VI. Fischer-Tropsch Catalysis

Although it is not readily apparent why the Electric Power Research Institute should support further research on the Fischer-Tropsch synthesis for the production of liquid fuels, the decision by the electric power industry to use jet aircraft turbine engines to generate peaking power makes such support necessary. Gas turbine engines have proved to be cheaper and more efficient than other means of generating electric power on a part-time basis. Since these engines run on jet fuels, the electric power industry should indeed be interested in processes for converting coal into these fuels.

A study by the National Electric Reliability Council predicts that in 1982 gas turbine engines will generate 67.3 million kilowatts of electricity using a total projected consumption of one million barrels of oil equivalent per day, made of half a million barrels of oil plus an equal amount of natural gas. These large numbers make it clear that refinery products are necessary for generating electric power during peaking periods, at least in the short run. Therefore, there is a very good reason to study processes for the production of these materials from coal.

According to W. K. Hall, "If we are to convert coal into liquid fuels, it seems almost certain that a large volume will be by the coal hydrogenation route to produce synthetic crude. This crude will vary markedly in composition from petroleum crudes in that it will be highly aromatic and contain a large polynucleararomatic fraction. Further hydrogenation of this crude will yield mainly light paraffins and aromatics with relatively short side-chains." Some of the paraffinic fraction between C_6 and C_{16} will be missing. This fraction is important in the production of fuels and can be supplied for blending using a Fischer-Tropsch synthesis. The fuels derived from this synthesis will be very clean with regard to ash and mineral content.

One of the limiting factors in earlier economic considerations of the Fischer-Tropsch synthesis was the large amount of methane produced, which was considered an economic loss. This should now be considered as a profitable by-product. (In fact, W. K. Hall suggests that enough methane can be made this way to make separate methanation plants unnecessary.) Within certain limits, the gas-to-oil ratio can be varied to meet seasonal and other demands. These gaseous and liquid fuels will burn more cleanly than coal since almost all of the sulfur will be removed during the processing.

The Fischer-Tropsch synthesis can produce a wide spectrum of liquid hydrocarbons from the synthesis gas produced in the primary coal gasification. The product distribution depends on the catalyst and reaction conditions used. There has been a large amount of work investigating catalysts for the reactions, particularly in conjunction with gasoline production in Germany prior to and during World War II, followed by investigation by the U.S.Bureau of Mines. The Sasol Plant in South Africe, operating with a capacity of 9000 bbl/day, has demonstrated the technical feasibility of the process.

However, the cost is still high and the Sasol Plant survives mostly because South Africa has no petroleum reserves and the government controls the plant operation, the gasoline market, and the petroleum imports.

The commercial synthesis in Germany from 1938 to 1944 used a catalyst composed of 100 Co: $5ThO_2$: 8MgO: 200 kieselguhr by weight. With the use of pressures of 5-15 atmospheres, the use of iron-alkali catalysts that were insufficiently active at lower pressures and temperatures came into use. Ruthenium catalysts at high pressures resulted in the production of very high molecular weight hydrocarbon waxes.

Perhaps if it is found that some hydrocarbon mixture that can be used as a fuel can be more readily or cheaply synthesized, some turbine generators could be modified to utilize this new fuel. Hydrocarbon mixtures that can be used without elaborate separation and refining steps should be given consideration in this regard. Methanol would not need refining and can be made by a Fischer-Tropsch synthesis. It will most likely be an excellent turbine fuel.

Recommendations

Further progress in the development of new and improved processes for the Fischer-Tropsch production of jet fuel and methanol will be more rapid when the mechanisms for the synthesis are more clearly understood. As is generally true with reaction systems that have immediate industrial application, studies of the kinetics and mechanisms of these syntheses have lagged behind the practical development studies. In most instances, the data available are limited to very specific catalysts over limited temperature and pressure ranges. Iron catalysts for the Fischer-Tropsch synthesis have been studied relatively extensively by physical chemists at the Bureau of Mines and elsewhere, by relatively modern methods. The ZnO and $ZnO \cdot Cr_2O_3$ methanol catalysts have also been extensively investigated. Nickel methanation catalysts have not yet been studied as extensively. According to R. B. Anderson, "The current work of the Bureau of Mines on sprayed Raney nickel is a remarkable development involving a fortunate intuitive engineering attack without appreciable scientific support." The following recommendations are designed to provide the needed scientific support.

The most obvious need is for improved catalysts for the Fischer-Tropsch process to produce liquid fuels including methanol. Although many materials have been tested for catalytic activity in these systems, there has not been much improvement since the 1930's. However, that doesn't mean that we should stop searching. The catalytic synthesis of ammonia which was developed in Germany in the 1908-1913 period has been studied more extensively during the last 60 years than any other catalytic reaction. Only recently, revolutionary nonferrous catalysts, severalfold more active than standard iron catalysts, have been prepared by Ozaki which throw new light on the mechanism of the catalytic synthesis of ammonia.

The desirable improvements in Fischer-Tropsch catalysts are:

1. <u>More Active Catalysts</u> (Catalysts useful at higher hourly space velocities)

The hydrogenation of carbon oxides in the processes we are considering are relatively slow reactions on the basis of weight of useful product per unit volume or weight of catalyst. The Synthane Process at the Bureau of Mines operates at ~2000 hourly space velocities, and the German Ruhrchemie Fischer-Tropsch plant operated between 1938 and 1944 used only 60-100 hourly space velocities. For comparison, space velocities of 20,000 or higher are used in the conventional ammonia synthesis. The relatively low space velocities now possible lead to a requirement for very large reactors which raises the capital equipment cost of the processes. More simply stated, the less active a catalyst is, the more of it that must be used to obtain a satisfactory conversion rate. (The methanol synthesis is now carried out at high space velocities [40,000-50,000 hr^{-1}], so this is not a problem in methanol production.)

One advantage of a more active catalyst for the Fischer-Tropsch Synthesis is that Producer gas which is cheaper than Synthesis gas could be used as a feed gas. Producer gas contains nitrogen and, therefore, the reactants (H_2 + CO) are diluted. However, experiments have shown that at the same space velocity, replacement of 16%-30% of the H_2 + CO by N_2 results in slightly larger yields of liquids and solids per cubic meter of ($2H_2$ + 1 CO). However, the volume of CO converted per volume of catalyst per hour decreases so that the increased yield doesn't compensate for the decreased volume of the reactants flowing over the catalyst. If higher space velocities could be used, then the dilution effect would be minimized and Producer gas would do nicely for the Fischer-Tropsch synthesis. (This is not true for methanation since the nitrogen would dilute the final product and lower its heating value.)

In order to find more active catalysts, R. B. Anderson recommends that small-scale studies should "examine metal catalysts including the iron-group metals and ruthenium, and other metals that are not normally effective in hydrogenation of oxides of carbon. Here, highly dispersed metals in the form of alloys and interstitial compounds such as carbides, nitrides, and borides should be tested."

2. Durability

In order to lower the operating costs of the processes under discussion, catalysts must be found that are active for long periods of time. The Raney nickel catalyst used in the Bureau of Mines' Synthane Process has proved to be useful for a period up to about four months. After this, there is a steady decrease in the amount of methane produced. The cobalt-based catalyst used by the Ruhrchemie Fischer-Tropsch plant during World War II had a useful lifetime of only about six months. This problem is greater in plants using fixed-bed catalysts than in those employing a fluidized catalyst since the fixed-bed plant must shut down for a short period of time to replace the catalyst when it becomes inactive, whereas the fluidized-bed plant can continually introduce new catalyst into the reaction system.

According to R. B. Anderson, "of immediate concern are iron-catalysts for the Fischer-Tropsch Synthesis that will withstand disintegration by elemental carbon deposition and oxidation, and for nickel methanation catalysts resistant to deactivation by elemental carbon deposition and carbide formation." For iron catalysts, the synthesis gas is initially a reducing and carbiding reagent but, as the H_2 and CO are consumed, H_2O and CO_2 become large enough to oxidize the metallic iron and iron carbides.

Since the reactions between CO and H_2 are highly exothermic, heat must be removed from the reaction chamber or the resulting temperature rise will sinter the catalyst, rendering it inactive, or lead to carbon deposition or carbide formation (which is all right for iron catalysts but not for cobalt or nickel). Carbon deposition is determined by the H_2:CO ratio, as well as by the conditions and catalysts used. Although it may have only a small effect on catalytic activity, it results in poor process efficiency and operating difficulties which arise from the carbon plugging the reactor tubes. This heat removal problem will become even more important when more active catalysts are found.

Longer-range research on other deactivation mechanisms and techniques for reactivation is also necessary. Also, catalysts must be developed with greater resistance to sintering at the higher temperatures that will result from higher hourly space velocities. The problem of catalyst life is extremely complex and more fundamental catalyst research must be done before concrete suggestions for maintaining and increasing catalyst lifetimes may be made.

3. Greater Tolerance to Sulfur

We are interested in producing low-sulfur fuel products since it is cheaper and easier to remove the sulfur as H_2S during processing than to remove it from the stack gas as SO_2 after combustion. Therefore, catalysts that will operate on raw, sulfur-containing synthesis gas may be of little economic value. However, the iron, cobalt, and nickel catalysts now in use are poisoned by sulfur in the synthesis gas in amounts greater than 1 to 2 mg.S/m^3 (0.7-1.4 ppm).

Increasing this limit to 5-10 ppm would bring the sulfur content within the capability of the hot carbonate scrubbing process for H_2S and COS. Removal of organic sulfur, mainly thiophenes, to this level would require other treatment such as activated charcoal or iron oxide. Molybdenum and tungsten-based catalysts have been tested since they are resistant to sulfur poisoning. However, these catalysts have very little activity for catalyzing Fischer-Tropsch reactions.

4. <u>More Selective Catalysts</u>

The products of the Fischer-Tropsch synthesis are very sensitive to the choice of the catalyst to be used. An important advantage of iron catalysts over those of cobalt is that they impart a great flexibility to the process. By variation in catalyst composition, method of preparation, method of reduction, composition of synthesis gas, and temperature and pressure condition, the reaction can be regulated for the production of a large fraction of wax, or gasoline, or jet fuel, or olefins, or alcohol, or high BTU gas.

In addition to the problem of catalyst development, the design of reactors for these processes involves difficult engineering problems, particularly concerning the removal of the reaction heat. However, R. B. Anderson feels that "these tasks seem within the scope of expertise and experience of chemical engineering in the United States." Designing effective catalysts with physical configurations appropriate to the reactor design (like the Tube Wall Reactor and low pressure-drop catalysts for hot-gas recycle processes) will be a continuing problem in engineering development. Anderson has listed the catalyst requirements for various reactor designs (Table 3).

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Table 3

Catalyst Requirements for Fischer-Tropsch Reactors

	Desirable Catalyst Characteristics*			
Type of Reactor	Activity	Mechanical Strength	Mechanical and Chemical Stability	Press. Drop Catalyst Bed
Externally cooled				
Fixed-Bed	H	M	H	L
Fluidized-Bed	M	H	H	U
Internally cooled, oil phase				
Fixed-Bed	H	M	H	L-M
Agitated-Bed	H	H	H	L-M
Slurry	H	U	U	U
Internally cooled, gas phase				
Hot gas recycle	M	H	H	L

*H = high; M = moderate; L = low; U = unimportant;
L-M = low to moderate

VII. Mechanisms of Bond Breaking in Coal; Center-Ring Cracking of Polynuclear Aromatic Structures

From the molecular standpoint, coal may be thought of as polynuclear aromatic or hydroaromatic structures joined together by short (1-4 carbon atom) aliphatic groups, ether linkages, sulfide and disulfide bonds, and biphenyl-type linkages. In bituminous coals, about 70 to 75% of the carbon is in aromatic rings. Six-membered aromatic rings predominate although significant quantities of five-membered configurations also exist. These account for most of the organic sulfur and some nitrogen. Hydroaromatic structures, where a part of the structure is saturated with respect to hydrogen, are also found. In general, about 15 to 25% of the carbon is associated with hydroaromatic structures. The average size of a fused configuration is about three rings and since some of the rings are single rings, others must be larger than three rings. These multi-ringed aggregates are solids at room temperature.

In order to liquify coal, its molecular structure must be transformed so that it contains very few three-ringed and almost no four- or more ringed aromatic molecules. Liquefaction processes must rupture not only the aliphatic links connecting the aromatic moities, but also must reduce the size of the polynuclear aromatic structures themselves. Since the normal melting point of anthracene (a three-ringed fused structure) is $> 200^{\circ}C$, and the solubility of napthacene (a four-ringed structure) in benzene is only

0.057 grams per 100 grams benzene, the amount of three-ringed or larger aromatic structures in a product that is liquid at room temperature must be limited. (Coals of lower rank contain more hydrogenated hydroaromatic constituents which melt at lower temperatures). Fused polynuclear aromatic structures cannot be ruptured by thermal means alone in the temperature range (400-500°C) used for liquefaction; these processes require catalysts and a considerable quantity of hydrogen. Catalysts are also necessary to promote the removal of organic sulfur as H_2S in order to produce a low-sulfur liquid product.

On the other hand, thermal rupture of the connecting links begins at 325-350°C when bituminous coal is pyrolyzed. Bonds connecting side chains to the clusters and other bonds of similar energy are also ruptured, and the extent of this bond rupture increases as the temperature is increased. Each bond rupture results in two free radicals which are extremely reactive and probably very short-lived. If the fragments are small enough, and if they can be stabilized by the addition of a hydrogen atom or a small radical group (like a methyl group), they will be evolved as part of the tar. If the fragment is too large, it will remain with the char. If no small entity (like a hydrogen atom or small radical group) is available, polymerization of the fragments will occur, yielding char or coke. Some fragments can provide stabilization within themselves through atomic rearrangement. A hydroaromatic fragment, for example, might accomplish this by hydrogen migration. A fully aromatic fragment may abstract a hydrogen **atom** from a hydroaromatic fragment to achieve stabilization. Catalysts are needed which can promote the most desirable stabilization routes and inhibit the others. Moreover, in order to obtain a high yield of liquid product, a very high percentage of the connecting links must be ruptured and this cannot be accomplished in the appropriate temperature range without the aid of a catalyst.

Studies of the catalytic hydrogenation of multi-ringed aromatic compounds (anthracene or phenanthrene) show that the molecule is worn down by saturating at least one end, followed by ring opening and splitting-off of methane and ethylene, then saturation of another ring, eventually yielding only one single-ringed compound (benzene, toluene, xylene, etc.) from each multi-ringed aggregate. Since hydrogenation of the ring precedes ring opening, a hydrogenation catalyst like Co-Mo is usually employed in this step. In order to maximize the yield of single-ringed aromatic compounds for use as high-octane gasoline or fuel oil, a selective catalyst is needed that will cleave a center ring, yielding at least two single-ringed compounds per polynuclear aromatic structure. This catalyst also must not catalyze the further hydrogenation of the single-ringed compounds produced.

Recommendations

According to G. A. Somorjai, "The investigation of the mechanism of bond breaking and coal catalysis is the major scientific question that faces us in trying to carry out important hydrogenation and hydrogenolysis reactions on coal. I am sure that one can develop metal-organic systems and other types of catalysts that would selectively hydrogenate and carry out hydrogenolysis of coal, perhaps even underground." What is needed are studies to determine which chemical bonds in the coal are attacked by which types of catalysts and why. Center-ring cracking is important mainly for the production of distillate from heavy coal liquids and other bond-breaking reactions are important for the conversion of coal to other kinds of heavy liquids that can be burned under boilers to generate electricity. In order to study center-ring cracking, benzanthracene, anthracene, phenanthrene, and napthacene should be used as model compounds. Carbon isotopic labeling would prove helpful in this study.

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