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Assessment of Advanced Process Concepts for Liquefaction of Low H_2:CO Ratio Synthesis Gas Based on the Kölbel Slurry Reactor and the Mobil-Gasoline Process

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PREFACE

This assessment study was requested by the Fossil Energy Division of Planning and Systems Analysis, DOE Headquarters. However, the author assumes responsibility for the opinions expressed and for any inaccuracies contained in the report.

The author wishes to acknowledge helpful discussions with Drs. H. Heinemann and R. Hildebrand during the course of the study.

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SUMMARY AND RECOMMENDATIONS

The "Kölbel reactor" is a three-phase Fischer-Tropsch reactor in which synthesis gas is passed upward through a slurry of finely divided catalyst in a heavy oil medium and products are removed overhead. Kölbel claimed that this reactor configuration allowed the processing of synthesis gas with low H_2:CO ratios at high single-pass conversion with excellent temperature control and without the rapid aging because of carbon deposition normally encountered with such feeds in other reactor types. These reactor characteristics might thus allow conversion of the low H_2:CO ratio output from second-generation coal gasifiers directly without preliminary water-gas shifting and without extensive recycle. Such operation should result in improved thermal efficiency and decreased processing costs. However, the product distribution reported was relatively conventional for Fischer-Tropsch performance so that the need for octane improvement for gasoline production would still exist.

The Mobil-Gasoline process converts methanol to high-octane gasoline in high efficiency. There are recent indications that the shape-selective zeolite catalyst used might also accept crude Fischer-Tropsch products as a feed instead of methanol. Conceptual combination of all these observations leads to an advanced indirect liquefaction scheme for coal consisting of a second-generation gasifier coupled to a slurry Fischer-Tropsch reactor coupled to a Mobil-Gasoline upgrading unit.

In a pilot-plant study in the early 1950's, Kölbel achieved 90% single-pass conversion of an H_2:CO = 0.67 feed with a precipitated, low alkali-content, Fe-based catalyst. The space-time yield was however

relatively low, even for Fischer-Tropsch experience. The average molecular weight of the product could be varied widely, presumably by manipulation of temperature and catalyst composition. Catalyst lifetime was claimed to be much greater than for corresponding operation in a conventional gas-solid reactor. The quantitative claim was for a useful catalyst life of ∿40 days with the ability to regenerate completely by oxidative treatment. Whether such a lifetime for this relatively cheap catalyst is practically viable would require a process economics study. Unfortunately, Kölbel did not provide detailed data on aging rate and the claims of complete regenerability were not illustrated with data.

A British group attempted to confirm Kölbel's experience but observed lower conversions and much more rapid aging with associated buildup of particulate carbon in the reactor. The conditions used were not dramatically different (Table I). Therefore, if Kölbel's report is taken as correct, we must conclude that catalyst aging and carbon deposition are subtle functions of conditions, especially of catalyst composition, in a fashion not yet completely understood. The requirement for an active catalyst which does not produce a heavy product may be crucial. Japanese workers also describe results from a reactor similar to Kölbel's but not enough time on stream was accumulated to make a judgment concerning catalyst lifetime. Workers at the Bureau of Mines also worked extensively with slurry reactors, generally with H_2:CO = 1 feeds, and observed more serious aging than did Kölbel. In light of these superficially conflicting reports, it would appear that additional experimental data with slurry reactors will be required for a rigorous understanding of the effects of catalyst composition and reactor parameters on aging rates. Any future studies should also consider in detail the fluid dynamic properties of such three-phase reactors.

The Mobil-Gasoline process requires temperatures some 100°C higher than typically used in the Fischer-Tropsch slurry reactor studies. Zeolite catalyst aging occurs over a time period similar to that of Kölbel's Fischer-Tropsch experience with Fe; oxidative regeneration of this inherently more expensive catalyst is quite effective. From studies with individual alternate feeds and from growing knowledge of the reaction mechanism, it appears that the Mobil catalyst should also convert light olefins and alcohols to gasoline. Under forcing enough conditions it may also upgrade paraffins and C_{11}+ materials, but more specific data in this regard would be useful.

The first hybrid process concept would use the output from a slurry Fischer-Tropsch reactor as the feed for the Mobil-Gasoline process, each reactor operating in its optimum mode. Such a two-step scheme has the advantages that each process could operate at different, individually optimized conditions and that the catalysts could be regenerated individually. These would need to be balanced against the disadvantages of a more complex process scheme. Such integration would require finding the optimum compromise between the product variability inherent in the Fischer-Tropsch process and the feed requirements of the zeolite-catalyzed process. As an initial estimate, it appears that the Fischer-Tropsch process should be operated under conditions to give the lightest, most olefin- and oxygenate-rich product possible, consistent with maintaining acceptable aging rates and minimal production of methane.

In this context, any future catalyst screening studies in the slurry reactor should consider catalyst variants which are now known to promote light olefin formation (e.g., Fe-Mn combinations) or oxygenate formation (e.g., nitrided Fe). These modified catalysts also show some evidence for inherently lower coking tendencies. Any such catalysts must however retain high shift activity so that the H_2:CO usage ratio remains comparable to the feed ratio. Detailed aging studies should distinguish between loss of conversion because of actual catalyst fouling or because of mass transport limitations which arise from increased viscosity of the oil medium when carbon particles form.

A second hybrid process concept would place both catalyst functions in a single slurry reactor. This is a challenging problem in catalyst design because synergistic interactions between the catalyst functions are in principle possible. Workers at Mobil have made recent progress in this direction with H_2:CO = 1:1 feeds in conventional reactors; again catalyst lifetime is a difficulty. Whether a slurry reactor would hold advantages for these dual-function catalysts applied to low H_2:CO ratio feeds remains to be seen. A slurry reactor has the inherent disadvantage that in situ regeneration appears very unlikely because of limits imposed by the thermal and oxidative stability of the oil medium. Even external regeneration offers a special challenge in this case because optimum regeneration conditions and schedules for the two catalyst entities will seldom coincide.

I. INTRODUCTION AND STATEMENT OF OBJECTIVE

Proposed processes for conversion of coal to liquid transportation fuels can be classified as either direct or indirect. In direct processes, the complex coal structural network is partially broken down and hydrogenated to the level required for the desired fuel application. In indirect processes, the coal structure is totally destroyed by gasification to a mixture of CO and H_2 (synthesis gas) followed by catalytic conversion to form liquid fuel products by condensation-hydrogenation of CO. In the classic Fischer-Tropsch synthesis, hydrogenation of CO over Fe- or Co-based catalysts produces a mixture of paraffins and olefins with a broad molecular weight distribution. A typical Fischer-Tropsch gasoline boiling-range product mixture requires extensive upgrading (octane improvement) because of its largely linear structure and low aromatic content. Recently, a second approach to indirect liquefaction has been provided by the two-step Mobil-Gasoline process. Synthesis gas is first converted to methanol in high selectivity by commercially well-established technology followed by conversion of methanol to high-octane gasoline by shape-selective zeolitic catalysts. Because the hydrocarbon mixture produced from methanol has a significant content of branched and aromatic components, further upgrading is unnecessary. Also, the overall selectivity to gasoline-range product is substantially greater than for traditional Fischer-Tropsch processes.

All approaches to indirect liquefaction of coal involve in principle three reactions: gasification to produce a raw gas whose composition (H_2:CO ratio and methane content) depends on the gasifier design and operating conditions; gas cleanup and water gas shift reaction to adjust the H_2:CO ratio to that required for the synthesis step; and the synthesis process itself. A major challenge in process conception and design is to couple these stages in the most economic, thermally efficient manner. Any one of the reactions may be forced to operate away from its inherently optimum conditions for the sake of integrated process efficiency. The concept being evaluated herein results from considerations forced upon the overall system by the H_2:CO ratio.

Recent economic calculations by Shinnar and Kuo[1] demonstrate that production of the lowest cost synthesis gas with the highest thermal efficiency would be achieved by second generation gasifiers (e.g., Slagging Lurgi, Texaco, Koppers-Totzek, Winkler) which use the minimum amounts of oxygen and steam feed. However, in contrast with the more established gasifiers, the gas so produced has a very low H_2:CO ratio in the range 0.6-0.7. Because of the dominant contribution of gasification to the total cost of indirect liquefaction, the ideal synthesis reaction would accept such feed ratios directly. Unfortunately, neither traditional Fischer-Tropsch processes nor methanol-forming processes will accept such a low feed ratio. In either case, the water gas shift reaction would first have to be applied to increase the proportion of H_2 present to $H_2:CO \gtrsim 2$ and reject some carbon as carbon dioxide. However, this leads to a loss in thermal efficiency and process simplicity as illustrated in the following paragraph.[2]

Consider a gasifier effluent with $H_2:CO = 0.5$. In principle, if a catalyst possessed both Fischer-Tropsch and water gas shift activity, this mixture could be converted directly to hydrocarbons with rejection of excess carbon as carbon dioxide:

$$2\,CO + H_2 \longrightarrow \frac{1}{n}(CH_2)_n + CO_2 \qquad (1)$$

If in reality water gas shift to $H_2:CO = 2$ is required before synthesis, however, two process steps are needed, each consuming one-half of the CO present:

$$CO + H_2O \longrightarrow H_2 + CO_2 \qquad (2)$$

$$CO + H_2\,(\text{initial}) + H_2\,(\text{from shift}) \longrightarrow$$

$$\frac{1}{n} \left(CH_2\right)_n + H_2O \qquad (3)$$

$$\overline{2\,CO + H_2 + H_2O \longrightarrow \frac{1}{n} \left(CH_2\right)_n + CO_2 + H_2O}$$

The overall stoichiometric result in both cases must of course be identical, but, in the two-step case, thermal efficiency will be decreased by the requirement to produce steam for the water gas shift and to recover (incompletely) its energy content after synthesis. Also, the two-step case is more complex and expensive because of the requirement for a separate water gas shift process step. In this context, a synthesis process which could accept low H_2:CO ratio feeds directly is desirable.[2,3]

The traditional Co-based Fischer-Tropsch catalysts have little inherent shift activity, water being the predominant synthesis coproduct (eqn. 3). In contrast, the more popular Fe-based catalysts do possess shift activity and, in principle, could perform according to the stoichiometry of eqn. 1. In fact however, Fe-based catalysts allow for still a third overall stoichiometry, the Boudouard reaction, eqn. (4). This conversion competes more and more successfully with Fischer-Tropsch synthesis

$$2\,CO \longrightarrow CO_2 + C \qquad (4)$$

as the H_2:CO ratio decreases and the temperature increases. The result is rapid catalyst aging because of fouling by the carbon produced. Thus H_2:CO ratios < 1 are generally considered incompatible with long-term Fischer-Tropsch operation in either fixed-bed or fluidized-bed configurations.

This chain of reasoning leads to consideration of the "Kölbel reactor" and slurry reactors in general. In the Kölbel reactor,[4,5] feed gas is bubbled upward through a suspension of finely divided Fischer-Tropsch catalyst in a relatively nonvolatile liquid carrier. Presumably because of the superior heat transfer properties of such a well-mixed, liquid-filled reactor, it was observed that the highly exothermic Fischer-Tropsch reaction could be carried at very high single-pass conversions without developing temperature gradients in the reactor. A second unique feature, compared with fixed- or fluidized-bed gas-solid reactors, was the purported ability to process feed ratios as low as H_2:CO = 0.6 without rapid catalyst fouling. If these claims to be able to process CO-rich synthesis gas without recycle prove correct, the potential compatibility of such slurry reactors with second-generation gasifiers becomes obvious.[2] Hence the first objective of this report in Sect. II is to review and assess the experience of Prof. Kölbel (Sect. II.A) and of other research groups (Sects. II.C—II.E) with slurry reactors.

The product distributions claimed for the Kölbel reactor are not markedly different from those for normal Fischer-Tropsch operation in fixed or fluidized beds. Hence the effluent from a "successful" second generator gasifier—slurry Fischer-Tropsch reactor combination would still require upgrading for gasoline use. Since there are now indications that the Mobil-Gasoline process may accept a much wider range of feeds than simply methanol, possibly including Fischer-Tropsch products, certain aspects of this process will be reviewed in Sect. III with stress on the basic chemistry which will have impact on the potential for coupled processes (Sect. V). In particular we will focus on its feed flexibility (Sect. III.B) since this may influence the operating conditions chosen for an upstream slurry Fischer-Tropsch reactor. In other words, the catalyst composition and operating parameters chosen for a slurry reactor may well differ if its output were tailored for further processing to gasoline over shape-selective zeolite catalysts than if it were to be used as a fuel or feedstock directly. Recent Fischer-Tropsch catalyst modifications and their use in a slurry reactor aimed at maximizing production of petrochemical olefin feedstocks (Sect. II.B) are of special interest in this regard.

For historical completeness, Sect. IV contains a short discussion of the "Kölbel-Engelhart reaction" in which the synthesis feed consists of CO and steam. However, it seems to have no direct impact on the subject at hand.

Finally, in Sect. V, potential hybrid processes coupling both technologies (slurry Fischer-Tropsch and Mobil-Gasoline) will be considered. Such coupling might occur either in a two-step sequential mode, each process operating at its optimum conditions (Sect. V.A), or in a more integrated one-step mode (Sect. V.B) in which the Fischer-Tropsch catalytic function and the upgrading (zeolitic) catalytic function are present in a single slurry reactor either by use of physical mixtures of catalysts or truly "hybrid" catalysts. Success in the one-step mode demands that a compatible set of operating conditions for the two catalytic functions be found (Sects. II and III.A) and that the possibilities for synergistic interactions between the catalytic functions be appreciated.

This report does not contain an exhaustive literature survey of the areas covered. Rather we hope to review key references, to point out apparent conflicts and questions requiring further research and development for clarification, and to provide some judgmental assessments of the overall area as we proceed through it. Recent reviews by Kölbel and Ralek[5] contain extensive compilations of references relating to slurry reactor performance.

II. SLURRY FISCHER-TROPSCH REACTORS

As a benchmark for comparison of the claimed performance of several slurry Fischer-Tropsch reactors, we will review briefly the operating parameters of the commercial Fischer-Tropsch reactors operated by Sasol.[4] The "ARGE" fixed-bed, multi-tube unit is operated at 220-250°C, 23-25 atm, a fresh feed composition of H_2:CO = 1.3-2.0, a fresh feed GHSV = 500-700 hr^{-1}, and a recycle ratio of 2.5. Under these conditions, a (CO + H_2) conversion of 70% is achieved with a catalyst lifetime of 9-12 months for the (Fe : Cu : K_2O : SiO_2 = 100 : 5 : 5 : 25) standard precipitated catalyst. The space-time yield of C_2+ products is 50-70 tons/day/40 m^3 catalyst or 47-68 g/ℓ/hr. A typical product distribution for the different boiling ranges of the hydrocarbon portion is C_{3-4} : C_{5-10}: 180-320°C : 320-460°C : > 460°C = 11 : 26 : 22 : 19 : 19 with 4.5% C_1-C_4 alcohols; the olefin content of the < 290°C product is 50-60%. The average molecular weight of the products can be decreased by decreasing the K_2O and SiO_2 levels in the catalyst.

The "Synthol" entrained fluidized-bed reactor is operated at higher temperature (∿350°C) and requires a correspondingly even higher H_2:CO ratio to prevent carbon formation. The space-time yield appears to be ∿90 g/ℓ/hr at 80% (CO + H_2) conversion and a recycle ratio of 2. Overall lifetime of the finely divided, fused catalyst is less than for fixed-bed operation, a typical operating period being 5-6 weeks. The total product is lighter, a typical distribution being C_1 : C_{2-4} : "light oil": "decanted oil" = 10 : 33 : 43 : 7, and each fraction is typically more olefinic. This performance characterizes commercially proven Fischer-Tropsch technology.

A. The Kölbel-Rheinpreussen-Koppers Experience. The early laboratory work by Prof. Kölbel on slurry reactors began in the late 1930's and culminated in the early 1950's in a 11.5 ton/day pilot plant operated under a cooperative agreement among Kölbel at the Technische Universität, Berlin-Charlottenburg, Rheinpreussen A. G. für Bergbau und Chemie, Hamburg, and Heinrich Koppers G.m.b.H., Essen.[5-8] The pilot plant represented a successful scale-up from the laboratory reactor by a factor of 1667-fold in volume. It is the largest slurry Fischer-Tropsch unit ever operated and thus should be the most reliable source of information.

Finely powdered catalyst of average particle size < 30 μm was dispersed in a high-boiling paraffin wax, itself a heavy Fischer-Tropsch product. Pressurized, preheated synthesis gas feed was passed upward through the cylindrical reactor as small bubbles at a velocity sufficient to maintain good catalyst dispersion and mixing in the three-phase system. Reaction heat was removed by internal cooling coils which produced steam at 30 atm. Products were removed overhead in the vapor phase and condensed downstream. Liquid level was maintained by a level-sensing float. If synthesis conditions were such that the liquid dispersion medium was gradually lost by vaporization, some of the heaviest product condensate was returned to the reactor. If, on the other hand, excess liquid medium was produced during reaction, it was recovered as a liquid after removal of catalyst by filtration of a slip-stream. Auxiliary equipment was available for preparation of the initial catalyst slurry and for separation of spent catalyst from the slurry by centrifugation. Hence continuous operation with gradual replenishment of spent catalyst was anticipated.

The pilot plant useful reactor volume was 10 m^3, the overall dimensions being 155 cm ID x 8.6 m high. At the feed throughputs employed, the total internal cooling surface required to maintain nearly isothermal operation (±1°C gradient) was < 115 m^2.

The Fe-based catalyst[5] was of the unsupported precipitation type which is relatively inexpensive and could be easily prepared at the plant site. It was prepared by rapid precipitation from nitrate solutions by ammonium hydroxide. Copper promoter (as nitrate) was added before precipitation and potassium promoter (as carbonate) was added to the filter cake. The final precipitate was dried, ground, charged to the reactor in the oxide form, and then activated in situ by reduction at 15-30°C above reaction temperature. The catalyst concentration in the slurry was 88 g/ℓ. A typical composition was Fe : Cu : K_2O = 100 : 0.1 : 0.05-0.5, this being an unusually low alkali level (see Sect. II.C). Catalysts for slurry operation were claimed not to have stringent requirements for mechanical attrition resistance. However, data on long-term catalyst particle size diminution are not available. The key physical property was stated to be good dispersability. The final particle size (a few μm) resulted from grinding the oxide followed by some further particle disintegration resulting from internal carbon deposition during activation and reaction.

The superficial upward gas velocity was ∿10 cm/sec. At this velocity, a bubble size of a few mm was achieved without elaborate gas dispersion devices. The key item in successful scaleup from the laboratory (6 ℓ reactor) to pilot plant-scale (10,000 ℓ reactor) was said to be maintenance of constant gas bubble residence time. Kölbel stressed that the low viscosity and surface tension of the paraffinic dispersing liquid used were crucial for maintaining small bubble size and hence good gas-liquid mass transfer characteristics. The need to maintain low viscosities was said to establish upper limits on the total solids content of the reactor. Under this set of flow conditions, the reactor was claimed to be reaction rate-limited with no mass transport limitations.

The most extensive operating data were reported for 268°C, 12 atm, and a feed ratio of H_2:CO = 0.67. At a GHSV of 270 hr^{-1}, 91% CO conversion was achieved in a single pass without recycle. Since the (CO + H_2) conversion was 89%, the actual usage ratio was very close to the feed ratio. Note that such behavior is a requirement for high-conversion, non-recycle operation to be chemically efficient. The space-time yield of C_3+ products was 39 g/ℓ reactor/hr (2.4 lbs/ft^3/hr) or 0.44 g/g contained Fe/hr. Increasing the temperature from 268°C to 280°C increased the productivity to 125 g/ℓ/hr. Compared with typical Fischer-Tropsch experience in other reactor types, these space-time yields are somewhat low. In fact, they are probably about what would be expected for operation at such low GHSV and high conversion levels. Indeed Kölbel consistently states that the catalytic performance per se in the slurry reactor is the same as predicted from parallel gas-phase operation. Incidentally, 91% conversion is indeed "high" but not "complete." Dependent on the fuel gas requirements of the plant, a small amount of recycle or staging might still be necessary. These operating parameters are summarized in Table I for comparison with other workers in Sects. II.C—II.E.

The key feature of this "Kölbel reactor" in the present context is the claim that "the catalyst will...process CO-rich gas without any disturbing carbon deposition." The actual pilot-plant data describe the production of 400 g C_3+ product/g Fe during its total life. Hence the actual lifetime can be calculated to have been $400 \frac{(\text{g product})}{(\text{g Fe})} \times \left(\frac{1}{(0.44 \text{ g product/g Fe/hr})}\right) = 38$ days. It is not clearly stated to what fraction of its initial activity the catalyst had decayed after that period, nor is it stated whether any formation of carbon particles occurred in the reactor. Catalyst lifetime associated with the 3-fold enhanced productivity at 280°C was not reported. Full restoration of activity by oxidative regeneration was said to be effective, and, in fact, the regenerated catalyst was said to have less tendency to form both carbon and methane than the fresh catalyst.[5] However, no explicit data are given to illustrate these claims. In summary, the data presented indeed show a substantial catalyst lifetime for such a low H_2:CO ratio feed; however, it would be reassuring to see detailed data on actual aging rates, regenerability, and the criteria used to define catalyst "lifetime."

TABLE I

Performance Data for Slurry Fischer-Tropsch Reactors

	Kölbel (averaged) Sect. II.A	British (initial) Sect. II.C	Japanese (99 hr) Sect. II.D	Bureau of Mines (21st day) Sect. II.E
Reactor dimensions (cm ID × m high)	155 × 8.6	25 × 8.5	5 × 6	7.6 × 3.05
Height/diameter ratio	5.6	34	120	40
Reactor volume (ℓ)	10,000	300	11.8	14
Catalyst concentration (g/ℓ)	88	37	26	300
Catalyst composition: Fe	100	100	100	100
Cu	0.1	1.25	0.3	10
K_2O	0.05-0.5	1.4	0.6-1.2	1
Superficial gas velocity (cm/sec)	9.5	7	3.8	2.75
Temperature (°C)	268	260	273	255
Pressure (atm)	12	10.5	11	10-14
H_2:CO feed ratio	0.67	"low"	0.53	1.00
GHSV (hr^{-1})	270	197		240
Conversion (%)	91 (CO)	63 (CO)	78.5 (CO)	73 (CO)
	89 (CO + H_2)	59 (CO + H_2)		45 (H_2)
Productivity (g C_3 + product/ ℓ reactor/hr)	39	$\sim$23	$\sim$17	$\sim$30
Productivity (g C_{3}+ product/ g Fe/hr)	0.44	$\sim$0.62	$\sim$0.65	$\sim$0.1

Two-stage operation with inter-stage scrubbing of CO_2 product was also demonstrated. With a first-stage conversion of ∿60%, a total conversion of 96-97% was reported with a 50% increase in catalyst productivity and a 2-fold increase in catalyst lifetime compared with single-stage operation.

The product distribution for the conditions just outlined (Table I) was C_{1-2} : C_{3-4} : gasoline (25-190°C) : diesel oil (190-310°C) : heavies (>310°C) = 7 : 17: 62 : 10 : 3. The olefin contents of the C_{3-4} gas, gasoline, and diesel oil fractions were 72, 74, and 45%, respectively. Hence the molecular weight distribution does not appear particularly unusual for Fe-based catalysts, the slurry reactor product being somewhat lighter than the lower-temperature ARGE product and heavier than the higher-temperature Synthol product. In general, H_2-poor feeds lead to decreased methanation, increased average molecular weight, and increased olefin content in the product.[9,10] In Table II are listed product distributions from slurry runs aimed at production of "medium" and "high" average carbon numbers rather than the "low" case just discussed. It appears[4,5] that most of these changes were achieved by changes in catalyst composition and operating temperature. Higher temperatures and lower alkali (K_2O) contents generally limit chain growth.[9]

For coupling with the Mobil-Gasoline process, conditions giving the lowest average carbon number product appear the most promising (Sect. III.B). In this regard, Kölbel[5] has described several other process modifications deduced from laboratory reactor results to promote selectivity to light, olefin-rich products. These include: (1) use of a regenerated catalyst at higher temperatures (274-278°C); (2) recycling the heavy products to the reactor; and (3) establishing a vertical temperature gradient within the reactor by placing the cooling surfaces in decreasing abundance from bottom to top.

B. The Kölbel-Ruhrchemie-Schering Experience. Kölbel's work in the 1950's was aimed at fuels production. The recent resurrection of interest in Germany has emphasized a new type of catalyst aimed at maximizing selectivity for C_2-C_4 olefins as petrochemical feedstocks.[5,11,12] Cooperative efforts with Ruhrchemie AG, Oberhausen-Holten and Schering AG have

Variations in Product Composition from the Kölbel Reactor

Molecular Weight Goal	"Low"[b]	"Medium"[c]	"High"[c]
Single-pass C_{3+} product yield (g/m^3 feed)[a]	166[d]	175	182
Distribution of C_{3+} products (%)			
C_{3-4}	18	7	2
Gasoline (C_5-190°C)	68	40	7
Diesel fuel (190-310°C)	11	26	8
310-450°C	2.5	18	33
>450°C	0.5	9	50

[a] Theoretical yield of <u>all</u> organic products is 208 g/m^3 if the usage ratio equals the feed ratio. [b] Further data in Table I and text. [c] Associated reaction parameters, productivity, and catalyst life data not given.

[d] 12 g/m^3 $C_1 + C_2$.

progressed to the point where a pilot unit for 10,000 m^3 feed gas/hr is planned for the early 1980's. Although feedstock production per se is not within the scope of this study, these efforts bear careful watching for at least three reasons. First, they will provide further operating experience with slurry reactors and low H_2:CO feeds. Secondly, it may be that the much lighter, more olefinic product would be a superior feed for gasoline production by zeolite catalysts (Sect. III.B) than a traditional Fischer-Tropsch product. Thirdly, there are hints that the modified catalysts have less tendency for carbon formation. Hence we will briefly review recent reports in this area.

Particular emphasis has been placed on catalysts prepared by coprecipitation of Mn and Fe oxides (8-10:1) followed by reduction by CO and then by H_2 in situ. [The active phase(s) present remain a subject of debate.] At 290°C, 12 atm, a feed ratio of H_2:CO = 0.79, and GHSV = 353 hr^{-1}, a conversion of 84.5% was achieved in a fixed-bed reactor with a productivity of 59 g/ℓ/hr. The product contained a ratio of CH_4 : C_{2-4} olefins : C_{2-4} paraffins : C_5+ plus oxygenated products = 12 : 40 : 10 : 38. Even without slurry operation, a laboratory lifetime of 83 days was reported for these Mn-rich catalysts without "obvious loss in synthesis activity." Thus this catalyst may be inherently less susceptible to carbon deposition at low H_2:CO feed ratios than traditional Fe catalysts.

The Mn-Fe catalyst was then evaluated as 40 μm particles (10% suspension) in a 2-m-high slurry reactor. At 299°C, 11 atm, a feed ratio of H_2:CO = 0.87, and GHSV = 2390 hr^{-1}, the conversion was only 53% [but note the unusually high GHSV]; the average carbon number increased and the olefinic content decreased compared with fixed-bed operation. A broader residence time distribution for the reactants was suggested as a contributor towards the higher average molecular weight in the slurry reactor. No lifetime data were given; thus potential advantages of the slurry reactor for this modified catalyst remain to be defined.

Several other groups[13] are actively searching for light olefin-specific catalysts. A complete survey is outside the scope of this study, and only Kölbel's work has been described here because of its relation to slurry reactors. However, for the reasons outlined above, this topic deserves the attention of future workers in the subject area of this study.

C. The British Experience. Hall, Gall, and Smith[14] at the British Fuel Research Station carried out a detailed comparative study of Fischer-Tropsch performance of a commercial, fused, ammonia-synthesis catalyst (3.4% MgO, 0.7% K_2O) in fixed-bed, fluidized-bed, and slurry (5 cm ID x 1.2 m high) reactors under identical temperature, pressure, and feed composition conditions. This could only be achieved with H_2-rich feeds and gas recycle so that the actual slurry reactor environment had H_2:CO = 3-4. Therefore the results are not directly applicable to the regime of this study and will not be reviewed in detail. Nevertheless, they should provide useful background information for any future slurry reactor studies. For operation at comparable conditions in the three reactor types, Hall's general conclusions included the following: (1) reaction rates in the slurry reactor are inherently lower (in contrast to Kölbel's opinion); (2) methanation is less of an interference in the slurry reactor because of good temperature control; and (3) the rate of carbon formation is a function of reaction parameters, particularly temperature and hydrogen partial pressure, but not of reactor configuration per se.

A larger slurry reactor was then constructed at the Warren Spring Laboratory and operated specifically with low H_2:CO ratio feeds,[15] but with less heartening results than obtained by Kölbel. This reactor was much smaller than Kölbel's with a larger height:diameter ratio, ∿0.3 m^3 volume, 25 cm ID x 8.5 m high (see Table I for comparison). Again the use of internal cooling coils allowed a temperature gradient of only ± 1°C to be maintained. The initial product composition (at 8°C lower temperature than Kölbel) was much heavier, and hence much more of the product failed to vaporize from the reactor. Thus much more elaborate auxiliary equipment became necessary to draw off continuously a liquid slip-stream from the reactor and recover the catalyst in a specially designed, multiple-stage, gravity-settling apparatus. Overall operation thus appears to have been more complex than in Kölbel's case. In the context of the present study, it would appear that minimization of production of materials nonvolatile at reaction conditions should be a goal of any future work so as to minimize catalyst handling.

The catalyst used was a precipitated Fe oxide with Fe : Cu : K_2O = 80 : 1 : 1.1 again activated in situ. The concentration of both additives was greater than used by Kölbel. After break-in, the average particle size was 1-3 μm. The catalyst concentration can be deduced to have been 37 g/ℓ, less than one-half that used by Kölbel. Catalyst composition was followed with time as activity declined (see below); the relative proportion of Fe_3O_4 increased and that of Fe_2C decreased. Such slow changes in phase composition of Fe-based Fischer-Tropsch catalysts are of course commonly observed.[9] However, since we still do not know with certainty the catalytic roles of the Fe, Fe_3O_4, and Fe_xC phases, it may be important in the future to know whether use of low H_2:CO feeds leads to a different equilibrium phase distribution and resulting catalytic performance than for traditional operation with more reducing feeds.

A difficulty in interpreting the British work is that the exact H_2:CO ratio is not stated although, from the motivation of the work,[3] it must have been "low." Nevertheless, to achieve high conversions, these workers found that the superficial gas velocity could not exceed 3 cm/sec, 3-fold lower than in Kölbel's study. This lower activity may have resulted from their using a lower starting temperature (260°C vs. 268°C), using less catalyst, and/or having an inherently less active catalyst. Whatever the cause, this low gas velocity did not achieve full expansion of the slurry. Therefore all later studies were conducted at ∿7 cm/sec at the sacrifice of conversion which decreased to ∿60% with a H_2:CO usage ratio of ∿0.55. At 260°C, 10.5 atm, GHSV = 197 hr^{-1}, and 63% CO conversion, the initial productivity of C_3+ products was ∿0.62 g/g Fe/hr or ∿23 g/ℓ reactor/hr, slightly larger than Kölbel's normalized to Fe content but smaller normalized to reactor volume.

The key feature of the British work which contrasts with the German studies was observation of gradual catalyst decay. Temperature was therefore gradually increased from 260°C to 280°C to attempt to maintain constant conversion. However after 18 days, conversion had decreased to 37% even at 280°C; the slurry had suffered a large increase in viscosity and was near "gelling" because of accumulation of finely divided carbon. Measurements of the slurry density allowed calculation of the volume fraction of gas phase in the reactor. The increased viscosity markedly increased bubble coallescence, decreased the gaseous volume fraction, and was thus felt to have contributed to the decline in catalytic activity.

As time-on-stream accumulated and temperature gradually increased, the product became lighter. Initially, 47% of the product was described as "reactor wax," a product clearly heavier than Kölbel's "low" molecular weight product (Table II); at the end of 18 days, this fraction had virtually disappeared. Whether this represents solely a temperature effect or also an inherent effect of catalyst aging cannot be determined from the data.

We must distinguish in principle between loss of catalytic performance because of actual catalyst fouling by internal coking (as implied by Kölbel's descriptions and recommendation of oxidative regeneration) or because of deterioration of hydrodynamic, mass transfer properties of the medium caused by the viscosity increase associated with formation of small carbon particles separate from the catalyst particles. In practice, we cannot deduce how much actual catalyst fouling occurred in the British work. In any future work, these performance decay mechanisms should be distinguished because their avoidance or reversal may require different approaches. Also, if formation of separate carbon particles is the major problem, they might be physically separable from the catalyst particles during operation based on different size, density, or magnetic properties.

Why then did the British group observe much more extensive carbon formation under conditions which do not differ in any obviously dramatic fashion from Kölbel's? To quote Hall:[3] "...we are inclined to think our poor performance was due to the use of an unsuitable catalyst.... It would appear that the catalyst was insufficiently active and tended to encourage carbon formation. In our experience it would be extremely difficult to increase the activity of the catalyst for promoting synthesis while reducing its activity for carbon formation, but this may well be what Professor Kölbel has achieved." One obvious difference in catalyst composition is the much higher K_2O level. In general increasing alkali level leads to increased activity, increased average carbon number, increased olefin content, increased oxygenate production, and increased carbon formation.[9] This difference might then rationalize the observations except for the inherently lower activity. Kölbel[5] has pointed out that the British catalyst also contained traces of sulfur, which resulted from its precipitation from sulfate rather than nitrate solutions; this may have acted as a poison. A second factor may relate directly to the initially heavier product composition, whatever its cause. It is not really known whether carbon formation occurs directly from CO as described by the formal stoichiometry of the Boudouard reaction or whether it also results from gradual chain lengthening of heavy olefinic products which accumulate in the liquid phase. All conjecture aside, the contrast of the British and German work suggests that further work at the PDU stage aimed specifically at determining the subtle factors which determine catalyst lifetime in slurry Fischer-Tropsch reactors will be necessary.

D. The Japanese Experience. Sakai and Kunugi[16] recently described results from a small slurry reactor patterned closely after Kölbel's laboratory reactor. The catalyst (Fe : Cu : K_2O = 100 : 0.3 : 0.6-1.2) was used at an initial slurry concentration of 10% Fe. However, since catalyst was gradually removed along with excess heavy oil product during the run, its concentration steadily dropped. Results are given in Table I for 99 hr on-stream, at which point a steady-state product composition was assumed to have been reached. The productivity results appear to be generally in accord with those of Kölbel, but the product (62% > C_{28}) was much heavier. Note again the higher alkali content of the catalyst. Although the authors report that the specific catalyst activity did not decline over the test period, it was not long enough (only 4 days) to serve as a legitimate test of catalyst aging characteristics. Therefore, these Japanese studies do little to assist our assessment of this key issue.

E. The Bureau of Mines Experience. An additional body of experience with slurry reactors is provided by the U. S. Bureau of Mines,[17,18] although their H_2:CO feed ratio was normally 1:1 so that the applicability to lower ratio feeds cannot be directly determined. The reactor dimensions were 7.6 cm ID x 3.05 m high, still smaller than either the German or British case (see Table I). To remove excess heavy oil produced, a parallel downflow slurry recycle line was attached containing a porous metal filter. In this relatively small test unit, no cooling coils were used although provision was made for reflux cooling by coils above the slurry bed.

Preliminary experiments showed that uniform catalyst dispersion could be maintained at a superficial gas velocity of only 2.75 cm/sec for a slurry containing 300 g catalyst/ℓ, i.e., a more concentrated slurry than either previous group used. The British claimed that such a velocity was too low to maintain effective fluidization at one-eighth the slurry concentration; these observations may be resolved by the Bureau of Mines' notation that more concentrated slurries were indeed easier to maintain uniform.

The catalyst was prepared by coprecipitation of Fe and Cu hydroxides followed by impregnation with K^+ ion to give Fe : Cu : $K_2O \cong 100 : 10 : 1$, the most Cu-rich of the cases discussed herein. Before activation in the reactor, the particle size was < 61 μm but no data are reported during use. These workers particularly stressed the importance of establishing optimum catalyst activation ("induction") procedures to achieve maximum productivity of a Fischer-Tropsch catalyst.

Operating data were collected for a period of 52 days during which temperature, pressure, and GHSV were varied in a general trend of increasing all three over the ranges 242-276°C, 6.8-17.0 atm, and 130-300 hr^{-1}. Certain upsets in maintaining slurry circulation through the recycle line may have confused the results somewhat, but a trend of gradually declining activity became obvious. Temperature was gradually increased to 275°C to compensate. A <u>reductive</u> reactivation with pure H_2 at the 42-day point restored the activity somewhat but not to the initial level.

Typical results at the 21-day point (Table I) showed 73% CO conversion and 45% H_2 conversion at 255°C, 10.2-13.6 atm, and GHSV = 240 hr^{-1}. The overall conversion level is thus again well below that claimed by Kölbel even with a 3.4-fold greater catalyst concentration and a higher H_2:CO ratio, albeit at 13°C lower temperature. Whether the aging phenomenon was comparable cannot be judged since unfortunately Kölbel did not provide his aging rate. Note that this catalyst gave a usage ratio of H_2:CO = 0.62, quite appropriate for a low ratio feed but out of balance for the 1:1 feed actually used.

Analyses of catalyst composition as a function of operating time showed a gradual buildup of carbon amounting to 0.064 g C/m^3 feed consumed/kg Fe. However, it is not clear how this carbon was distributed between free carbon particles, carbon within the catalyst pellets, and gradual conversion of Fe and/or Fe_3O_4 to Fe_xC.

The product composition for the conditions just described was C_{1-2} : C_{3-5} : gasoline (25-204°C) : diesel oil (204-343°C) : heavies (>343°C) = 12 : 23 : 27 : 10 : 28. Going from 255°C to 276°C to compensate for decreasing activity (as well as simultaneously going from 13.6 to 17.0 atm and from 240 to 300 hr^{-1}) reduced the amount of heavies four-fold. [In such cases where the initial conditions are seldom reestablished experimentally, one must exercise some caution in ascribing all charges in product composition to reaction parameters; an inherent product selectivity change may accompany catalyst aging.] The product thus appears slightly heavier than Kölbel's but lighter than the British. Water soluble alcohols made up a small fraction of the total product.

A second data set from the Bureau of Mines[19] resulted from efforts to utilize the ability of nitrided Fe catalysts to produce atypically high proportions of oxygenated products.[20,21] These data must be perturbed to some degree by the slow conversion of nitride to carbonitride during synthesis but nevertheless are of interest in the present context. The same reactor was used but the slurry recycle tube was eliminated by incorporating a short section of porous bronze tubing into the main reactor tube, through which excess liquid phase could be withdrawn as required.

The original oxidic catalyst preparation, either fused or precipitated, was ground to <60 μm and then reduced with H_2 and nitrided with NH_3 in situ. After use, the particle size had been reduced to ∿1 μm, and particle rupture because of carbon deposition and/or nitride-to-carbide phase conversion was suggested as a more probable cause of particle disintegration than simple mechanical breakdown in the slurry. The catalyst fraction used in the slurry was not stated.

Since this operation stressed maximum production of oxygenates as the key dependent variable, temperatures tended to be rather low (240-250° C). Continuous operation for periods up to 133 days were reported, longer than any other slurry experience described, albeit with 1:1 feed. For our purposes, conversion values and product compositions under the more forcing conditions (at the expense of selectivity to oxygenates) are most pertinent, although it must be remembered that most of the time-on-stream accumulated was under less forcing conditions. At 258°C, 20.4 atm, and GHSV = 200 hr^{-1} with the fused, nitrided catalyst, the ($CO + H_2$) conversion was 71.4% at a usage ratio of 0.81. The product was lighter and more oxygen-rich than for a non-nitrided catalyst. The ratio of C_{1-2} : C_3+ hydrocarbons : oxygenates was 37 : 46 : 17.

For a precipitated, nitrided catalyst with 1:1 feed, the following grouped values of temperature, GHSV, and ($CO + H_2$) conversion are given as a function of catalyst age: 250°C, 300 hr^{-1}, 38.4% at 10-15 days; 250°C, 200 hr^{-1}, 43.7% at 16-34 days; 259°C, 200 hr^{-1}, 47.0% at 35-38 days. Although both variables were changed at once, there seems to be little evidence for major catalyst decay. To the extent that a light, oxygen-rich product may be ideal for conversion to gasoline by zeolites (Sect. III.B) and to the extent that these data show rather impressive catalyst lifetimes, albeit at lower temperatures and a higher H_2:CO ratio than earlier studies, the use of nitrided catalysts in slurry reactors at lower feed ratios deserves reevaluation. For example, does the nitrided catalyst show an inherently reduced tendency to form coke and can this hint be used in further catalyst design?

A second line of investigation at the Bureau of Mines[22] involving use of catalysts in a liquid medium led to development of the oil recirculation process. This differs from the slurry processes described so far in that heat removal was accomplished by continuous recirculation of the oil phase through an external heat exchanger rather than by use of internal cooling coils. Such operation requires some additional energy input for oil circulation and sets some (not clearly defined) lower limit on catalyst particle size to prevent extensive catalyst carry-over with the oil. After experiencing difficulties with a fixed catalyst bed because of gradual particle aggregation, these workers increased the upward oil velocity to the point (3-5 cm/sec) where the bed expanded with use of an intermediate catalyst size (20-42 mesh). However, temperature gradients of 5-10°C still occurred in contrast to the slurry cases discussed above where the oil phase did not leave the reactor and backmixing was surely more extensive. In the initial work, a H_2:CO = 1 feed ratio was used with recycle. The combination of all these operating factors makes this work of only peripheral interest to the problem at hand, and no further review will be given here. This process concept was also applied to nitrided Fe catalysts.[21]

In a later study[23] with 6-20 mesh fused-Fe catalyst in the expanded-bed, oil-recirculation mode, some direct comparisons were made for H_2:CO = 0.7:1 feed compared with a 1:1 feed. The following changes were observed for the more CO-rich feed: a slightly higher temperature was required for a given conversion level; the liquid product had a larger average molecular weight and was more olefinic; and carbon formation and catalyst particle disintegration were accelerated, especially above 270°C. While these conclusions regarding the effects of the H_2:CO ratio may not carry over completely to a slurry reactor with finely divided catalyst, they appear reasonable in light of other Fischer-Tropsch experiences. The accelerated aging results at H_2:CO = 0.7 thus temper somewhat any conclusions above regarding the Bureau of Mines slurry reactor operated at H_2:CO = 1.1 and reinforce the need for further experimental evaluation.

F. Overview. The work of Kölbel and his German associates shows obvious potential for achieving high single-pass conversion of low H_2:CO ratio synthesis gas with relatively slow catalyst aging to give a rather typical Fischer-Tropsch product mixture rather low in methane and high in olefin content. Kölbel also suggests that slurry reactors are inherently more flexible than other reactor types with respect to achieving varied product compositions because any given design for a slurry reactor allows more latitude in choice of reactor parameters. For detailed economic evaluation, however, we must understand the relationships among catalyst life, regenerability, and cost and the economic penalties of downtime for catalyst replacement and/or regeneration. A weakness which then emerges when attempting to use Kölbel's data is that the quantitative criteria for assessing catalyst aging and regeneration were not given. We do not know what fraction of initial catalyst activity was lost over the "life" of the catalyst and data are not presented to support the claim of complete oxidative regeneration.

The British and American work suggests that aging rate may be highly dependent on rather subtle factors of catalyst composition and operating parameters. The three major studies differ enough in exact detail to make any further rigorous comparison impossible. However, they clearly point up the need for additional data on aging rates and regeneration capabilities as a function of catalyst composition and operating parameters.

Aging rate [or more exactly, the optimum compromise between aging rate and catalyst cost] may not be the only measure of process desirability. Formation of a product slate most amenable to further conversion to high-octane gasoline may be equally important (Sect. III.B). The existing information regarding product distribution—catalyst composition relationships for Fischer-Tropsch catalysts should be judiciously applied when selecting catalysts for any further aging tests in slurry reactors.

We may speculate concerning reasons for suppression of carbon deposition in the slurry reactor, but a definitive answer is not apparent. Excellent temperature control[5,14] to avoid hot spots surely is a major contributor to inhibit both methanation and carbon formation. Less severe temperature gradients within each catalyst particle as well as the absence of locally high CO concentrations because of its small diameter compared with fixed bed catalysts may also be factors.

We have made no explicit attempt in this study to consider the fluid dynamics of three-phase bubble-column reactors. Discussions are available by Kölbel and Ralek[5] and by Satterfield and Huff.[24] This area deserves careful attention in any future work for several reasons. Firstly, the reactor conditions for which mass transfer, particularly across the gas bubble—liquid phase interface, becomes rate-limiting should be known.

Kölbel[5,25] has consistently concluded that his studies (Table I) were performed under conditions where the catalytic surface reactions were rate-controlling. However, recent analysis by Satterfield[24] of several previous experimental studies and by Hall[14] conclude otherwise for rather similar reaction conditions. Further clarification is demanded. Secondly, product selectivity may be affected by changes in gas residence time, by the extent of liquid backmixing, and by other fluid dynamics factors. Finally, there are important consequences for future catalyst testing programs in slurry reactors in terms of minimum reliably useable reactor size. For example, how small diameter a reactor can be used to evaluate slurry performance without the occurrence of slugging and gas bypass? The answer will dominate the practical logistics of a testing program. If a reactor as large as that used by Kölbel in 1953 (10 m^3) were necessary, the number of catalysts which could be tested for extended periods obviously would be much smaller than if, say, a 2-inch ID bench-scale reactor could be used reliably.

Finally, we note parenthetically that recent experience has been obtained with slurry reactors for converting synthesis gas to both methane and methanol, especially by Chem Systems research personnel. We make no attempt to review this subject here but recommend its consideration by any future researchers working on the present problem.

III. THE MOBIL-GASOLINE PROCESS

The purpose of this section is not to review the Mobil-Gasoline process concept in detail but rather to highlight those features which relate directly to the chances for coupling the process with a slurry Fischer-Tropsch reactor operating with low H_2:CO feed (Sect. V). To reiterate, such coupling could be either in a two-step mode, each process operating at its optimum conditions, or in a single-reactor mode, operating at a compromise set of conditions.

A. Basic Process Conditions and Chemistry. The Mobil process[26] converts methanol or aqueous methanol-dimethyl ether mixtures in high selectivity to C_5-C_{11} hydrocarbons having a much higher octane number than traditional Fischer-Tropsch "gasoline" because of the presence of aromatic and branched aliphatic hydrocarbons. The key to the process is a shape-selective, high-silica zeolite catalyst, typified by ZSM-5. Initial process development studies were carried out in a two-stage, fixed-bed configuration where the methanol-dimethyl ether-water equilibrium was established in a first reactor to assist in heat management. Later studies focused on fluidized-bed operation, most recently at a 4 bbl/day scale. Two chemical features of special concern herein are the flexibility of the zeolite catalyst to accept feeds other than methanol and the minimum reaction conditions, especially temperature, required to achieve high conversion to high-quality gasoline. The first will influence the viability of a two-step slurry Fischer-Tropsch—Mobil-Gasoline process and the second, the prospects for a hybrid, single-reactor process.

We will describe briefly results[27] from fixed-bed studies because they reveal general process features needed to answer these questions. Screening tests in a microreactor showed that methanol conversions of $99^{+}\%$ at 1 atm and WHSV = 0.8 hr^{-1} required temperatures of at least 370°C, i.e., ∿100°C higher than typical for the Kölbel Fischer-Tropsch reactor. Still higher temperatures, however, were disadvantageous since they decreased C_5+ yields and enhanced light gas formation. Increasing pressure increased the proportion of polymethylbenzenes such as durene which appear to arise from alkylation of initially formed aromatics by residual methanol.[28] A fix-bed PDU (3.2 cm ID containing 220 cc of catalyst) was operated in which the feed was a near-equilibrium methanol-dimethyl ether-water mixture along with a molar recycle ratio of 3-4. Typical conditions were 343°C inlet temperature, ∿455°C outlet temperature, 13.6-23.1 atm pressure, and WHSV (methanol) = 1.5-5.0 hr^{-1}. Gradual catalyst aging and methanol breakthrough resulted from coking. However, the catalyst could be reactivated by burnoff and a total methanol consumption of 8000 g/g catalyst was achieved over a period of 200 days with an average cycle time between regenerations of 22 days.[29] Such catalyst aging could be a serious problem in a single-reactor, integrated process with a physical mixture of Fischer-Tropsch and zeolite catalysts because not only a single set of reaction conditions but also a single set of *regeneration conditions* would need to be found. Note that the zeolitic catalyst is inherently more expensive than typical Fischer-Tropsch catalysts.

Development efforts[30] then turned to a small fluidized-bed unit (4.1 cm ID) because of its superior heat-transfer properties and because, although the raw product contained less C_5+ gasoline and more light olefins, the overall gasoline selectivity, after alkylation, was greater. Provision was made for periodic catalyst burnoff *in situ* up to 590°C. A systematic study of the effects of reaction variables on methanol conversion and product composition was made as a function of time on stream. Methanol conversion increased with increasing temperature and contact time as expected. At 2.7 atm pressure and WHSV = 2-3 hr^{-1}, a temperature $\gtrsim$ 370°C was again required for high methanol conversion. Increased pressure increased the rate modestly, but much less than anticipated for first-order behavior. A detailed aging test was conducted at 399°C, 2.7 atm pressure, and WHSV = 2 hr^{-1}. During a typical operational period of $\sim$350 g methanol/g catalyst, conversion decreased from 99 to 82%. Oxidative regeneration restored most but not all activity until, after six regenerations, initial catalyst activity had decreased $\sim$50%; this irreversible effect was attributed to the well-recognized effects of high-temperature steaming on zeolite structures.

A 4 bbl/day fluidized-bed pilot plant (10.2 cm ID x 7.6 m high) was then operated.[29,30] Runs of 34 and 75 days were completed over the operating range: 388-427°C, 2.4-3.7 atm pressure, and WHSV = 0.5-1.5 hr^{-1}, with $\sim$20% of the catalyst inventory being reactivated every 2 days in batch operation. The results cited in the preceding few paragraphs summarize the overall process conditions required for the Mobil-Gasoline process with its normal methanol feed, especially the need for temperatures near 400°C.

Detailed chemical studies[31] have revealed that the process occurs by the following consecutive steps:

$$2\ CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$CH_3OCH_3 \longrightarrow \text{light olefins} + H_2O$$

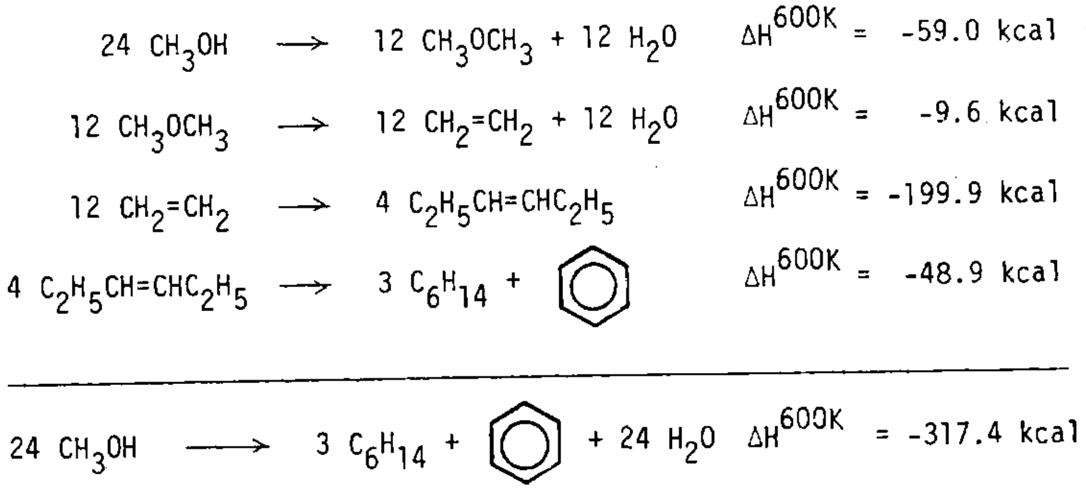
$$\text{light olefins} \longrightarrow C_5\text{+ olefins}$$

$$C_5\text{+ olefins} \longrightarrow \text{paraffins and aromatics}$$

Recent evidence[32] points to an autocatalytic character of the dimethyl ether consumption step because at least part of the methanol/dimethyl-ether disappears by rapid secondary reactions with initially formed olefins; at very low conversion levels, propylene exceeds ethylene among the initially formed olefins.

Additional mechanistic data supporting this gross reaction sequence from alcohols to higher hydrocarbons have been presented by Derouane and coworkers[33] for studies with methanol and ethanol as feeds, both of which give similar product mixtures at high conversion. Similar studies by Anderson and coworkers[34] also support the key role of olefins as intermediates on the route to aromatics, although this group reported ethylene generally to be less reactive than propylene. At 400°C over HZSM-5, C_6 paraffins were also cracked and aromatized, albeit at a much lower rate than methanol or propylene is converted. Recent Mobil patents[28,35] describe process variants aimed at maximizing production of these intermediate light olefins by using less severe reaction conditions than those required to maximize gasoline selectivity. For example, with a methanol: water = 83:17 feed at 299°C, 1.4 atm pressure, and WHSV = 0.4 hr^{-1} in a small fluidized-bed reactor, the methanol conversion was only 52% but with 48% selectivity to C_{2-5} olefins; the olefin-to-paraffin-plus-aromatics conversion appears to require at least 50°C higher temperature.[31] On the basis of these results, a single-step conversion of synthesis gas to gasoline with mixed catalysts (Sect. V.B) would appear to be difficult because a temperature high enough to maximize gasoline selectivity (350-400°C) would seem inimical to lifetime of most Fischer-Tropsch components, and probably would also be inconsistent with stability of the oil liquid phase medium in a slurry reactor.

As already noted, the conversion of methanol to gasoline is highly exothermic. However, the breakdown into individual steps, with use of C_6 as an example:[36]



shows that much of the heat is released in the hydrocarbon-condensation steps. Hence in a two-step process (Sect. V.A), there would be less heat load on the zeolite-catalyzed step with crude Fischer-Tropsch feed than with methanol feed.

B. Feed Flexibility. Implicit in the discussion above has been the assumption that the Mobil catalyst might indeed accept a Fischer-Tropsch product rather than methanol as the feed; we will now examine the evidence. Chang and coworkers[31] described the use of several oxygenated feeds besides methanol at 371°C. High conversions were achieved for *t*-butanol, 1-heptanol, propionaldehyde, and acetone to give remarkably similar product compositions. The French and Belgian workers[33] demonstrated the suitability of ethanol. Hence we conclude that the minor, oxygenated, largely alcoholic component of a typical Fischer-Tropsch product could probably be upgraded to gasoline. Both these groups[31,33] and the Australian group[34] demonstrated the reaction sequence given earlier in which olefins serve as intermediates before hydrogen redistribution to form paraffins and aromatics. Hence the more important olefinic component should also be an acceptable feed. Anderson's results[34] show that under vigorous enough conditions even the paraffinic component would probably be converted, i.e., isomerized and/or aromatized to improve its octane number. Specific data for individual compounds are not available concerning whether the zeolite catalyst would degrade the C_{11}+ component of a Fischer-Tropsch product. However, to the extent that the acidic HZSM-5 serves as a carbenium ion catalyst and to the extent that the temperatures for the Mobil-Gasoline process are approximately those where olefin oligomerization and catalytic cracking of olefins and paraffins are thermodynamically balanced, breakdown of larger molecules into the gasoline range may be feasible. For example, the free energy of cracking n-hexadecane to n-octane and 1-octene becomes negative above 275°C.[36] The predominantly linear nature of a Fischer-Tropsch product should be advantageous in this regard since it could still penetrate the shape-selective catalyst. In fact, the Mobil Distillate Dewaxing process[37] appears to operate on just this principle by selectivity cracking the least bulky components of fuel oils.

These observations and considerations taken together suggest that typical Fischer-Tropsch products could be upgraded by ZSM-5 catalysts at a high enough temperature, but that the optimum feed for the upgrading stage of a two-step process would be derived from a Fischer-Tropsch catalyst and process which emphasizes formation of highly olefinic or oxygenated products of as low an average molecular weight as possible without excessive methane formation.

C. Overview. The remarkable ability of the ZSM-5 catalyst to convert methanol to gasoline stands as a tribute to modern catalyst design. For the present purpose, however, for consideration of two-step processes, more specific data are needed on its ability to transform typical Fischer-Tropsch product mixtures as a function of temperature (Sect. V.A) and on its aging characteristics as a function of the feed. For one-step processes with mixed catalysts (Sect. V.B), the temperature optima of presently known Fischer-Tropsch and zeolite catalysts are not as well matched as would be desirable.

IV. THE KÖLBEL-ENGELHARDT REACTION

The extreme case of using low H_2:CO ratio feeds for Fischer-Tropsch synthesis was pioneered by Kölbel and Engelhardt[6,38,39] who demonstrated conditions for supplying the needed hydrogen solely as water. By careful control of the feed ratio, CO could be converted to hydrocarbons over Fe-based catalysts by feeding only steam in the absence of molecular hydrogen.

$$3\ CO + H_2O \longrightarrow \frac{1}{n} \left(CH_2 \right)_n + 2\ CO_2$$

This work was first reported in the early 1950's, but some recent revival of interest[40] has occurred, particularly regarding the extent of mechanistic coupling between the water gas shift and synthesis components of the reaction.

The applicability of the Kölbel-Engelhardt reaction was originally proposed and appears still to be for dilute CO-containing streams not containing H_2 (e.g., blast furnace off-gas) rather than for synthesis gas itself. Hence it has no direct impact for the present study except that it provides one more data set for the behavior of the Kölbel reactor.[6] Kölbel and associates described the conversion of CO-H_2O feeds in a much smaller reactor (5 cm ID x 5 m long; 300 g Fe in 7 ℓ of slurry) than used for the CO-H_2 feeds. At 240-280°C, 15-20 atm pressure, and GHSV = 220 hr^{-1} for a blast furnace gas containing 34% CO to which steam had been added to give CO : H_2O = 3 : 1.15, a space-time yield of C_3+ hydrocarbons of 11.3 g/ℓ/hr was reported at 93% CO single-pass conversion. Again improved catalyst lifetime compared with gas-phase operation was claimed. The actual life datum presented was very similar to that for the CO:H_2 feed, i.e., 405 g C_3+ product/g Fe during "its life."

V. HYBRID PROCESS CONCEPTS

A. Two-Step Operation. As stated above, one advanced process concept would use the total crude product from a slurry Fischer-Tropsch reactor operating with low H_2:CO ratio gas as the feed for a downstream Mobil-Gasoline reactor of optimum design. [Whether or not interstage CO_2

removal would be used may depend on the feasibility of high-temperature scrubbing.] In this case each process could operate at its preferred process parameters (T,P,SV) to optimize overall product yield and quality. Decoupling the reaction parameters for each step may be most advantageous for temperature since it appears that the optimum for the Mobil-Gasoline process is some 100°C higher than for the Kölbel reactor. A second advantage is that the catalyst for each process could be regenerated separately, again each under its optimum conditions and schedule. To compare such two-step operation with one-step, these advantages would need to be compared with the disadvantages of probably greater investment and operating costs.

From the viewpoint of catalyst design, the challenge of two-step operation would be to correlate the feed requirements of the zeolitic catalyst with the product slate of the Fischer-Tropsch catalyst. We have already pointed out the probability that adjusting the Fischer-Tropsch catalyst and process conditions to give the highest olefinic and oxygenated product content and the lowest average molecular weight (without undue methane formation) would be desirable to obtain the most extensive upgrading by the zeolite. We make no attempt here to review but simply call attention to the continually growing literature on product selectivity of Fischer-Tropsch catalysts as a function of composition and reaction conditions. For traditional Fe-based catalysts, the product requirements just outlined probably demand as high an operating temperature as possible, consistent with excessive methanation and aging, and a low alkali content. For compositionally more complex catalysts, we stress again the recent discoveries regarding catalysts which optimize light olefin selectivity (Sect. II.B).

At least one recent patent disclosure[41] is related to the second step of this approach. A gasoline-range Fischer-Tropsch product (C_5 - 204°C, RON = 66) was processed over HZSM-5 at $\sim$265°C, 48 atm pressure, and LHSV $\sim$0.6 hr^{-1} to give an octane-improved gasoline fraction and a higher-boiling (204-343°C) fuel oil fraction with minimal gas formation. The yield loss to fuel oil associated with an improvement in RON to 81 was 12%; increasing severity gave only modest further octane improvement but at the expense of further yield loss. The upgraded gasoline had a relatively high olefin:aromatic ratio. The net chemical result thus was an increase in average molecular weight and production of some hydrocarbons heavier than C_{11}, in contrast with the parent Mobil-Gasoline process. The reason presumably is the very low temperature used in this example, a temperature actually more typical of Fischer-Tropsch operation than Mobil-Gasoline operation. Note also that the improved octane level achieved was still lower than for the gasoline prepared directly from methanol. Hence this example enhances the view that the second step of a two-step process would need to operate in the 350-400°C temperature range not only because of activity considerations but also because of gasoline yield and quality considerations. It is noteworthy that this example[41] was performed with advantage at high enough pressure to maintain a liquid phase (to avoid accelerated aging), a necessary requirement if the zeolitic catalysts are ever to perform in a slurry reactor (Sect. V.B.).

B. One-Step Operation. A more integrated approach from the reactor engineering viewpoint would be to include both the Fischer-Tropsch and the upgrading catalytic activities in a single reactor. In the present context this would be a slurry reactor with a low H_2:CO feed ratio. We are not aware of published results for either of these criteria, let alone both. However, there are recent data on attempted one-step operation in more traditional reactors and with $H_2:CO \geq 1$ feed which will be reviewed shortly.

The one-step approach demands a common reaction temperature. If the zeolite catalysts require operation in the 350-400°C range for optimum performance (Sect. V.A), then we must ask whether there exist Fischer-Tropsch catalysts which will operate in this regime without excessive coking and/or methanation. No obvious candidates emerge from past history with Fe- and Co-based materials, but less well-trodden areas,[9] such as the isosynthesis or "Synol" processes, may deserve renewed attantion in this context.

The catalyst for one-step operation could be simply a physical mixture of the individual catalysts. In the slurry case, this may require a careful balancing of particle size and density of the two materials to achieve a uniform distribution throughout the reactor. Or, a truly "hybrid" catalyst can be imagined, i.e., one in which the two catalytic functions are "mixed" at the molecular levels. A fine dispersion of the Fischer-Tropsch metal within the zeolitic pore structure would be a prototype conceptualization.

In one-stage operation, each catalytic function will almost surely be forced to operate somewhat removed from its optimum conditions of temperature and pressure. This disadvantage may however be countered (or compounded) by the more subtle question of interactions between the catalytic functions mediated by migration of intermediates from one type of particle or active site within a particle to another. Thus "hybrid" catalysts can produce a result not anticipated from the simple sum of their individual activities and hence leave opportunity for discovery. In the present case, the design of catalysts for one-step operation would not be simply an extrapolation from previous data but a significant research problem in its own right.

Recent studies from Mobil[42,43] have demonstrated in the case at hand the principle that mixtures of catalysts can produce results differing from the simple sum of their known behavior if an intermediate formed on one catalyst particle can diffuse to another catalyst particle of the second kind where it serves as the substrate. A 1:4 intimate mixture of separate 12-25 mesh particles of K_2O-promoted, ammonia-synthesis Fe catalyst and ZSM-5 catalyst was tested in a fixed-bed microreactor at 330°C. Compared with a similar Fe catalyst alone, the carbon number distribution of the product was truncated at $\sim C_{11}$. The yield of gasoline-range product ($\sim$60%) was higher, and its octane was greater because of more branching. Omitting the zeolite led to gradual reactor plugging because of wax formation. A sequential arrangement rather than intimate mixture of the catalyst particles did not provide the synergistic result. Therefore Caesar and coworkers[43] proposed that α-olefins are free intermediates in the Fischer-Tropsch reaction, many of which are readsorbed and grow further.[44] However, they can therefore also be intercepted by the zeolite and converted to aromatics, branched olefins, etc. Further examples of synergistic interactions between catalyst particles were provided by Chang and coworkers[42] for mixtures of ZSM-5 and methanol-forming catalysts.

Additional examples appear in recent patent literature from the same group.[45] For example, a mixture of Fe-based ammonia synthesis catalyst and ZSM-5 catalyst operated at 370°C, 18 atm pressure, a feed ratio of H_2:CO = 1:1, and contact time = 15 sec gave 98.4% CO conversion to produce CH_4 : C_{2-4} : C_5+ in a ratio of 53 : 41 :6 whereas the Fe catalyst alone gave 93.5% conversion and a product ratio of 45 : 50 :5 [note the uncharacteristically low average molecular weight for Fe resulting from the uncharacteristically high temperature]. The major difference was a 15% aromatic content in the C_5+ fraction in the former case compared with only 1.4% in the latter. Using the catalysts sequentially rather than intimately mixed did not give this enhancement in aromatics. A disturbing example in this patent describes the failure of sequential, two-step operation to achieve any significant upgrading even for a Fischer-Tropsch product containing 50% C_2-C_4 hydrocarbons and at temperatures characteristic of the Mobil-Gasoline process. This observation appears counter to the suggestions made in Sect. V.A.; further clarification is clearly in order.

The most extensive data from Mobil[29,46] concerns the performance in both fixed- and fluidized-bed operation of a set of proprietary catalysts for direct synthesis gas-to-gasoline conversion. Their composition has not been revealed; however since it has been specifically stated[29] that the success achieved resulted from the unique character of the zeolitic component chosen, in contrast with the generally disappointing results of several other research groups[47-49] with metal-exchanged or metal-loaded zeolites of other types, we will assume that these are similar to those discussed in the recent papers[42,43] and patents.[45]

We describe here results in fluidized-bed operation only for catalyst "SGF-A-3," which possesses inherent shift ability. In a bench-scale unit at 293°C, 14.6 atm pressure, and GHSV = 1000 hr^{-1} for a feed ratio of H_2:CO = 1:1, the (H_2 + CO) conversion was 70% to give a product ratio of C_{1-2} : C_{3-4} : C_5 - 200°C : 200°C^+ of 28 : 16 : 56 : trace. The gasoline fraction had an octane number of 92 and a 16% aromatic content. The much higher octane value than a typical Fischer-Tropsch product resulted not only from the (modest) aromatic content but also from the branched nature of the nonaromatic, highly olefinic portion. Catalyst aging was a general phenomenon, but multiple oxidative regenerations were achieved. These hybrid catalysts appear to be the most dramatic example to date of direct conversion catalysts which give a product which differs from Fischer-Tropsch products both in its molecular weight distribution (not controlled by the Schulz-Flory polymerization model[43]) and structure (branched and aromatic). Remaining problems to be solved appear to be improved gasoline selectivity with elimination of C_{1-2} gas and especially improved lifetime. In this regard, the necessity to operate at $\geq 300°C$ at $H_2:CO<1$ will obviously be a challenge both to avoid inefficiency to methane and aging.

In extended tests with this class of catalyst, the Mobil workers abandoned fixed-bed operation in favor of fluidized beds because of serious problems of temperature control and carbon deposition even for high $H_2:CO$ feed ratios in fixed beds. The question now remains of whether performance and lifetime would be further improved by slurry operation and allow even lower $H_2:CO$ feed ratios than 1:1 within the constraints set by the upper temperature limits of the oil slurry medium.

Oxidative regeneration in a normal fluidized bed can be accomplished in situ, but note that this cannot be done for a slurry containing oxidizable oil as the medium. If such regeneration cannot be completely avoided for these inherently costly catalysts, it would have to be accomplished in a separate reactor after catalyst separation with attendant introduction of process complexity. Alternatively, hydrogenative regeneration may deserve attention, although the upper temperature limits imposed by oil volatility and thermal stability may still be overly restrictive.

VI. References

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