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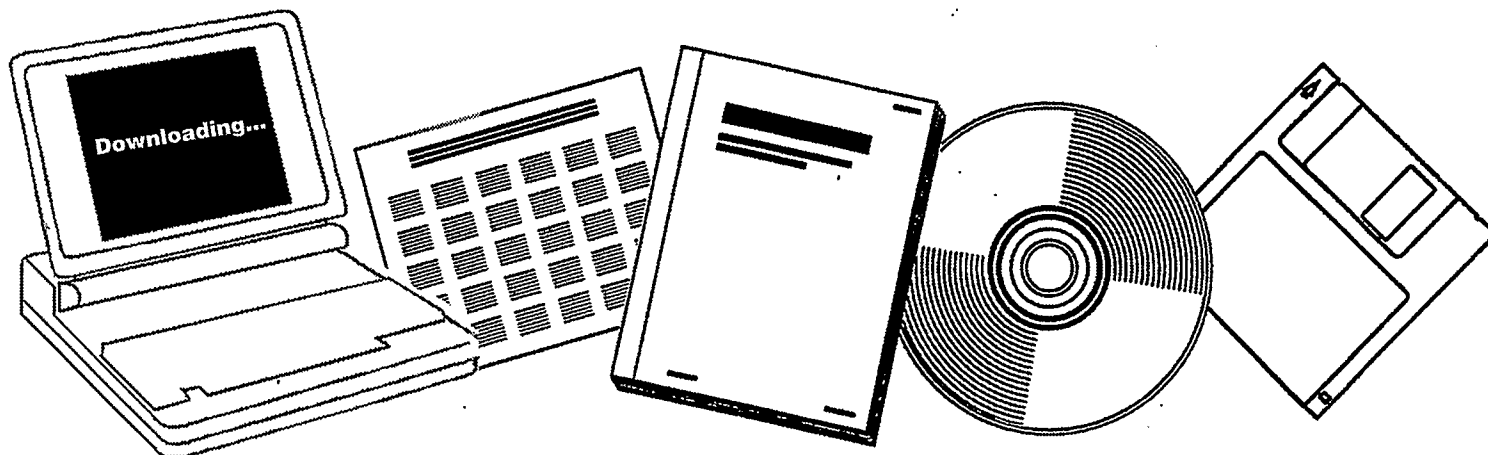
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DOE INDIRECT LIQUEFACTION PROGRAM

DEPARTMENT OF ENERGY, PITTSBURGH, PA.
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DOE INDIRECT LIQUEFACTION PROGRAM

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ABSTRACT

Processes for the hydrogenation of carbon monoxide have had commercial importance since about 1920, when the commercial production of methanol and higher alcohols on oxide catalysts began. Soon thereafter Fischer and Tropsch discovered that liquid hydrocarbons could be synthesized from carbon monoxide and hydrogen over Group VIII metal catalysts. Following extensive catalyst and process development efforts, this technology provided Germany with a source of liquid fuels during World War II. The period following the War saw an acceleration in research and development on the Fischer-Tropsch process, but the only commercial application that was to emerge was the SASOL process in the Union of South Africa.

The oil crises of the 1970's have rekindled worldwide interest in indirect liquefaction technologies for the production of clean, high-quality motor fuels from coal. The development of more efficient coal gasification processes and the advent of molecular sieve catalysts that allow tailoring of product distributions have set the stage for revolutionary improvements in process designs over state of the art technology.

This paper reviews, in brief, the research and development projects that the Department of Energy is sponsoring in the area of synthesis gas conversion to liquid fuels. These projects range from pilot-plant-scale operations, such as the fluidized-bed MTG plant in Wesseling, FRG, to basic research into reaction mechanisms at universities and government laboratories.

INTRODUCTION

As part of the Department of Energy program for the successful production of alternative liquid fuels from coal, the indirect liquefaction program is dedicated to investigating new and significantly improved approaches to the conversion of coal-derived synthesis gas to desirable liquid fuels.

The research and development program that has been formulated involves four major elements:

- o Improved integration of gasification with liquefaction. This involves the use of low H_2/CO ratio synthesis gas in the hydrocarbon formation step.
- o Improved selectivity by use of shape-selective catalysts. Classical Fischer-Tropsch chemistry is subject to limitations due to the chain growth mechanisms. Shape-selective catalysts can circumvent this limitation by an intermediate that can be formed in high selectivity (e.g., methanol) or by inhibition of the chain growth mechanism.
- o More thermally efficient liquefaction reactions. Use of the liquid phase reactor can increase single-pass conversion, thus reducing recycle requirements, can improve temperature control, and can result in the recovery of the heat of reaction at higher temperatures.
- o Simplified product-upgrading methods. Conventional methods for upgrading Fischer-Tropsch liquids lead to a very complex process sequence. The use of new catalyst systems can provide greatly simplified upgrading methods.

The purpose of this paper is to elaborate on the technical background of the research and development projects that the Department of Energy is sponsoring within the indirect liquefaction program.

Mobil Methanol-to-Gasoline Process

Most researchers in the field of synthesis gas chemistry subscribe to the chain growth mechanism for the formation of hydrocarbons from synthesis gas over classical Fischer-Tropsch catalysts (1, 2). According to this mechanism, each hydrocarbon chain developing on the surface of a catalyst has the same probability of continuing to grow by adding one more carbon atom. This type of chain growth is well known in polymer chemistry and may be described by the "Most Probable Distribution" of Schulz and Flory (3). The Fischer-Tropsch product distribution can be controlled, to some extent, by catalyst composition and reaction conditions, although an upper limit is placed on the amount of product that can be formed directly within a given desired carbon number range. For instance, the maximum fraction of the total product that can be formed in the gasoline range is about 50%, which is concomitant with the formation of significant quantities of fuel gas (C_1 and C_2) and heavy wax.

In the early 1970's, Mobil discovered a new family of medium pore (5-6 Å) zeolites that opened a new avenue to the production of fuels and chemicals from synthesis gas. The most publicized member of this family, ZSM-5, converts alcohols and olefins to gasoline in high yield without rapid coking (4). The unique structural characteristics of this zeolite not only inhibit the formation of carbonaceous deposits within the catalyst pores but also restrict the formation of hydrocarbons greater than about C_{11} . Fortuitously, this corresponds very closely to the end point of the gasoline boiling range.

After discovering the properties of ZSM-5, Mobil began work to optimize the catalyst and to develop a process to convert methanol to gasoline. These studies were continued in 1975-1976 under a DOE (formerly ERDA) contract. This work was jointly funded by DOE and Mobil. The results of this project provided data for the fixed-bed Mobil MTG process (5).

Commercialization of the MTG process is in progress. The New Zealand government has decided to build a 14,000 bbl/day liquefaction plant based on the MTG fixed-bed process (6). Natural gas from the offshore Maui Field will be steam-reformed to synthesis gas, which will then be converted to methanol and finally to high octane gasoline via the MTG process (7). About 85% of the total hydrocarbons formed from methanol fall in the gasoline range. This includes the alkylate that can be formed from the light olefins produced. The remaining product consists of LPG and fuel gas (C_1 - C_2).

Mobil is also conducting process development studies on a fluidized-bed MTG process. Again, under a cost-shared contract with ERDA that began in 1976, the Mobil Research and Development Corporation designed, built, and successfully operated a 4 bbl/day fluidized-bed unit (8). Operation of the unit was so promising that soon thereafter the foundation was laid for a cooperative effort to demonstrate the process in a semiworks unit in the Federal Republic of Germany (FRG).

The fluidized-bed version of the MTG process offers several potentially significant advantages over the fixed bed. The fluidized bed allows low pressure operation (270 kPa) and, as a result of good fluidized-bed heat transfer characteristics, may be operated nearly isothermally, with no gas recycle requirements. Another important feature of the fluidized-bed catalytic reactor is that it provides for the continuous withdrawal and regeneration of catalyst, so that optimal catalytic activity can be maintained. The fixed-bed MTG reactors must be taken off-stream periodically to regenerate the catalyst beds by coke burn-off. Operating conditions and product yields for the fixed-bed and fluidized-bed processes are compared in Table 1 (9). These data were obtained from comparably sized process development units.

The semiworks unit in Germany is designed to be capable of converting 100 to 200 bbl/day of methanol into gasoline. The project began in early 1980 as a cooperative agreement between the German Federal Ministry for Research and Technology, the U. S. Department of Energy, and three industrial partners: Mobil, Uhde, and Union Rheinische Braunkohlen Kraftstoff (URBK). The development program, scheduled to be completed in 1986, will examine two methods (Figure 1) for removing the exothermic heat of reaction from the fluidized bed (10). In one mode of operation, the catalyst is continuously circulated to an external heat exchanger, where it is fluidized with inert gas. The catalyst, at a lower temperature, is then returned to the reactor. The second mode of operation involves the direct removal of reaction heat by heat exchanger tubes submerged in the reactor fluidized bed.

TABLE 1. Comparison of Operating Conditions and Product Yields
For Fixed-Bed and Fluidized-Bed MTG Process

<u>OPERATING CONDITIONS</u>	<u>FLUIDIZED-BED</u>	<u>FIXED-BED</u>
Temperature, Avg. Bed, °C	410	-
Inlet, °C	-	360
Outlet, °C	-	415
Pressure, kPa	270	2170
Recycle Ratio, Mole	0.0	9.0
Methanol Space Velocity, WHSV	1.0	1.6
YIELDS, WT% OF METHANOL CHARGE		
Methanol + Ether	0.2	0.0
Hydrocarbons	43.5	43.6
Water	56.0	56.0
CO, CO ₂ , Coke, Other	0.3	0.4
HYDROCARBON PRODUCT, WT%		
Light Gas	5.6	1.4
Propane	5.9	5.5
Propylene	5.0	0.2
i-Butane	14.5	8.6
n-Butane	1.7	3.3
Butenes	7.3	1.1
C ₅ + Gasoline	60.0	79.9
Gasoline (including alkylate)	88.0	85.0
LPG	6.4	13.6
Light Gas	5.6	1.4

Reference: Fitch, F. B., and Lee, W., paper presented at
International Pacific Conference on Automotive Engineering,
Honolulu, Hawaii, November 16-19, 1981.

INTERNAL COOLING

EXTERNAL COOLING

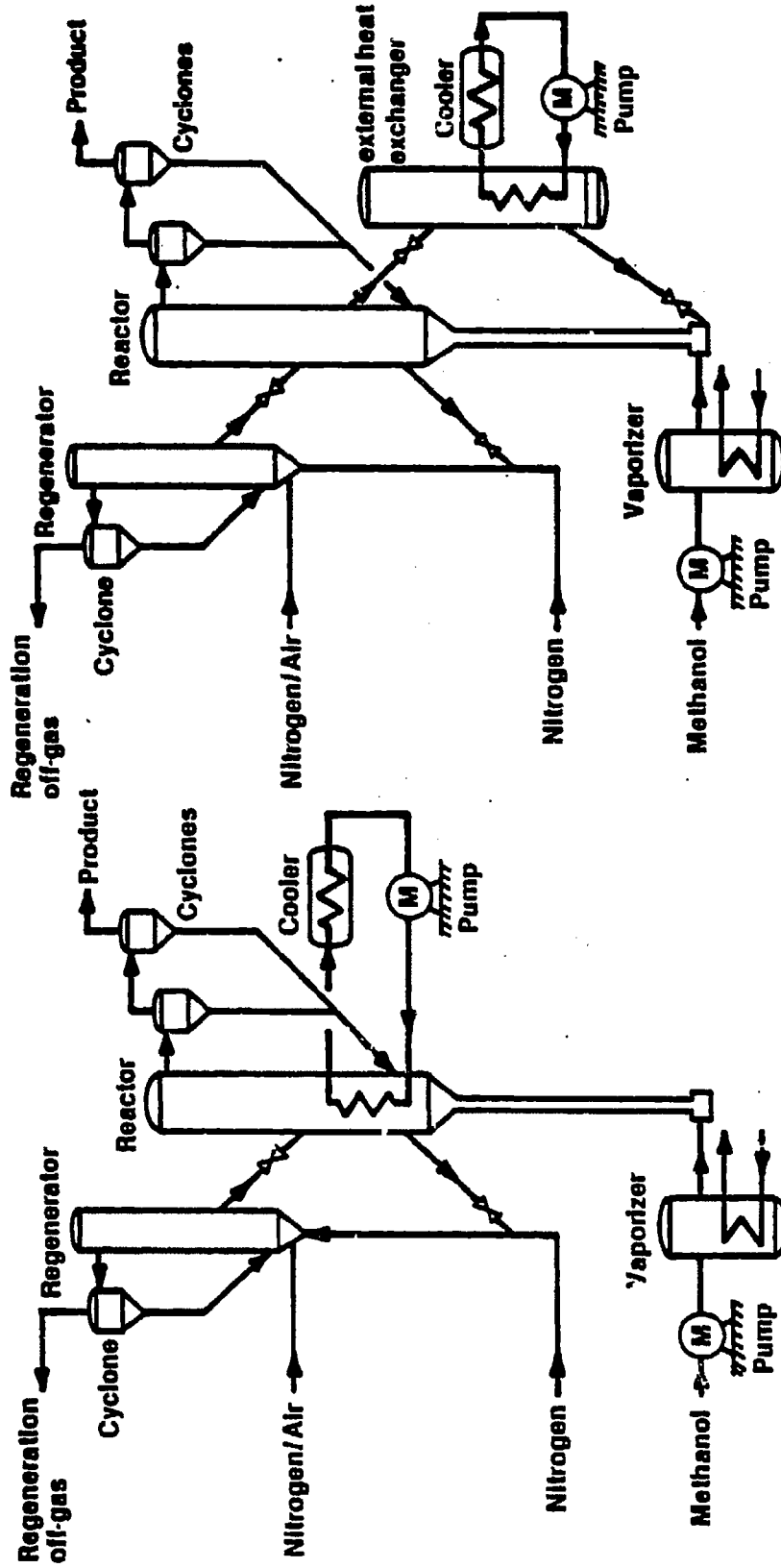


Figure 1. Fluidized-Bed Methanol-to-Gasoline Pilot Plant

Reference: Dolkemeyer, Von W., Flatow, D., Thiagarajan, N., and Gould, R.M., Paper Presented at Synthetic Fuels Conference, Essen, Germany, Nov. 26-27, 1981

Liquid Phase Fischer-Tropsch Synthesis

Synthesis gas conversion reactions are highly exothermic, and good temperature control is required to maintain desired product selectivity as well as minimize adverse side reactions, such as carbon deposition. The three-phase slurry reactor (11, 12), first investigated by the Germans during the 1930's, provides excellent temperature control by the high heat capacity and thorough mixing of the slurry. Coupled with appropriate catalysts having both Fischer-Tropsch synthesis and water-gas shift activity, the slurry reactor is capable of processing low H_2/CO ratio syngas without the rapid catalyst deactivation that would be observed in vapor phase systems.

Air Products and Chemicals, Inc., is exploring the application of three-phase reactors to the synthesis of both hydrocarbons and methanol. In one project (13), jointly funded with the U.S. Department of Energy, a 35 bbl/day unit located in La Porte, Texas, was recently put into operation to provide engineering scale-up data for a liquid phase process developed by Chem Systems, Inc., to convert synthesis gas to methanol. A detailed discussion of this project is given in these proceedings by J. Klosek and R. Mednick.

In a second project (14), also jointly funded with the U.S. Department of Energy, Air Products and Chemicals, Inc., is investigating new catalytic materials with application to three-phase Fischer-Tropsch synthesis. The objectives of this work are to improve the yield of gasoline- and diesel-range hydrocarbons and to investigate the hydrodynamic behavior of bubble columns.

The advantages of the three-phase reactor led the Mobil Research and Development Corporation to investigate the feasibility of converting low H_2/CO ratio synthesis gas to high octane gasoline in a two-stage process, using a slurry phase Fischer-Tropsch reactor in the first stage, followed by an upgrading reactor containing a ZSM-5 class catalyst (15). Mobil is currently conducting this study, under a jointly funded contract with the U. S. Department of Energy, with a slurry bubble-column reactor (5.2-cm-diameter x 7.6-m-tall), followed by a fixed-bed reactor containing the upgrading zeolite catalyst (16). Heavy hydrocarbons (C_{12}^+ liquid) produced in the slurry reactor are effectively converted to lower boiling range material, and significant amounts of aromatics are formed in the second-stage reactor. Table 2 shows a comparison of the hydrocarbon distributions of the raw Fischer-Tropsch product before and after upgrading over the zeolite bed (17). This approach offers the advantage of

Table 2. Comparison of Product Distributions From a Slurry Fischer-Tropsch Reactor Before and After Upgrading Over Zeolite Catalyst

<u>Yield, wt%</u>	<u>Before Second Stage</u>	<u>After Second Stage (After Alkylation)</u>
C ₁	7.5	7.7
C ₂ =/C ₂	1.6/3.0	1.1/3.1
C ₃ =/C ₃	8.0/2.0	0/5.1
C ₄ =	6.6	0
i-C ₃ /n-C ₄	0/2.0	(2.2)/4.3
C ₅ -C ₁₁	33.5	71.2
C ₁₂ + (Liquid)	27.8	1.7
Reactor-Wax	<u>8.0</u>	<u>8.0</u>
	100.0	100.0
Gasoline + Heavy Liquid	--	84.2
<u>Gasoline Properties</u>		
RVP, psi		10
PONA, vol%		66/13/4/17
R + O		90
M + O		83

*Required from other sources for alkylation.

Reference: Kuo, J.C.W., Leib, T.M., Gupte, K.M., and Kyan, C.P., paper presented at the AIChE 1984 Spring National Meeting, Anaheim, California, May 20-23, 1984.

allowing the Fischer-Tropsch catalyst and the zeolite catalyst to be operated at their preferred process conditions. An additional advantage is that each catalyst could be regenerated, as required, under its own optimum conditions.

The slurry-phase reactor also appears capable of high diesel oil yields if operated under conditions such that a large fraction of the product boils above 350°C. Recent studies at SASOL indicate that as much as 87% of the total upgraded C₅+ product can be diesel oil with a cetane number of 67 (18). The diesel fraction consists of straight run diesel, oligomerized C₃ to C₆ olefins,

and hydrocracked wax. Thus, by varying the upgrading process configuration and/or processing conditions, a high degree of product flexibility (high octane gasoline vs. high cetane diesel oil) is possible with the two-stage concept.

Conversion of Synthesis Gas Over Shape-Selective Catalysts

The emergence of the methanol-to-gasoline technology soon spawned the idea of combining a Fischer-Tropsch type catalyst with shape-selective catalysts, such as ZSM-5, to produce high octane gasoline directly from synthesis gas. Chang et al. (19) and Caesar et al. (20) demonstrated that intimate mixtures of ZSM-5 with methanol or Fischer-Tropsch synthesis catalysts are capable of producing gasoline-range hydrocarbons, high in aromatic content, in yields greater than those predicted by Schulz-Flory polymerization kinetics. In one example, a 25% fused-iron ammonia synthesis catalyst mixed with 75% ZSM-5 increased the gasoline-range product by as much as 50% over that produced when fused-iron catalyst was tested under identical conditions but without ZSM-5 present. Furthermore, the composite catalyst produced only trace amounts of hydrocarbons greater than C₁₁. Since other experiments, conducted in such a way that the iron and zeolite were arranged sequentially, did not result in the same synergism, Caesar and coworkers (20) were led to propose that at higher temperatures, α -olefins are free intermediates in the Fischer-Tropsch reaction and are capable of readsorption on catalytic sites and of initiating new growing chains. In the presence of ZSM-5, however, these α -olefins may be intercepted by the zeolite and converted to internal olefins, aromatics, or branched aliphatics that do not readily complex with the iron sites to undergo further reaction.

Research groups have continued studies of the metal-zeolite catalyst system. In particular, research efforts at the Pittsburgh Energy Technology Center are directed toward developing a better understanding of such things as the effect that the method of metal incorporation with the zeolite has on metal-zeolite interactions (21). The Union Carbide Corporation is also working under a cost-shared research contract with the U. S. Department of Energy to investigate the direct conversion of synthesis gas to gasoline- and diesel-range hydrocarbons using Union Carbide molecular sieve catalysts in conjunction with Fischer-Tropsch components (22). Two major problems remain a challenge to researchers: (a) The one-step approach necessitates that both catalyst components function at the same reaction temperature. Reported data for the MTG process would indicate that the optimum operating temperature for ZSM-5 may be 100°C to 150°C higher

than temperatures used for typical Fischer-Tropsch catalysts. Thus, one is forced to compromise and operate at some intermediate temperature, which sometimes leads to excessive yields of methane and ethane and/or inefficient conversion of the reaction intermediates to high octane components by the ZSM-5.

(b) Dual-functional, direct-synthesis gas conversion catalysts deactivate with use and require periodic regeneration in order to maintain useful activity. Brennan (23) demonstrated that multiple oxidative or hydrogenative reactivation was possible in a fluidized-bed system, although frequently activity and selectivity deteriorate with increasing number of regenerations. Once again, conditions required to regenerate one component of the catalyst may have adverse effects on the other component. For example, repeated high temperature coke burn-off of the zeolite component may cause irreversible deactivation of the transition metal component through sintering of metal crystallites and loss of active metal surface area.

CONCLUSION

In addition to the research and development projects discussed above, the Department of Energy is also sponsoring a number of smaller projects with universities, national laboratories, and industrial laboratories. This research is directed at developing a better fundamental understanding of the chemical and physical processes associated with the catalytic conversion of coal-derived synthesis gas to liquid fuels. Emphasis is placed on characterization and testing of new catalyst formulations to provide insight into the factors affecting catalyst activity, stability, and selectivity. Other studies seek to establish a quantitative understanding of mass and heat transfer related factors that affect catalyst performance in slurry- and fluidized-bed synthesis reactors.

In April, 1984, the Department of Energy announced that eleven university and industrial laboratories had been selected to investigate advanced techniques for converting coal to synthetic gasoline, diesel fuel, or jet fuel. The research projects fall into four categories: (1) basic research on catalyst promoters, activation and regeneration, methane formation, and carbon formation, (2) broadening of the data base for solubility and diffusivity of reactants and products in slurry media, and research on the hydrodynamic behavior of slurry bubble columns, (3) research on new catalyst or process concepts for the

conversion of synthesis gas to hydrocarbon fuels, and (4) research on new catalyst or process concepts for the conversion of synthesis gas to higher alcohols. Contract talks with the organizations are currently in progress.

It is believed that success in the research areas outlined in this paper, as well as in the gasification of coal to produce clean synthesis gas, could significantly improve the competitiveness of converting coal to quality transportation fuels.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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