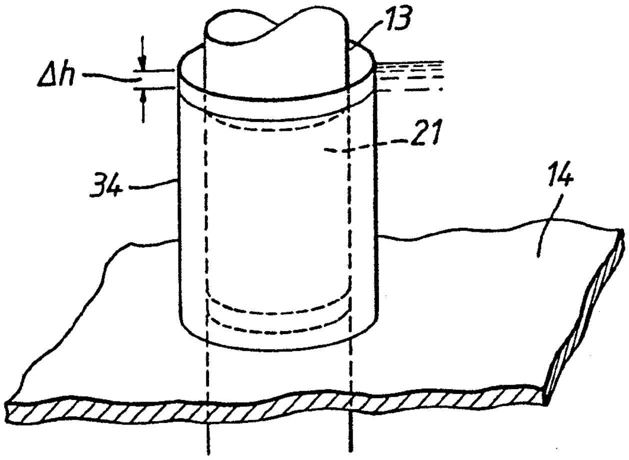

Figure XIII.11. Schematic of sleeve on reactor tube in Figure 10 to maintain slurry level in each reactor tube (from ref. XIII.19).

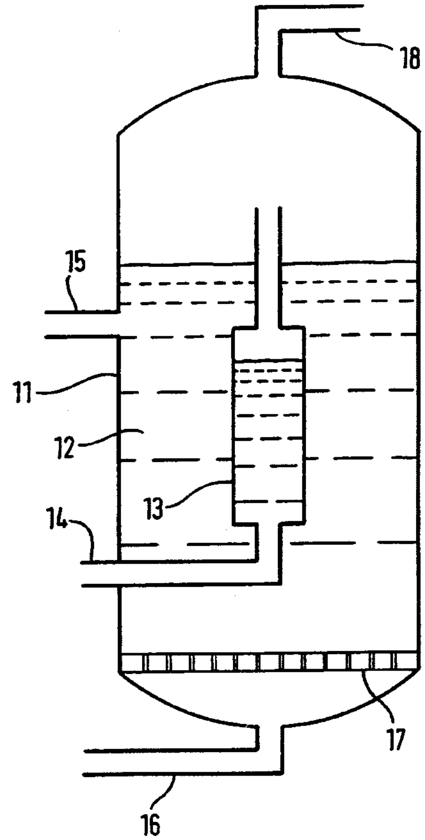

Figure XIII.12. Schematic of slurry phase reactor with internal wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

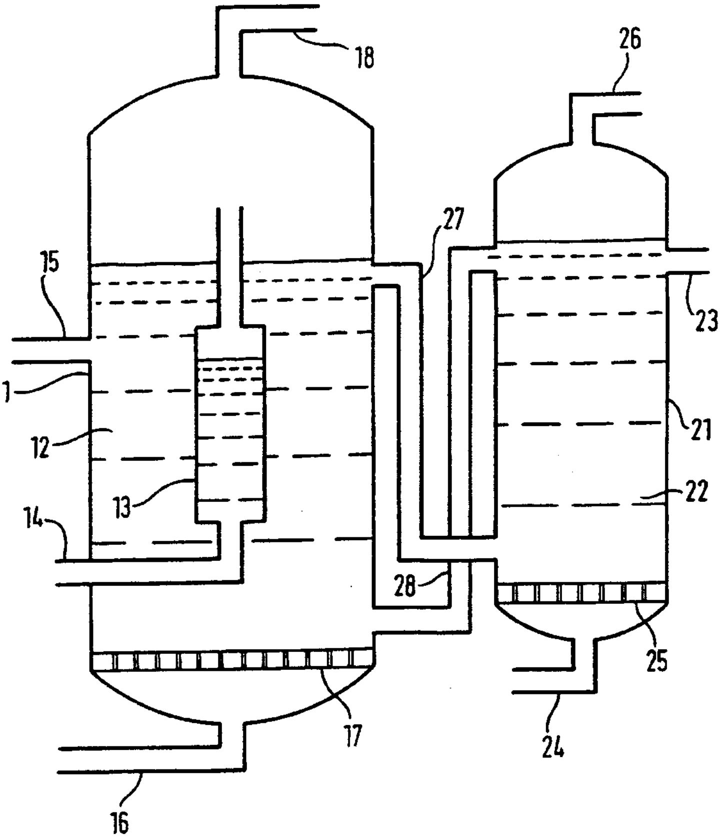

Figure XIII.13. Schematic of slurry phase reactor with external wax/catalyst separation unit that can be used for regeneration of a Fischer-Tropsch catalyst (from ref. XIII.21).

ATTACHMENT XIV

Review of Fischer-Tropsch Work by Rentech

Rentech has obtained eight patents to date [October 10, 1996] [XIV.1-XIV.8]. The drawings, background of the invention and objectives of the invention are identical [except for combining some paragraphs and minor changes in a few paragraphs such as "A further object ..." rather than "It is yet another objective..."]

The background provides a brief description of earlier work [XIV.9-XIV.14]. They indicate that today there are two primary methods for producing syngas from methane: steam reforming and partial oxidation. The primary advantage of partial oxidation over steam reforming is indicated to be that the reaction is self-sustaining and the only heat that must be added is the initial preheating of the reactants. Another advantage is that a lower ratio of H_2/CO is produced, and that it more nearly matches that needed for the FTS. In addition, the CO_2 and/or hydrogen need not be removed from the syngas prior to the synthesis.

The authors indicate that "...the Fischer-Tropsch reactor must typically be able to convert at least 90% of the incoming carbon monoxide."

They discuss the advantages of the two materials they consider to be attracting the most attention: cobalt and iron based catalysts. They indicate that, theoretically, a cobalt catalyst can produce higher conversion yields than an iron based-catalyst since the cobalt catalyst can approach 100% carbon conversion efficiency but that an iron catalyst tends toward 50% carbon conversion to hydrocarbons due to the extent of the water-gas-shift (WGS) reaction. They indicate that cobalt is much higher in cost, and this is likely to increase even further if the demand for cobalt increases to meet widespread development of Fischer-Tropsch synthesis (FTS).

It is indicated that recycle of the tail-gas is usually utilized to achieve 90% conversion of CO. Too much water is considered to be an inhibitor for FTS and the maximum attainable in single-pas operation is 70% CO conversion. On the other hand, the WGS activity of the iron catalyst permits operation at 90% conversion per pass without difficulty. It has been reported, contrary to this view, that even with an iron catalyst, the rate of CO conversion may decline rapidly at CO conversions above about 60% [XIV.15].

The present inventions are claimed to "...include a solution to the problems of reducing the formation of excess hydrogen from the reformer or partial oxidation unit and increasing the conversion efficiency for the entire carbon input to the system when using specifically prepared promoted iron catalysts." The patents demonstrate the use of recycle of the carbon dioxide produced during the FTS to the reformer in order to control the excess hydrogen and to improve the carbon conversion efficiency problems.

It is stated that olefins, alcohols and aldehydes are readsorbed on the catalyst and thereby participate in further chain growth. Naphtha and light diesel fractions are considered to be rich in olefins and to contain relatively large amounts of alcohols. Thus, the authors indicate that it is possible to force the reaction toward higher molecular weight by recycle of olefins, alcohols and aldehydes.

It is also proposed to convert the excess hydrogen as well as the carbon dioxide that is produced through the WGS reaction in a second FTS reactor.

A schematic of one of the process schemes is provided in figure 1. Indicated in this process is the recycle of carbon dioxide and/or recovered gas (streams 9 and 19).

The preferred catalyst is a precipitated iron catalyst that is promoted with a predetermined amount of potassium and copper. The amount of promoters depends upon the desired extent of chain growth and the product molecular weight distribution.

The preferred catalyst is unsupported. To accomplish catalyst preparation, iron and copper metal is dissolved in nitric acid. However, to minimize the emission of oxides of nitrogen, oxygen is bubbled through the solution while the metals are being dissolved.

The catalyst precursor was prepared by precipitation by the addition of ammonium hydroxide (ambient temperature) to the hot (up to 150°C copper/iron solution to produce a pH of 7.4. After cooling to 80°F, the pH is adjusted to 7.2. The slurry is pumped to a holding tank, the solid settles and the solution is removed; subsequent washings to remove ammonium nitrate are with "high quality water free of chloride". A drum filter, with water spray bars, is used to complete the washing and collection of the slurry. Aqueous potassium carbonate of the desired amount is added to the slurry and it is then thoroughly mixed. Drying, such as in a spray drier, is used to produce spherical catalyst in the size range of about 1 to 5 up to about 40 to 50 microns. The last step is heating to 600°F in a fluidized bed to remove residual moisture and to convert the hydrous iron oxide to hematite (Fe_2O_3).

The authors report that "Determining the "best" activating procedure for a catalyst is difficult at best..." In their study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure used carbon monoxide at 325°C at 0.1 atm. pressure. The authors indicate that it may be preferable to activate in synthesis gas, and give a recipe for doing this in a controlled manner. They heat the catalyst precursor in an inert gas to 500°F and then to 540°F in synthesis gas until the heat of reaction becomes sufficient to heat the catalyst bed at a faster rate than the applied external heat; at this point heating is terminated and cooling is effected to keep the temperature at 540°F until the CO conversion is 90%. At this point the temperature is lowered to the desired reaction temperature (450 to 525 °F) and the reactor pressure is raised from the activation pressure of 150 psig to below about 450 psig. The flow rate is adjusted to a space velocity in the range of 240 to 300 per hour.

It was reported that the activity and selectivity of the iron catalyst is improved by exposure to a hydrogen-rich synthesis gas at elevated temperature and pressure. The production of water is believed to prevent over-carburization of the catalyst, and thereby inducing the improved activity and selectivity [XIV.16].

The authors prefer a reactor design similar to that utilized by Bureau of Mines workers [XIV.17]. The gas distributor may consist of orifices or of porous metal spargers. Preferably a design using concentric rings of manifolds arranged to conform to the reactor; i.e., the largest diameter ring is at the highest and the smallest diameter at the bottom of the reactor. The reactor diameter should be selected to give a superficial velocity (actual volumetric flow rate of feed gases divided by empty reactor cross-sectional area) between about 0.02 to 0.2 meters per second. This flow should expand the bed by 30 to 45% over that of no flow conditions.

The authors prefer between 5 and 15 wt.% by weight of iron in the slurry, more preferably between 7.5 and 12.5, and most preferably 10 wt.% iron. This corresponds to 30 to 90 grams of iron per liter of expanded bed, and the most preferred is 60 g/L.

Heat removal utilizes heat exchanger tubes that commence about 1 meter above the gas distributor and extends to the top of the expanded slurry. Pressurized steam is the preferred heat transfer medium.

The preferred iron catalyst particle is between 10 and 40 microns, with 30 microns being most preferred. The preferred ratio of potassium (as carbonate) to iron is about 0.010 (0.005 and 0.015). The copper to iron ratio is preferably about 0.010.

The means of removing wax from the catalyst employed a cross flow filter. The advantage of this means is that the flow velocity of the slurry through the porous filter tubes is about 10 feet/sec and this slows down the rate of building a catalyst layer on the tube wall. When the flow has declined to a predetermined level, an inert gas is used to pressurize the shell side to remove the layer of catalyst into the slurry stream, which flows back to the reactor. They described rates for a cross-flow filter from Mott Metallurgical Corp., a filter and procedure which were found to be unsuitable for the operation at the LaPorte, Texas plant.

Catalyst can be removed from the reactor periodically by employing a slipstream.

The gaseous product stream (20, figure 1) can be used directly for process heat.

The quality of the diesel obtained from the Fischer-Tropsch synthesis are illustrated in Tables XIV.1 and XIV.2.

According to the data, the material contains 3.05 wt.% oxygen and the average carbon number is C_{14}. Assuming that the oxygen is distributed on the same basis as the hydrocarbons, then we calculate that the F/T diesel must contain about 38 wt.% alcohols in order to contain 3.05 wt.% oxygen. This value for the alcohol content appears consistent with the composition included at the bottom of Table V of U.S.

Patent 5,324,335. This would appear to be the highest content of alcohols that has been reported for Fischer-Tropsch products.

One of the catalysts utilized in the studies produces a chain-growth probability of 0.73 for carbon numbers from 1 to 9. Like Satterfield and coworkers, the patents reported that two different chain-growth probabilities were obtained.

In example 1, the authors indicate a means of calculating the carbon conversion efficiency for the overall process which is defined as the rate of production of carbon contained in the C_{5+} product in the FTS divided by the carbon atoms in the process feed. The authors state that, "Table VIII lists the product yields and carbon efficiency along with operating parameters for Example 1 and several examples discussed below." However, Table VIII does not contain a column giving efficiencies and the yield given in Table VIII is for C_{7+} rather than C_{5+} as given in the definition. It is not obvious how one can obtain the efficiencies, as defined, from the data in Table VIII. Efficiencies are given in some of the examples together with some indication of the mode of recycle; these are complied in Table XIV.3 by the reviewer.

The carbon dioxide produced in the FTS can be recovered by absorption from the FTS tail gas and can then be recycled to the gasifier, vented to the atmosphere or stored for later sale or use.

When additional diesel fuel is desired, the wax can be heated to 410^{o}C to effect thermal cracking. It was shown that the diesel from wax cracking contained only 0.16% oxygen whereas the diesel produced in the FTS contained 3.05% oxygen.

After removing the carbon dioxide, the tail gases from the FTS can be recycled to the FTS reactor to "...enable further chain growth of olefins and alcohols."

Examples 2 through 11 were ..."modeled using the conditions listed. The modeling is based on the experience with various conditions used in pilot plant studies and represents the expected results using the conditions employed."

In Example 2, the authors write that, "The large carbon dioxide content (approximately 18%) of the gases leaving the separation vessel is undesirable for the synthesis reactor feed. Therefore, the next step in synthesis gas preparation is reduction of the carbon dioxide content to less than about 5% by volume, and in the example to less than 2%."

Examples 3-10 involve various carbon dioxide and/or light gas recycle and some of these results are summarized in Table XIV.3.

In example 11 it is stated that, "...it was found that the tail gases from the Fischer-Tropsch reactor which consist chiefly of hydrogen and carbon dioxide can be converted to liquid hydrocarbons in a second Fischer-Tropsch reactor... A test was conducted in a small slurry reactor using the same iron-based catalyst that was used in the Fischer-Tropsch synthesis. The temperature, pressure and space velocity were also kept the same. The carbon dioxide conversion was 25% for a feed having hydrogen to carbon dioxide ratios of 2:1 and also 1.5:1. Conversion of the hydrogen was 42%, and 88% of the carbon monoxide produced in the water gas shift reaction was converted to hydrocarbons in the Fischer-Tropsch reaction. The chain growth (α) was the same as in the conventional Fischer-Tropsch synthesis."

Apart from the claims, references XIV.1, XIV.6 and XIV.7 are essentially identical. The patent of reference XIV.1 claims the production of an oxygen containing diesel fuel using FTS. The claims in references XIV.6 and XIV.7 cover a variety of carbon dioxide and/or light gaseous product recycle schemes that include both stream(s) and the fraction of each stream to be recycled.

Another grouping of three patents are essentially identical except for the claims [XIV.2-XIV.4]. These three patents are to show, "Several Fischer-Tropsch reaction schemes using a promoted iron catalyst in a slurry reactor produce oxygenated naphtha and diesel fractions on distillation that reduce particulate emissions in diesel engines. High carbon conversion efficiencies and optimum chain growth are characteristics of the process."

These three patents are identical to the above three patents up to the Detailed Description of the Invention and, apart from the one difference described below, this section is the same in the two sets of three patents. In references XIV.2-XIV.4 the paragraph in references XIV.1, XIV.6 and XIV.7:

> "The steam reforming reactor 5 can be of conventional design employing a commercial nickel catalyst such as obtained from Katalco and designated **23-1**. Preferably, the reactor should be operated at from about 1292°F (700°C) to about 1652°F (900°) at system pressure of about 12 psia (82.7 kPa) to about 500 pais (3447 kPa). The flow of input gases through the reactor catalyst bed should be approximately 300 lbs/hr/ft^3 catalyst."

has been replaced by examples of approaches to reduce the amount of carbon monoxide in town gas to a specified level, for example 10% by volume.

It is shown that the water gas shift reaction could be used to reduce the level of CO in the output from the gasifier; however, this approach significantly reduces the heating value of the resulting town gas. It is shown that the removal of the CO_2

produced during the WGS will increase the heat content of the town gas but, in order to have 10% CO in the product, the extent of WGS must be even greater.

The objective of these patents [XIV.2-XIV.4] is to replace the shift reactor with a FTS reactor to remove the excess CO. Thus, a portion of the gas from the gasifier is fed to the FTS reactor while about 20% of the gas bypasses the FTS reactor (Case III in ref. XIV.2-XIV.4). The composition of the blending streams and the town gas are shown in Table XIV.4.

In addition to the town gas, the FTS produces 11.8 barrels of hydrocarbon liquids having five or greater carbon atoms (based on 1.0 MMSCF feed from the gasifier).

Removing the CO_2 will permit the heating value of the town gas of Case III to be increased but this will require a greater fraction of the effluent from the gasifier passing through the FTS reactor (Table XIV.5).

In this instance 12.6 barrels of C_{5+}-hydrocarbons will be obtained.

In another scenario, a WGS reactor is included in the process that can be utilized when the FTS reactor is inoperable or, in another scenario, both the FTS and WGS reactors can be utilized in parallel.

The catalyst activation and the test results of this group of three patents [XIV.2-XIV.4] are identical to those in the first group of three patents [XIV.1,XIV.6,XIV.7]. The examples in references XIV.2-XIV.4 are essentially the same as those in references XIV.1, XIV.6 and XIV.7.

Reference XIV.2 claims a method of thermally cracking a wax produced by a FTS reaction using an iron-based catalyst in a slurry reaction at a temperature of 770^{o}F (410^{o}C) for a sufficient period of time to produce diesel and naphtha fractions.

Reference XIV.3 claims a method for preparing and activating with synthesis gas a material that is catalytically active for Fischer-Tropsch synthesis.

Reference XIV.4 claims a FTS method suitable for producing a diesel product that is cleaner than commercially available that is derived from crude oil and having a cetane number which is higher than 45 and aromatics less than 1% and the same product that contains more than 2 wt.% oxygen.

The final two patents [XIV.5,XIV.8] are essentially identical to each other and, except for a section describing the use in conjunction with power generation and the claims, are identical to references XIV.2-XIV.4. The Fischer-Tropsch processes are used in combination with electric power generation. The example considers a 300 MW off-peak power production rate (during 17 hours of the 24 hour day) in a plant with a thermal efficiency of 33%. The feed gas requirements for the peak and off-peak conditions are 14.87 and 11.15 million standard cubic feet per hour (MMSCFH), respectively. This requires a FTS reactor to handle 3.72 MMSCFH of coal gas during off-peak hours. To prevent slurry bed slumping, the FTS reactor would require an additional 0.45 MMSCFH during peak operation. During peak operation, the FTS conditions would be changed from 250 to 100 psi to maintain an adequate superficial velocity in the FTS reactor. The average production of liquid hydrocarbons would be about 2100 barrels per day.

Reference XIV.5 claims: (1) a FTS process for producing liquid hydrocarbons from a synthesis using an iron catalyst in a slurry reactor with recycle of CO_2 to the gasifier, (2) claim 1 using coal derived synthesis gas and (3) the method of claim 2 wherein the FTS is used in combination with an electric power generation system.

Reference XIV.8 has one claim for a diesel fuel additive for reducing particulate emissions by utilizing the oxygenates in the FTS product so that the diesel contains at least 2 wt.% oxygen.

The discussion in the sections of these patents provides an excellent overview of FTS using an iron catalyst and of process concepts to improve the efficiency of carbon utilization. At times it is difficult for the reader to easily discern whether the data is from modeling or produced by experiment. Rentech has operated a 6-inch 8-foot tall slurry reactor both with and without CO_2 removal in advance of the FTS reactor [XIV.8]. In 1992 it was reported that the longest run was for a two-week period but it is understood that subsequent runs have been made for periods of 60 days or more; however, data for these longer runs do not appear to be available in the public domain.

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XIV.18. C. B. Benham, "A decade of research and development in Fischer-Tropsch applications, Pittsburgh Coal Conf, October 15, 1992.

Table XIV.1

	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel
Cetane Index ASTM 976-80	45 min.	40 min.	62
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*
Temperature ^oF ASTM D56 Viscosity @ 40^oC	550^oF-max.	540^oF-min. 640^oF0Max.	556^oF
cSt.	1.4 min.	1.9 min.	1.8
ASTM D445-82	2.5 max.	4.1 max.	
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02
Flash Point ^oF, min. Corrected to 760 mm Hg ASTM D56-82	100^oF	125^oF	122^oF
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%
API Gravity ASTM D1298	38-41	34.7	48.7
BTU/lb ASTM D240	16,000-17,000	19,810	19,371
Oxygen Content, Wt.%	N/A	N/A	3.05%

* Analyses were below limits of detection.
(1) ASTM D975-81, #1 Diesel
(2) ASTM D975-81, #2 Diesel

Table XIV.2

Test	Method		Results
Flash Point, ^oF	ASTM D56		122
API Gravity @ 60^oF	ASTM D1298		48.7
Sulfur Content, Wt.%	Horiba Analyzer		<0.0001
Kinematic Viscosity @ 40^oC, cSt.	ASTM D445-82		1.80
Distillation Range	ASTM D86	IBP	314
		90%	566
		FBP	627
Conradson Carbon on 10% Residuum, Wt.%	ASTM D189-80		0.02
Saturates, Wt.%	NMR/90 MHz		30
Alpha-Olefins			45
Internal Olefins			9
Alcohols and Others			16
Oxygen Content, Wt.%	Elemental Analysis		3.05
Average Carbon Chain Length	GC/FID		C_{14}
Cetane Index	ASTM D976		62
Heat of Combustion, BTU/lb	ASTM D240		19,371

Table XIV.3

Efficiencies Taken from Description of Examples
Feed 1,000,000 Std. Cubic Feet/Day

Example	Efficiency	C_{5+} bbl/day	CO_2 Recycle
1	58.1	80.7	
2	50		Yes, reactor and reformer
3	36.8	51.8	No
4	43.6	61.3	Yes, from reformer inlet
5	60.5%	85.2	Yes, reformer and 1/2 FT tail gas
6	71.3%	94.6	Yes, ~ all CO_2 and 1/2 FT tail gas hydrocarbons
7	43.7[a]	60.0	

a. Same as example 5 except $\alpha = 0.7$.

Table XIV.4
Stream Compositions for Case III

Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.15
CO	26.9	3.69	10.00
CO_2	2.0	17.88	13.56
CH_4	14.1	19.75	18.21
C_2H_6	1.3	2.05	1.84
C_2H_8	0.0	0.19	0.14
C_4H_{10}	0.0	0.12	0.09
LHV (B/ft.3)	388.3	387.1	387.4
Volume (MMSCF)	1.0	0.572	0.786

Table XIV.5
Stream Compositions for Case IV

Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Mixed Gas (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.17	65.34
CO	26.9	3.69	8.59	10.00
CO_2	2.0	17.88	14.52	0.60
CH_4	14.1	19.75	18.57	21.57
C_2H_6	1.3	2.05	1.89	2.20
C_2H_8	0.0	0.19	0.16	0.18
C_4H_{10}	0.0	0.12	0.10	0.11
LHV (B/ft.3)	388.3	387.1	387.7	450.9
Volume (MMSCF)	1.0	0.572	0.773	0.664

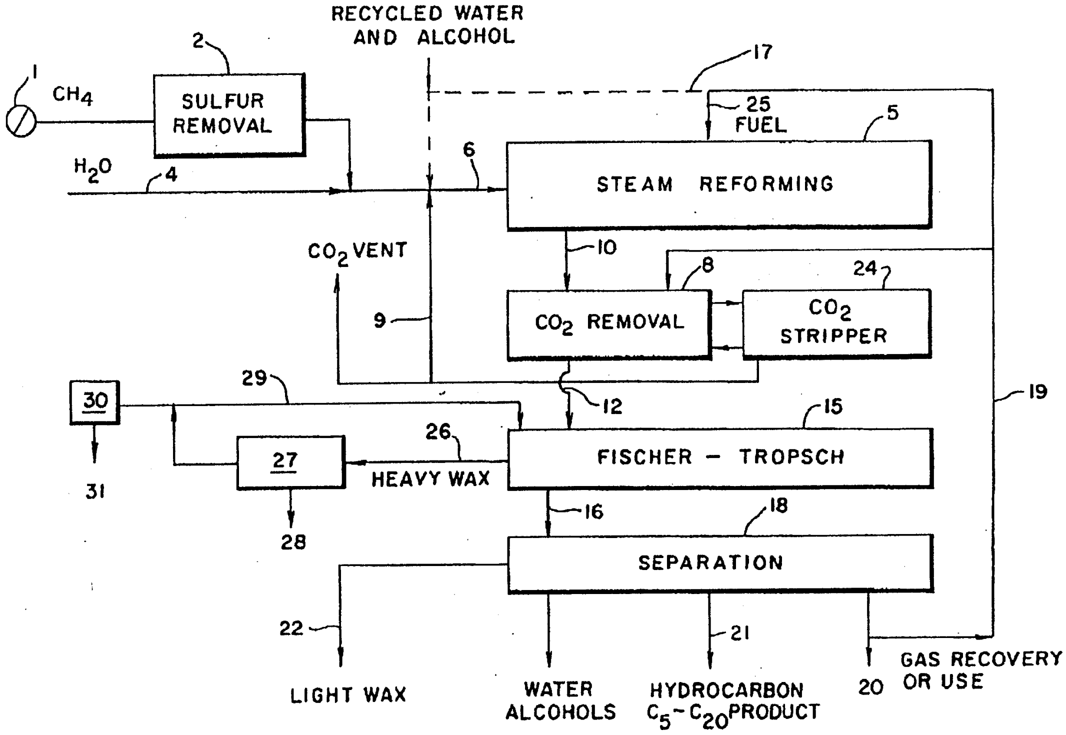

Figure XIV.1. Recycled water and alcohol.