

backflush column was a 6 inch x 1/8 inch SS Carbosieve S column with a carrier gas rate of 15 cc/min helium. The column operated in series for 1.1 min. (allowing hydrogen, argon, carbon monoxide, methane, and carbon dioxide through) with the rest of the time in backflush mode under a reversed flow condition. Integration for the Hewlett-Packard gas chromatograph was taken over by a Spectra Physics SP 4000 at the same time that the backflush valve was added to the Carle. Also at this time, the stainless steel column in the Hewlett-Packard instrument was also replaced by a 6 foot x 1/4 inch O.D. glass column packed with 80/100 mesh Porapak QS. This analytical system was used for the remainder of the vapor phase tests. A typical chromatogram for this system is shown in Figure IV-8.

4. Analytical Procedure For Slurry Autoclave Tests

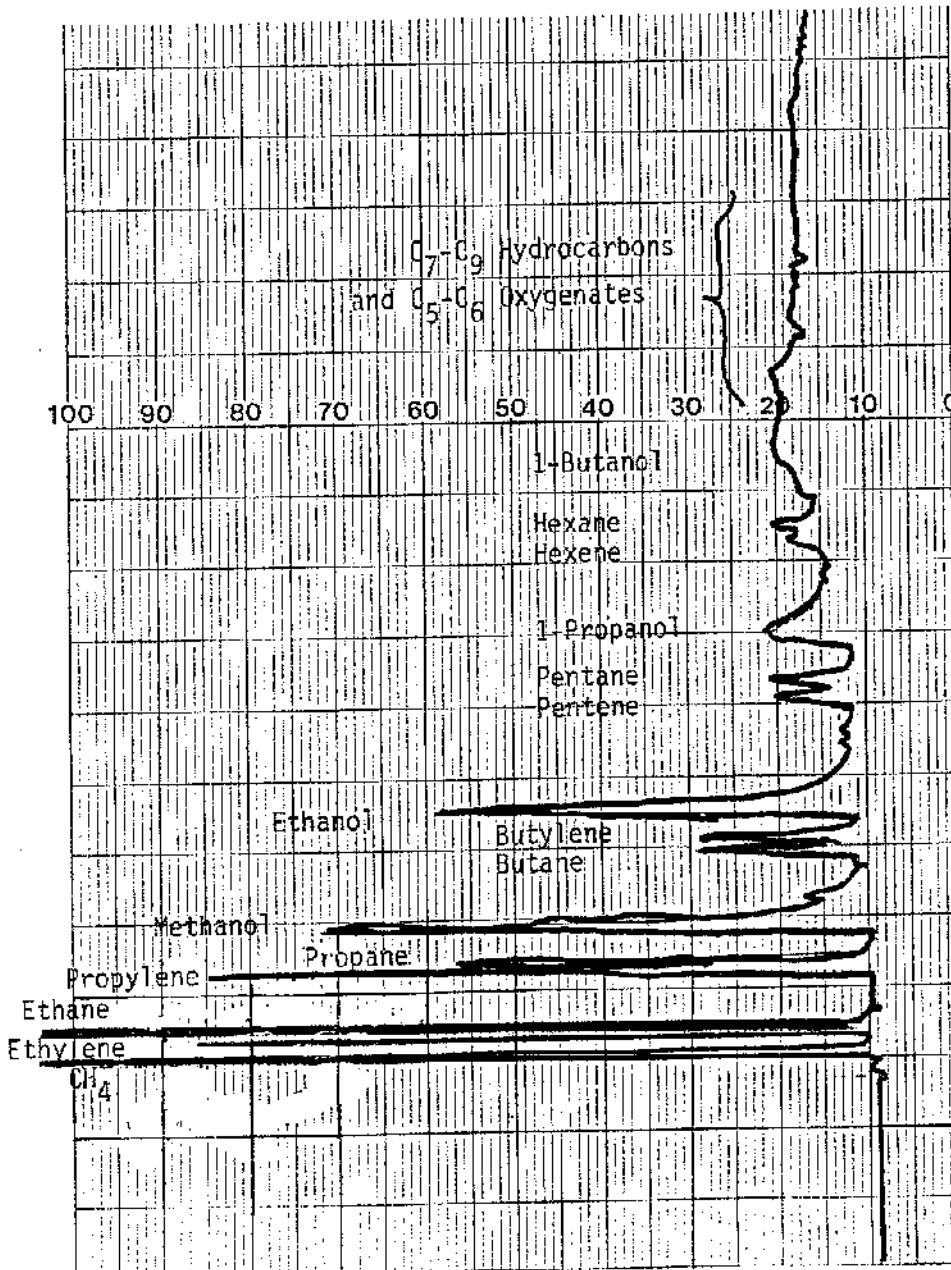
When work started in the slurry-phase autoclave reaction system, it was immediately apparent that the analytical system would have to be modified, as the slurry oil in the sample damaged the columns in the Hewlett-Packard instrument. To alleviate this problem, a second backflush column was added to allow only components through C_9 hydrocarbons into the chromatograph. In addition, the valve oven temperatures were increased to 220°C to prevent condensation of slurry oil in the sampling system. The new backflush column was a 3 foot x 1/8 inch O.D. SS column packed with 10 percent SE-30 on Anakrom ABS 60/70 mesh, N.P. A carrier flow of 15 ml/min helium was used for both backflush columns in operation. Due to problems with the temperature control unit towards the end of the project, the Hewlett-Packard 5720A was replaced with a Shimadzu Mini 2 gas chromatograph equipped with twin flame ionization detectors and two 9 foot x 1/4 inch O.D. glass columns packed with Porapak QS 80/100 mesh. The twin columns eliminated baseline drift due to temperature programming. The carrier flows and temperature programming were not changed.

E. Catalyst Activation Procedures

Two types of catalyst activation procedures were employed. The type most often used involved reducing the catalyst with a dilute mixture of hydrogen in nitrogen (usually 2 percent hydrogen). The initial

FIGURE IV-8

SAMPLE CHROMATOGRAM AND INTEGRATION FOR
VAPOR-PHASE ANALYSIS OF ALKANOLS SYNTHESIS PRODUCTS



TIME	AREA
13	494
43 CH ₄	878439 2
76 Ethylene	24463 2
89 Ethane	129165 2
189 Propylene	3443 2
202 Propane	57195 2
258 Methanol	17363 1
311 Acet. Aldi	2459 1
333	1348 1
341	1149 1
349	1001 1
371	2561 2
393 Butylene	32949 2
410 Butane	36855 2
460 Ethanol	132997 3
577	1035 1
599	1343 1
653 Pentene	16027 1
681 Pentane	19325 1
747 Propanol	56603 2
835	833 2
857	9051 3
913 Hexene	3602 2
933 Hexane	11864 3
1011	4664 2
1049	22417 3
1197	3679
1471	4609 2
1511	316 2
1539	113 3
1639	3517 2
	1485679T

temperature during the reduction was maintained at 200°C until hydrogen breakthrough occurred. The temperature was then raised in 10°C increments until the final reduction temperature was reached. This temperature was maintained until hydrogen uptake was completed. Final reduction temperatures of 240°C, 350°C, and 450°C were studied. Reduction gas feed rates of 500 l/hr/l catalyst and 1000 l/hr/l catalyst were studied. All reductions of this type were carried out at ambient pressure. During reductions in the Berty reactor, the impeller speed was maintained at 1000 rpm.

After the reduction, the reactor was purged with nitrogen and allowed to cool to about 200°C before pressurization with synthesis feed gas for the case of reduction in the vapor-phase units (plug-flow or Berty). The typical time required for this reduction procedure was 48 hours.

The second type of activation procedure is referred to as an in-situ reduction. This procedure involved introducing synthesis feed gas (generally one with a 2/1 hydrogen/carbon monoxide ratio and 5 percent carbon dioxide content) to the catalyst bed at 230 to 240°C and at atmospheric pressure. As this reduction process evolved a considerable amount of heat, it was only tested in the Berty reactor under careful temperature control. As with the last procedure, progress of reduction was determined by measuring hydrogen uptake with the Carle gas chromatograph. This activation procedure required only 1-2 hours, after which the system was then brought up to reaction pressure.

V. DISCUSSION OF RESULTS OF CATALYST FORMULATION AND SCREENING STUDIES (TASK 1)

A. Literature Review

1. Review of Early Catalyst Development

The production of chemicals and clean fuels from synthesis gas has been known for over fifty years, and research and development efforts in this area have taken many directions. The initial foundation for the development of this chemistry began in the 1920's with the well-known work of Fischer and Tropsch^(1,2,3,4) for producing liquid hydrocarbons from synthesis gas. The reaction between carbon monoxide and hydrogen were carried out at pressures between 100 and 150 atm, at temperatures of 400 to 450°C in the presence of an alkali-activated, iron oxide catalyst.

The scientific and industrial importance of this chemistry was so apparent that experimental research on the subject was initiated in laboratories throughout the world. The research centered on the development of improved catalysts for the Fischer-Tropsch synthesis as well as on other chemical routes to alcohols. The various processes for obtaining higher alcohols for carbon and hydrogen can be classified into three groups:

1. Synthesis by catalytic processes aimed at producing hydrocarbons from carbon monoxide and hydrogen (Fischer-Tropsch);
2. Synthesis with modified methanol catalysts;
3. Oxo synthesis from carbon monoxide, hydrogen and olefins.

The Oxo synthesis (hydroformylation) was originated in Germany during World War II as a process for the production of higher alcohols. However, its utilization was limited by the requirement for the additional olefinic reactant.

The discovery and concomitant improvements in the ZnO-Cr₂O₃-based catalysts during the 1920's through the 1950's represented a decisive step in the selective synthesis of higher alcohols. The first high yields of methanol in the presence of these catalysts were reported by BASF⁽⁵⁾ in 1923. Natta and Strada⁽⁶⁾ in 1930 found that the highest yields of alcohols were obtained with ZnO-based catalysts promoted by potassium, rubidium or cesium ion. A few years later, Morgan and coworkers⁽⁷⁾ studied the quantitative influence of the addition of five different alkali ions to a chromium oxide-manganese oxide catalyst. Although they found Li⁺, Na⁺, K⁺ (added as hydroxides) to inhibit the overall reaction yield, they did not observe this phenomenon when Rb⁺ or Cs⁺ was present. Other researchers^(8,9) also found that alkaline metals can be used as promoters for the synthesis of higher alcohols. The overall conclusion from a recent review⁽¹⁰⁾ of this older work is that the catalytic synthesis of higher alcohols is not selective and the resultant alcohol mixtures have methanol as a predominant component.

The following types of catalysts have been proposed⁽¹¹⁾ for the synthesis of higher alcohols:

1. ZnO-based catalysts with alkaline promoters;
2. ZnO-Cr₂O₃-based catalysts with alkaline promoters;
3. Oxides of zinc, manganese, chromium-activated with alkaline promoters;
4. Copper, ZnO, Cr₂O₃ catalysts activated with alkaline promoters;
5. Copper and oxides of zinc, chromium, manganese, calcium, lead, aluminum, thorium, etc. activated with alkaline metals and;
6. Catalysts containing cobalt.

Catalysts containing cobalt result in a fundamentally different product spectrum. The modified methanol catalysts mentioned above lead mainly to the formation of primary isobutanol among other higher alcohols. On the other hand, the catalysts containing cobalt lead to the formation of high

amounts of ethanol. High yields of ethanol were observed by Taylor⁽¹²⁾ working with a catalyst containing Cu, Mn and Co. Operating at 400°C and 200 atm at high space velocities, the selectivity to ethanol was up to 22 wt percent. High selectivities of ethanol equivalent to 29 wt percent of the condensed product were also obtained by Klyukvin, et. al.⁽¹³⁾ using a catalyst composed of ZnO:CoO = 3:1, and operating at 320-330°C and 120 atm. In general, the higher alcohols obtained with catalysts containing cobalt are predominantly of the linear type, whereas with the modified methanol catalysts, they appear mainly as the branched type.

A marked change in product composition was noted by Rao, et. al.⁽¹⁴⁾ in their recent work on the synthesis of gasoline range hydrocarbons from synthesis gas. The incorporation of cobalt into the catalyst (Fe/ZSM-5) reduced the aromatic fraction and increased the olefinic and oxygenate fractions. They also found that the extent of the water gas shift reaction was substantially reduced with this cobalt-promoted catalyst.

High yields of methanol and iso-alcohols, in particular isobutanol, were obtained by BASF⁽¹⁵⁾ with catalysts containing oxides of zirconium, indium, titanium and potassium at 435°C, 250 atm and space velocities (NTP) of 7500 hr⁻¹.

2. Recent Literature Review

In the previous section, we reviewed the early literature regarding synthesis of alcohols from carbon monoxide and hydrogen. In this section, we have summarized more recent developments in synthesis gas conversion catalysts.

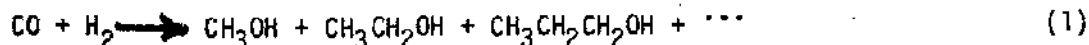
Until recently, the synthesis of methanol was carried out at high pressures (usually greater 250 atms) and temperatures (in the region of 400°C). Improvements in catalyst performance by ICI⁽¹⁶⁾ have enabled the synthesis reaction to be operated at lower pressures and temperatures. The ICI catalyst comprised of copper-zinc-alumina operates at 50-60 atms and in the range of 260°C. Similar breakthroughs in the

developments of low pressure catalysts for methanol synthesis were made by Lurgi⁽¹⁷⁾ using a copper-based catalyst and Japan Gas Chemical⁽¹⁸⁾ using a copper-zinc-chromium formulation.

Although not in commercial use, supported precious metal catalyst including Pt, Pd, Rh, Ir were widely employed in the mechanistic studies of both Fischer-Tropsch and methanol synthesis^(19,20) from carbon monoxide and hydrogen. These catalysts were very selective for methanol or two-carbon oxygenates such as acetic acid, acetaldehyde and ethanol.

A considerable amount of industrial research has also focused on liquid-phase homologation routes to higher alcohols. According to the current state-of-the art, very high reaction pressures are required, reaction rates are less than practical and selectivity is low. The active catalyst species for the reactions of methanol with synthesis gas is generally believed to be a cobalt carbonyl complex. Recently, a similar homologation reaction with methanol and synthesis gas was carried out using a supported precious metal catalyst⁽²¹⁾. The major product from this reaction was ethanol⁽²²⁾, but a recent result by Koermer, et. al.⁽²³⁾ shows that the homologation reaction is not so selective to ethanol as previously reported. They were able to identify more than twenty reaction products. The selectivity to ethanol was about 40 percent at a methanol conversion of 30-50 percent. Attempts to improve the selectivity or activity of the cobalt catalyst via various ligand additions such as phosphines, amines, nitriles, pyridines, and phenols, and via co-catalysts consisting of other metal carbonyls of iron, chromium, and rhenium or soluble metal complexes of rhodium, platinum, copper and vanadium, have not been successful.

In 1978, Institut Francais du Petrole (IFP)⁽²⁴⁾ reported that when using a catalyst containing a mixture of copper and cobalt oxides and alkali metal salts along with the oxides of either chromium, iron, vanadium or manganese, much higher yields of normal unbranched alcohols with two or more carbon atoms, particularly ethanol, can be obtained.



At 121°C and 60 atm, conversion was 35 percent per pass. The selectivity to alcohols was reported to be over 95 percent with carbon dioxide and methane accounting for the major portion of the yield loss. Selectivity to normal two carbon or higher alcohols was in excess of 71 percent with ethanol being the major product. In contrast to the isobutanol synthesis, the branched and/or iso-alcohol to normal linear alcohol ratio was quite low. The rate of alcohol formation was high compared to Fischer-Tropsch processes, and reaction temperatures and pressures were moderate.

A variety of catalyst compositions have been reported by IFP to be effective for alcohol production. A typical product distribution of alcohols is shown below:

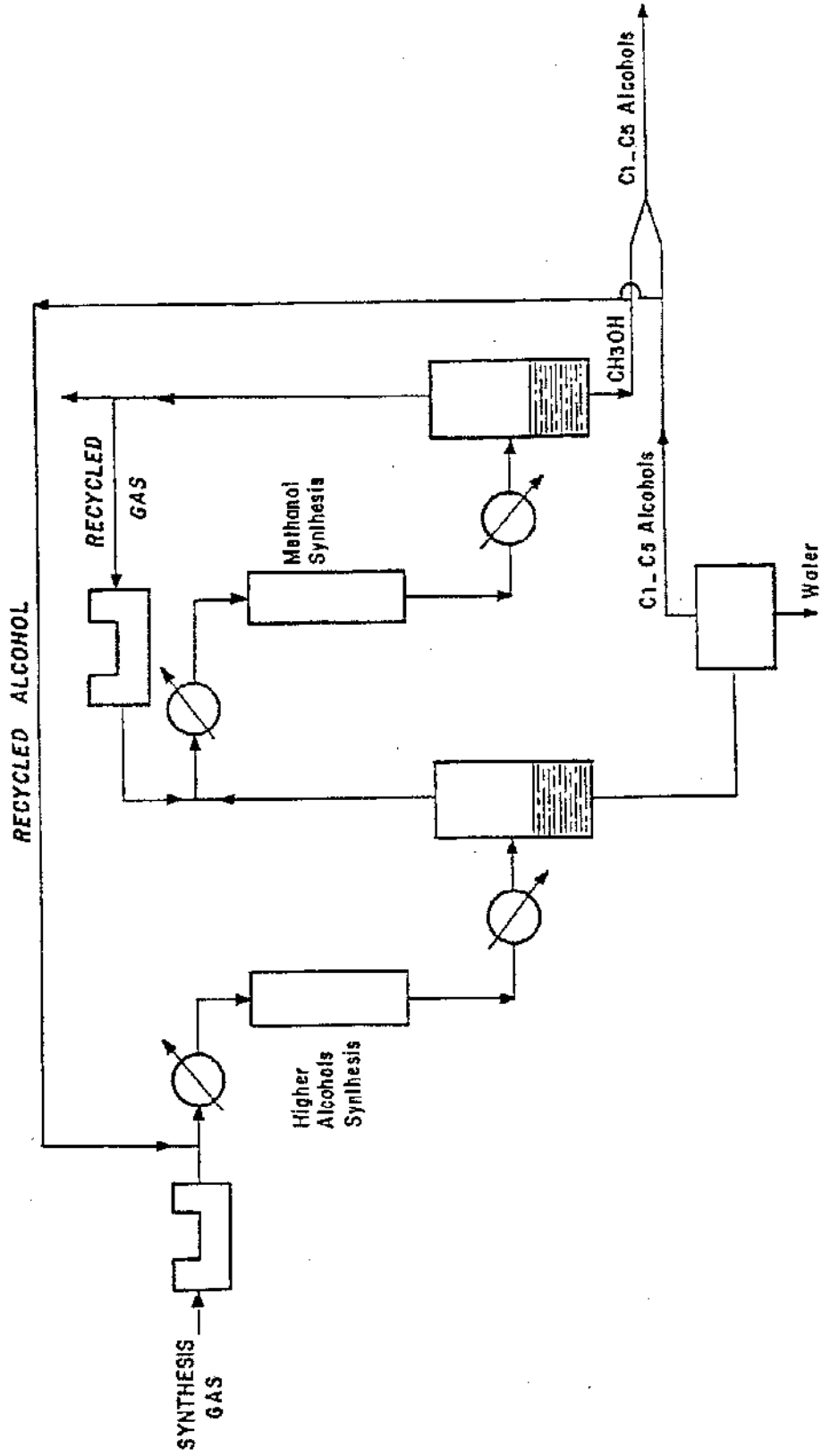
TABLE V-1
TYPICAL ALCOHOL PRODUCT DISTRIBUTION
(weight percent)

Methanol	20
Ethanol	38
n-Propanol	21
i-Propanol	3
n-Butanol	17
i-Butanol	--
TOTAL	<u>99</u>

The IFP process is described in Figure V-1. Synthesis gas is compressed to a pressure of 60-100 atms and is then sent to a higher alcohols synthesis reactor where 15-20 percent of the gas is transformed. The unreacted synthesis gas is not recycled but sent to a separate methanol synthesis unit. The reaction product (alcohols and water) is sent to the separation section, where water is removed from the mixture, so that the alcohols (C₁-C₅) can subsequently be mixed with the methanol produced in the methanol unit. If an increased production of higher alcohols is required, at least a fraction of the methanol and the ethanol is recycled to the higher alcohols synthesis reactor. As a consequence of this recycling, the unwanted methanation reaction will be greatly reduced. IFP's economic evaluation shows that, due to the fact that the synthesis gas is not recycled through the higher alcohols section, this process has the potential to produce a cheap mixture of alcohols suitable for use as a

FIGURE V-1

IFP'S C₁-C₅ ALCOHOLS FROM SYNTHESIS GAS PROCESS



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gasoline blending component. An interesting point made by IFP is that their methanol and higher alcohols catalysts are not pelletized but are made as spheroid droplets that have a certain size distribution that can be altered. They saw no problems in making a slurry catalyst in the 20 to 100 micron range.

IFP also filed a U.K. patent application⁽²⁵⁾ for a process to manufacture alcohols similar to the earlier method described in West German and U.S. patents⁽²⁴⁾. The major difference is the enlargement of the scope of catalyst composition to include 5-40 percent of a rare earth metal in addition to copper, cobalt, alkali or alkaline earth metal and a transition metal of atomic Number 23 to 26 inclusive. The catalyst can also contain zinc and/or a noble metal from Group VII of the periodic table. The following catalyst formulations were reported to result in high space yields and selectivities of 90-98 percent higher alcohols:

1. $\text{CuCoCr}_{0.8}\text{K}_{0.09}$
2. $\text{CuCoMn}_{0.8}\text{K}_{0.12}$
3. $\text{CuCoFe}_{0.8}\text{K}_{0.12}$
4. $\text{CuCoV}_{0.8}\text{K}_{0.12}$
5. $\text{CuCoCr}_{0.5}\text{La}_{0.3}\text{K}_{0.09}$
6. $\text{CuCoCr}_{0.5}\text{Ce}_{0.3}\text{K}_{0.09}$
7. $\text{CuCoMn}_{0.5}\text{Nd}_{0.21}\text{Pr}_{0.09}\text{K}_{0.09}$
8. $\text{CuCoFe}_{0.5}\text{La}_{0.3}\text{K}_{0.09}$
9. $\text{CuCoV}_{0.5}\text{La}_{0.3}\text{K}_{0.09}$
10. $\text{CuCr}_{0.4}\text{Co}_{0.8}\text{AlBa}_{0.1}$
11. $\text{CuCr}_{0.2}\text{Co}_{0.8}\text{Al}_{0.4}\text{La}_{0.8}\text{Ba}_{0.1}$

A recent development in ethanol production from synthesis gas was reported by Gulf⁽²⁶⁾ for a two-step process to convert synthesis gas to methanol over Cu-Zn synthesis catalyst followed by methanol homologation using a cobalt carbonyl-type catalyst. The catalyst system for the carbonylation step was prepared from cobalt-rhodium complexes with ligand modifiers such as triphenyl phosphine, triphenyl stilbene or triphenyl arsine and an iodine promoter with iodine/cobalt ratios less than 1.0. The addition of ruthenium to the catalyst also improves selectivity and productivity to

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ethanol. Overall product selectivity consisted of 92 percent "ethyl fuel" (80 percent ethanol, 12 percent methyl acetate), 4 percent dimethyl ether, 1 percent diethyl ether and 3 percent others at a methanol conversion of 30 percent. Optimal operating conditions resulted in a product mix with an ethanol/ methyl acetate ratio of 6.7/1. This mixture and a 50/50 mixture of ethanol and methyl acetate were tested as gasoline extenders. Both blends were added to conventional unleaded gasoline with resulting octane numbers comparable to but slightly lower than those obtained using pure ethanol as an extender. There was no significant difference between the ethyl fuel blends and pure ethanol blends with unleaded gasoline in terms of corrosivity or water tolerance.

In November, 1979, Amoco applied for a European patent⁽²⁷⁾ describing a catalyst system to produce methanol and higher alcohols from synthesis gas for blending with gasoline using a catalyst having the general formula $Cu_aThM_bA_cO_x$ where:

- M = Ca, Mo, Rh, Mn, Pt, Ce, Cr, Zn, Al, Ti, La, V, U, Re, Ru, or Pd
- A = alkali metal
- a = 0.5 - 2.5 atomic ratio
- b = 0.01 - 1.0 atomic ratio
- c = 0.05 - 0.9 atomic ratio

This catalyst system differs from the IFP catalyst system in that it contains no cobalt; must contain thorium as an active element; and is limited to only four metallic species as compared to five for the IFP catalyst system.

In February, 1982, BP⁽²⁸⁾ disclosed a catalytic process for the conversion of synthesis gases to C_1 - C_4 oxygenates utilizing a catalyst system comprised primarily of silver and rhodium supported on silica. The catalyst does not appear to be controlled by a Schulz-Flory mechanism with the predominant products appearing in the C_2 region as ethanol, acetaldehyde and acetic acid. Methanol, propanol and butanols were also reported to be produced at high selectivities. In order to utilize these

products as transportation fuels, additional processing will be required to recover acetaldehyde and acetic acid components from the crude synthesis products and convert them to ethanol.

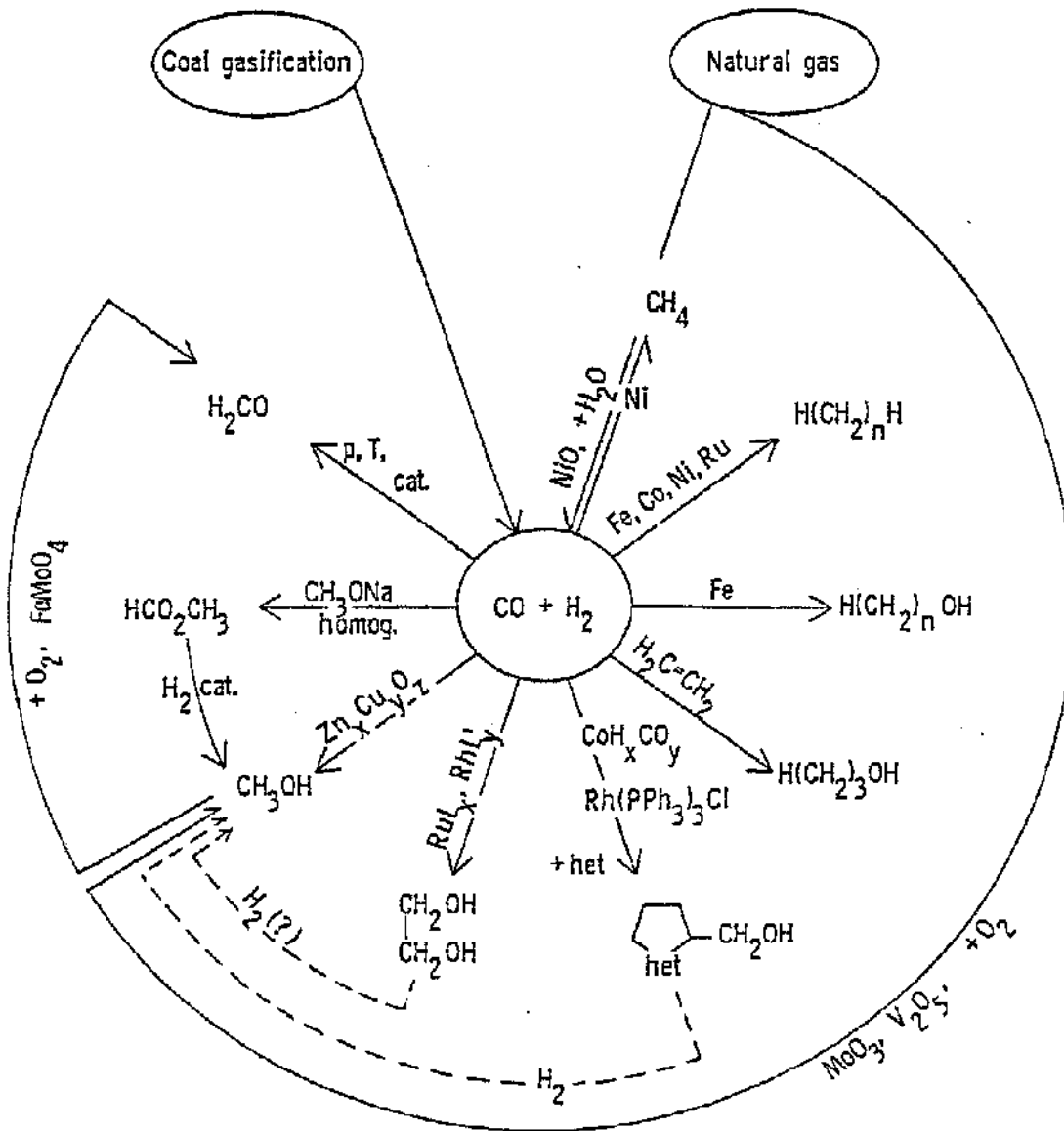
The improved catalyst may contain as much as 10% silver and as much as 10% rhodium. The catalyst can be produced by impregnation of the silica support with a soluble silver compound such as silver nitrate followed by reimpregnation of the silver-impregnated silica with rhodium trichloride. The finished catalyst is produced by evaporation at 120°C followed by reduction at 450°C. Typical synthesis conditions include temperatures of the order of 310°C, pressures of 50 atm and space velocities as high as 50,000 V/hr/V. The high space velocity leads to per pass carbon monoxide conversions below 20 percent but favors the high desired selectivities to C₁-C₄ oxygenates.

In April, 1982, Snamprogetti SPA⁽²⁹⁾ disclosed a process for a mixture of methanol and higher alcohols in the presence of a copper-free oxide catalyst comprised of chromium, zinc and at least one alkali metal, preferably potassium. The catalyst can be prepared by either reduction of a mixture of chromate, zinc oxide and alkali metal hydroxide or by precipitation of chromium and zinc nitrates with ammonia. The ratio of zinc/chromium varies from 5/1 to 1/1 with an alkali metal content of 0.5-5 wt percent as oxide. The preferred reaction conditions are 350-450°C reactor temperature, 49-128 atm reactor pressure and using a synthesis gas having a hydrogen/carbon monoxide ratio ranging from 0.1/1 to 5/1.

3. Review of Chemical Mechanisms

The chemistry of hydrogenation of carbon monoxide is extremely complex and literally hundreds of hydrocarbon and oxygenated products can result. The nature of the catalyst utilized in the synthesis is the key to product selectivity (and productivity). This has been quite effectively depicted by Klier⁽³⁰⁾ in Figure V-2 showing the variety of products that can be obtained by the use of three basic groups of catalysts: metals, organo-metallics, and metal oxides.

FIGURE V-2
REACTIONS OF CARBON MONOXIDE AND HYDROGEN



The following notable researchers have hypothesized mechanisms for the synthesis of higher alcohols which will be briefly summarized below:

1. Fischer-Tropsch (1-4)

Homologation via an acetic acid intermediate

2. Natta (6)

Homologation via formation of fatty acid salt intermediates

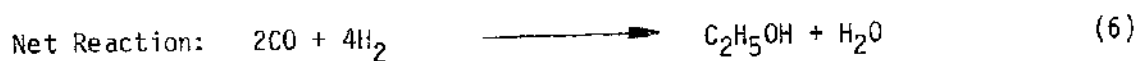
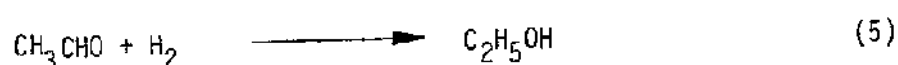
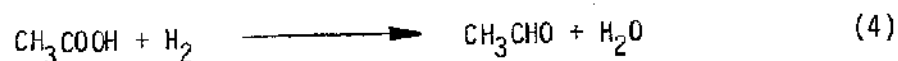
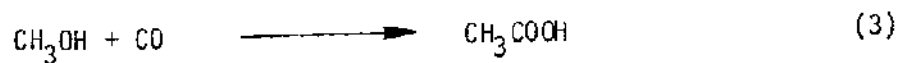
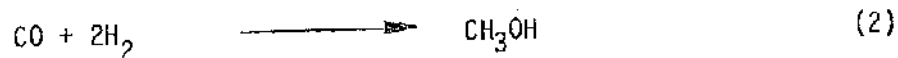
3. Morgan (7)

Aldolic condensation of formaldehyde

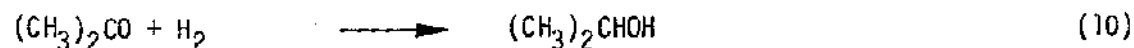
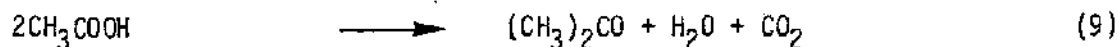
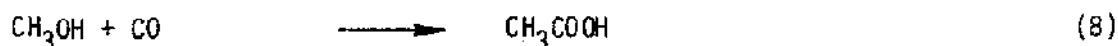
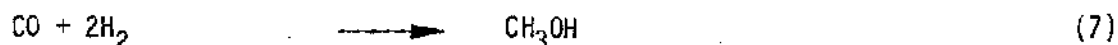
4. Wender (31)

Direct homologation of methanol

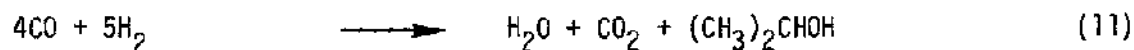
Fischer and Tropsch⁽¹⁻⁴⁾ suggested that higher alcohols are formed by methanol through the following consecutive reactions:



and so forth for primary linear higher alcohols. Iso-alcohols are formed by the transformation of acetic acid into acetone which then undergoes reduction to isopropyl alcohol:



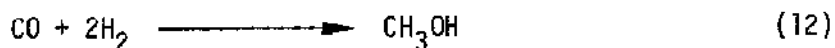
Net Reaction:



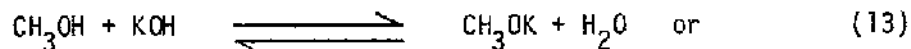
A further addition of carbon monoxide and hydrogen to isopropyl alcohol leads to the formation of isobutyl alcohol.

Natta's hypothesis⁽⁶⁾ implies that the catalysts play a fundamental role in the formation of intermediate fatty acid salts. A five-step consecutive sequence proceeds as follows:

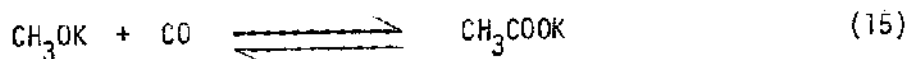
1. Synthesis of methanol by ZnO catalysis:



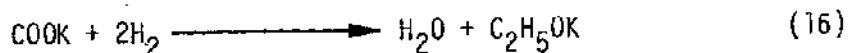
2. Formation of potassium methylate by either reaction with alkali or alkali zincate:



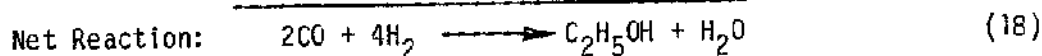
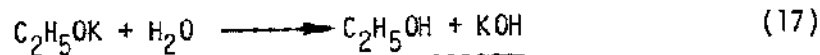
3. Reaction of alkali methylate and carbon monoxide with the formation of alkali acetate:



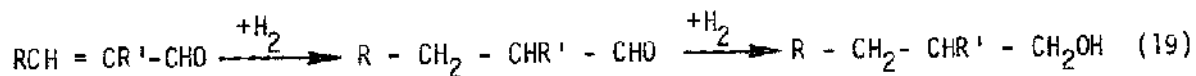
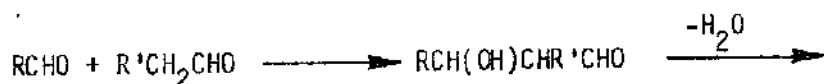
4. Hydrogenation of alkali acetate to alkali ethylate:



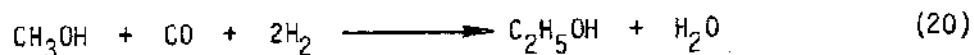
5. Hydrolysis of the alcoholate:



Morgan and coworkers⁽⁷⁾ based their hypothesis upon the fact that a number of aldehydes, including unsaturated and hydroxyaldehydes, have been identified in the synthesis product stream. Presumably, these aldehydes formed through the intermediate formation of fatty acid salts, as in the Natta mechanism. Morgan's hypothesis is that higher alcohols are formed through an aldolic condensation of formaldehyde as follows:

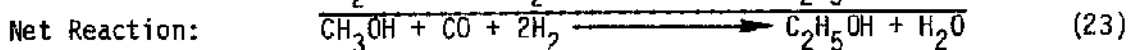
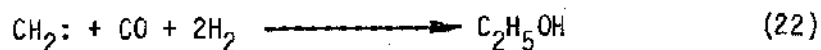
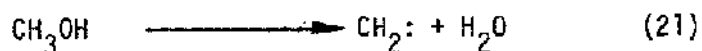


Wender and coworkers⁽²¹⁾ suggested a direct homologation mechanism based on their synthesis of ethanol in the presence of cobalt-based catalysts:



Methanol is more reactive towards homologation than ethanol and synthesis products, therefore, should be richer in ethanol if this mechanism were correct, but this is in contrast with experimental evidence. Natta⁽⁹⁾

has also hypothesized that methanol in place of olefin may participate in oxo-synthesis reactions. In other words, Wender's homologation mechanism can be considered as belonging to the oxo-synthesis reaction type if the formation of free methylene radicals through dehydration of methanol is assumed:



Further homologation of ethanol by formation of ethylidene radicals can hydroformylate to form propanol and so on. However, the rate of reaction of these higher homologations becomes decreasingly lower as carbon number increases.

Several other hypothesis have been formulated by various investigators but none of them appear to be entirely satisfactory. A review of these is presented by Emmett⁽¹¹⁾. From these reviews, the following conclusions can be made:

- Methanol is an intermediate product in the synthesis of higher alcohols;
- Higher alcohol synthesis is a strong function of basicity of the catalyst;
- Above 400°C with ZnO-based catalysts, isobutanol and n-propanol are formed in large proportions along with methanol;
- Below 400°C, higher alcohols can be produced when using certain transition metal catalysts (in particular, metals of the iron group);

- Catalysis with metals of the iron group (or with ThO_2) results in hydrocarbon formation together with higher alcohols. With ZnO-based catalysts in the absence of iron group metals and dehydrating catalysts (like alumina), the formation of hydrocarbons is almost completely prevented.

4. Schulz-Flory Distribution

Fischer-Tropsch synthesis has been considered to be a polymerization process since the molecular weight distribution of the primary products, i.e., hydrocarbons and alcohols, obeys the Schulz-Flory distribution of the primary products, i.e., hydrocarbons and alcohols, obeys the Schulz-Flory distribution equation. Consequently, the process may be treated in terms of polymerization kinetics for mechanistic evaluations.

A theoretical analysis of the molecular size distribution was first formulated by Schulz⁽³²⁾ for the case of radical polymerization of vinyl monomers, i.e., addition polymerization. Flory⁽³³⁾ published his equation for the case of linear condensation polymers. Both equations are essentially equivalent, although entirely different sets of conditions were used. Later, a similar distribution equation was developed by Friedel and Anderson⁽³⁴⁾ including branched products resulting from Fischer-Tropsch synthesis.

The Schulz-Flory distribution of molecular weights is given by⁽³⁵⁾:

$$M_p = (1-a)^2 P a^{P-1} \quad (24)$$

Where M_p represents the weight fraction of the polymers of a certain degree of polymerization P (here same as the number of carbons in the chain), and "a" is the probability of chain growth defined as:

$$a = \frac{g_p}{g_p + g_t} \quad (25)$$

Where g_p = rate of chain growth;
 g_t = rate of chain termination.

According to the mechanism suggested by Henrici-Olive and Olive⁽³⁶⁾, the chain termination reaction is the same as the chain transfer reaction in the course of which the chain leaves the metal, and a new chain can be started at the metal.

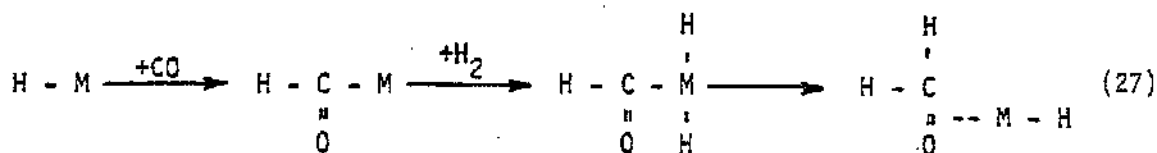
The above Schulz-Flory equation may be expressed in logarithmic form:

$$\ln \frac{M_p}{P} = 2 \ln (1-a) + (P-1) \ln a \quad (26)$$

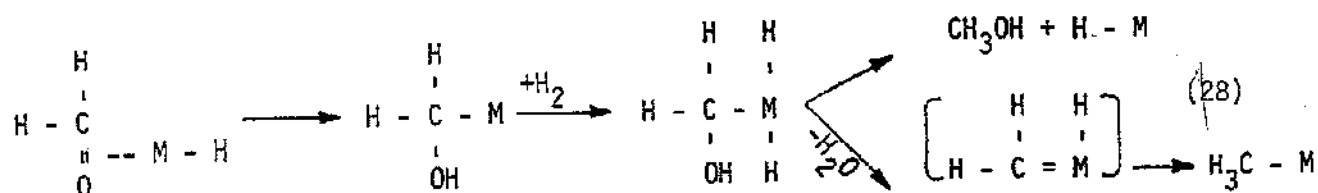
The weight fraction, M_p is the sum of olefins and paraffins, having the same carbon number, P . In our system in which a mixture of paraffins, olefins, alcohols and other oxygenates are formed, we have modified the Schulz-Flory definition of M_p to include the cumulative weight fraction of all products having the same carbon number, P .

If the graphical representation of $\ln M_p/P$ vs. P gives a straight line, and "a" determined from the slope ($\ln a$) and "a" determined from the intercept (at $P = 0$) are in good agreement, the molecular weight distribution obeys the modified Schulz-Flory distribution law. It also permits the estimate of the highest attainable selectivity for a given molecular weight range for a given "a". We have computed the Schulz-Flory probability parameters for several of the catalysts tested in the Bertly, plug-flow, and slurry reactors, and the resultant data are presented in Section V-D.

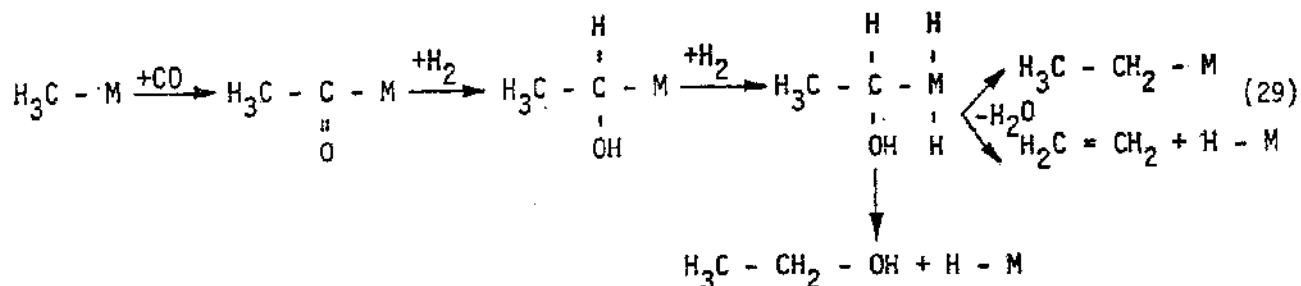
A mechanism for chain growth to produce higher alcohols with the product distribution following that of Schulz-Flory^(33,34) was suggested by Henrici-Olive and Olive⁽³⁶⁾. This mechanism is described here. The first step involves carbon monoxide insertion into the M-H bond, followed by hydrogen addition to the metal center, and scission to formaldehyde and metal hydride:



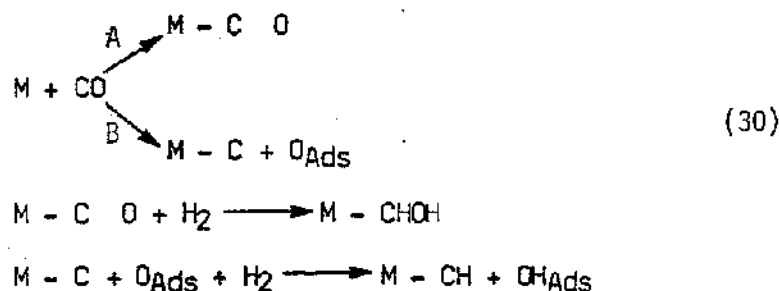
The next step is a rearrangement between the hydride and the C=O function of the aldehyde, followed by another addition of hydrogen to the metal center. The resulting intermediate then can proceed either to give methanol and a metal hydride to initiate another kinetic chain, or to rearrange to give a methyl ligand after elimination of water:



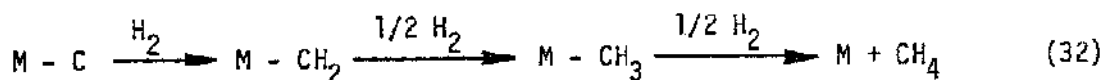
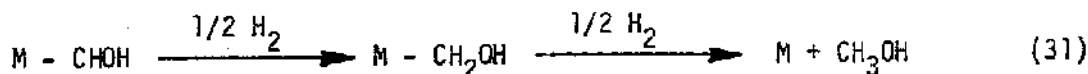
The chain growth continues by carbon monoxide insertion, followed by hydrogen addition (similar to earlier steps). The carbon chain is now increased by one unit. The resulting intermediate can react further either to produce ethanol and metal hydride, or to form an alkyl group by hydrogen elimination. These alkyl metal compounds may continue the chain propagation by carbon monoxide insertion, or produce alpha-olefins (i.e., ethylene) by hydrogen abstraction. Metal hydrides newly formed via alcohol and alpha-olefin formations initiate the kinetic chain:



There is recent evidence to suggest that for higher alcohols production, a catalyst must possess sites capable of adsorbing carbon monoxide associatively with hydrogenation to methanol or a methanol-like intermediate and also dissociatively with formation of a hydrocarbon intermediate⁽³⁷⁻⁴¹⁾, i.e.,

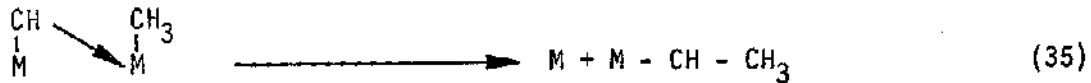


Where M is an active metal or metal oxide site. M - CHOH and M - C can undergo facile hydrogenation as follows:



Both modes of adsorption A and B are important and in addition, the two sites which promote the two types of adsorption must be in proximity so that the methanol-like and hydrocarbon-like moieties can interact to produce higher alcohols (and higher hydrocarbons). This suggests an extremely well dispersed catalyst, i.e., a "homogeneous" heterogeneous catalyst:

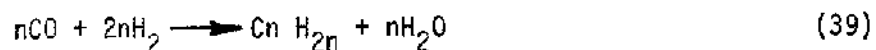
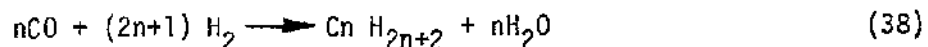
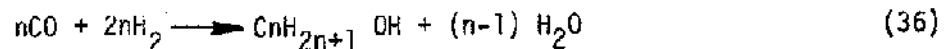




There is some evidence to say that in general, associative adsorption of carbon monoxide takes place on metal oxides (e.g., carbon monoxide on Cu^{I} in $\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}\text{O}_x$, which is the active site for methanol formation) although it can take place on metals. Dissociative adsorption of carbon monoxide takes place on metals (e.g., carbon monoxide on cobalt, nickel) although it is possible that metal oxides are involved as well.

5. Other Considerations

An analysis of the thermodynamics and stoichiometry of the ALKANOLS synthesis reactions was performed. The ALKANOLS synthesis is based on the following generalized reaction stoichiometries:



Reaction (36) represents the primary alcohols synthesis reactions. When n is unity, as for the case of the methanol synthesis, reaction (36) is equilibrium-limited. For higher alcohols, the equilibrium is far to the right with essentially complete conversion of carbon monoxide to higher alcohols possible. Reaction (37) represents the water-gas shift activity of the ALKANOLS synthesis catalysts. The last two reactions represent the Fischer-Tropsch activity of the catalyst with reaction (38) being the route to producing paraffinic hydrocarbons and reaction (39) being the route to olefinic hydrocarbons.

Table V-2 summarizes the theoretical stoichiometry and thermodynamic limitations of the three synthesis gas conversion processes for a hypothetical synthesis gas containing hydrogen and carbon monoxide only. The data in the table indicate that the range of energy content of synfuel products derived from the conversion of synthesis gas varies from 93,000 Btu/lbmol of synthesis gas (lower limit - all hydrocarbon product) to 104,374 Btu/lbmol of synthesis gas (upper limit - methanol). It is obvious that any synthesis gas conversion route results in downgrading the energy content of the neat synthesis gas.

B. Catalyst Preparation Procedures

1. Classification of Catalyst Types

Seven main types of catalyst preparations were used. They are: a) evaporation of metal salt solutions; b) coprecipitation; c) impregnation of active catalyst species onto supports; d) impregnation of metal salts onto existing catalysts; e) detergent dispersion; f) cobalt carbonyl impregnation; and g) mechanical blending of metal nitrates or oxides. Moreover, these catalysts have been classified (see Appendix) according to eight general group types based on composition.

2. Preparation Methods

a. Evaporation

In this method, a solution of metal nitrates was prepared in deionized water such that the atomic ratios of the metals in solution were the same as those of the desired catalyst formulation. About 0.1 mole of a complexing agent (usually citric acid) per mole metals was added to the solution, which was then evaporated at 100°C to form a viscous glassy mass. The resultant material was then calcined according to the temperature program shown in Figure V-3.

Sterotex HM, a fatty acid-based lubricant and binder, was added in an amount to make up 3 wt percent of the catalyst mixture. The resultant catalyst mixture was then pelletized using one of two procedures. The

TABLE Y-2

COMPARISON OF STOICHIOMETRY AND THERMODYNAMICS
OF SYNTHESIS GAS CONVERSION PROCESSES

<u>Synfuel</u>	<u>Energy Content</u>		<u>Volumetric</u>
	<u>Btu/lbmol</u> <u>Syn Gas</u>	<u>% of</u> <u>Syn Gas</u> <u>Content</u>	<u>Yield</u> <u>Gal/lbmol</u> <u>Syn Gas</u>
<u>Syn Gas</u>	122,439	100.0	--
<u>Methanol Synthesis</u> (CO + 2H ₂ → CH ₃ OH)	104,374	85.2	1.62
<u>ALKANOLS Synthesis</u> (2CO + 4H ₂ → C ₂ H ₅ OH + H ₂ O)	98,000	80.0	1.17
(3CO + 6H ₂ → C ₃ H ₇ OH + 2H ₂ O)	96,000	78.4	1.03
(7CO + 14H ₂ → C ₇ H ₁₅ OH + 6H ₂ O)	94,705	77.3	0.81
<u>MTG-Gasoline</u> (8CO + 16H ₂ → C ₈ H ₁₆ + 8H ₂ O)	93,000	76.0	0.77

FIGURE 4.3
TEMPERATURE PROGRAMMING OF CALCININS OVER

