

LIQUID FUELS FROM COAL DERIVED SYNTHESIS GAS

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INTRODUCTION

Modern synthesis gas chemistry has evolved from technology first developed in Germany early this century. Since that time worldwide interest in the production of liquid fuels from coal has gone through cycles reflecting the perceived availability of petroleum.

In the U.S., the Department of Energy (DOE) has supported an indirect coal liquefaction program to investigate new techniques for the production of liquid hydrocarbon and alcohol fuels. The liquid synthesis is based on utilizing a feedstock of low hydrogen content synthesis gas generated by advanced, more efficient, coal gasifiers. Research topics include improved reactor and catalyst developments as well as more fundamental studies of the reaction chemistry. This presentation summarizes results of a number of these projects and provides some comparisons with existing commercial liquid synthesis technology. Fuels of interest include gasoline, diesel and jet fuel, methanol and higher alcohols. Achievements in liquid phase synthesis of hydrocarbons and methanol are described along with the Methanol to Gasoline (MTG) process. Catalyst research is briefly reviewed and an assessment made of needs and prospects for future research.

Alcohol Fuels

Alcohols can perform well as fuels in both internal combustion and diesel engines, under appropriate conditions. Methanol is available now for evaluation as a direct replacement for petroleum derived gasoline, and the worldwide trend to low lead content gasoline provides a continuing interest in various oxygenates for use as octane enhancers in gasoline. Chem Systems, Inc. has developed a liquid phase reactor system to improve the thermal efficiency of methanol production (1). This Liquid Phase Methanol process is being further investigated under a cost shared contract in a 5 TPD process development unit (PDU) which is located at La Porte, Texas, on a site owned by the prime contractor Air Products and Chemicals, Inc. The PDU has operated very successfully with a Cu/Zn catalyst powder less than 50 microns in diameter slurried in an inert oil in the reactor through which the synthesis gas is passed. Operating conditions are 5.27 MPa (765 psia) and 250°C (482°F). During its most recent 40-day run (May-June 1985) the PDU operated with a nominal 25 wt. percent catalyst slurry and the catalyst activity declined 0.34 percent per day. The process is being developed for use with a modern coal gasifier to produce "once through" methanol to be available as a peak fuel while the unconverted gas is a baseload turbine fuel in an electric power plant. With a different feed gas (Table 1), the reactor can be used to produce "all methanol."

The production of higher alcohols requires more selective catalysts than are currently available. Union Carbide Corp. (S. Charleston, W.VA) is investigating homogeneous catalysts for this purpose under a cost sharing contract. Although existing commercial systems for production of chemicals require excessive operating pressure (20.78 MPa, 3015 psia), a successful catalyst will provide excellent selectivity and simple operations, particularly if the pressure can be

reduced. At Lehigh University modified heterogeneous Cu/Zn catalysts are being investigated in the pressure range of 3.45 MPa to 7.58 MPa (500 psia to 1100 psia) for the production of mixtures of methanol and higher alcohols. The alcohol product typically contains 40 percent methanol and about 25 percent isobutanol, for example (2).

Liquid Hydrocarbons

Historically, liquid hydrocarbons have been synthesized from hydrogen/carbon monoxide mixtures via Fischer-Tropsch technology using iron based catalysts. Another option is now being demonstrated commercially in New Zealand where methanol is produced from synthesis gas and immediately converted to high octane gasoline via the Methanol to Gasoline (MTG) process. Mobil Research and Development Corporation has developed this process based on a ZSM-5 catalyst, under a cost shared contract with DOE. A fixed bed reactor system was first developed with yields as shown in Table 2. In recent years, a more efficient fluid bed concept has been demonstrated in a 100 bpd (methanol feed) pilot plant located in West Germany. The plant operated very well at all levels including a much higher than designed throughput. Most recently operating conditions for the pilot plant were changed in order to produce light olefins rather than gasoline. The olefins can be converted commercially to diesel fuel and/or gasoline to offer the market another option. This project in West Germany has been supported equally by the U.S. Government, the W. German Government and an industrial consortium consisting of two German firms with Mobil.

Mobil also has been active in a cost-shared project using a liquid phase Fischer-Tropsch reactor followed by a second stage reactor with zeolite catalyst to produce gasoline and wax which can readily be cracked to produce diesel fuel (3) (4). Table 3 provides data on yield selectivity from the first stage in low wax mode of operation. This project provided an empirical correlation between methane and wax yields using a precipitated iron, copper, potassium catalyst. Mobil's bench scale research has also included first stage reactor operation in a high wax mode.

The base line technology against which process improvements are measured is that found at the Sasol plants in South Africa. These commercial plants owned by the South African Coal, Oil, and Gas Corp., Ltd. produce an estimated 90,000 bpd of diesel fuel and gasoline. Lurgi dry bottom coal gasifiers provide the synthesis gas while Arge fixed bed reactors, and Synthol fast fluid bed reactors, produce a broad mixture of fuels and chemicals which have to be further processed to marketable products (5).

During recent years, the MITRE Corp. McLean, VA, has put the Sasol and other process schemes on a common basis so that product costs can be compared. Table 4 provides relative costs for diesel fuel or gasoline (both having the same market value). All plants are considered to be located in the U.S. and the feed coal is Western subbituminous. For the advanced processes, the British Gas Corp. (BGC) Lurgi gasifier is used. The liquid phase Mobil two-stage process is compared with the liquid phase data reported by Prof. H. Kolbel from operations in Germany during the 1950's (4).

Catalyst Research

Practical catalysts must meet several criteria but one property has eluded researchers interested in producing hydrocarbons with more than one carbon atom. That property is selectivity to produce precisely the desired product. When one thinks of selectivity, one thinks of shape selective supported catalysts, homogeneous catalysts and enzymes or other biological approaches. While working

with a synthesis gas feedstock, one is tempted also by the possibility of combining the carbon monoxide activation/hydrogenation steps with shape selectivity in one catalyst formulation, in one reactor. All of these concepts are being investigated in a continuing research effort with the expectation that the results will better describe the reaction chemistry leading in turn to new and greatly improved catalysts.

Reactor Technology

Liquid, or slurry phase, reactors are recognized as having a potential to significantly improve thermal efficiency over more traditional reactor designs for highly exothermic reactions. A number of existing projects are investigating liquid phase reactors, but we need much more data describing the hydrodynamics of such systems under process conditions. Actual operating data are required from a reactor which can be operated in a commercially viable churn turbulent flow regime. Results from research to date are encouraging in processing a lower H_2/CO ratio syngas and producing a flexible product slate. The liquid phase Fischer-Tropsch reactor also operates at a higher, more productive, temperature (260°C-270°C) than is feasible with the Arge or Synthol reactors using the current iron catalyst at Sasol.

CONCLUSION

It is a pleasure to report, however briefly, the progress being made in new approaches to the synthesis of liquid fuels from coal derived syngas. The recently demonstrated selectivity and efficiency of producing hydrocarbon fuels from methanol is outstanding. Improvements are being demonstrated in selectivity for higher alcohol production and in making efficient use of liquid or slurry phase reactors.

Nevertheless, we have to conclude that no one has the technology today to produce liquid fuels from coal derived synthesis gas at a cost competitive with near term petroleum derived fuels in a typical industrial environment. Although the feed gas accounts for about two-thirds of the cost of the liquid fuel in a Fischer-Tropsch plant, the liquid synthesis can be greatly improved to contribute major savings. Existing technology to directly convert synthesis gas to liquid hydrocarbons is non-selective requiring extensive downstream processing. Liquid fuel production via methanol uses two selective process schemes, but they cannot be closely integrated, at present, for maximum efficiency. New approaches may provide solutions but until then we need to pursue avenues suggested by current research. A slurry reactor offers constant temperature operation with catalyst addition and withdrawal capability. Can productivity be improved with higher catalyst loading? Can wax produced in the reactor be efficiently removed and separated from the catalyst? What is the potential for new reactor designs? For continuous stirred tank reactors? Does catalyst metal particle size affect or control selectivity? Do homogeneous catalysts have any role in hydrocarbon, as distinct from alcohol, synthesis? Can practical bi-functional catalysts be developed to convert syngas to hydrocarbon liquids? Can by-product methane be converted directly and efficiently to liquid fuel?

Successful results from research efforts now underway will go far in answering these questions, and the data will be available for use by industry whenever it is required in the United States.

TABLE 1. Liquid Phase Methanol Process
Typical Reactor Feed Gas Compositions (6)

	Methanol/Power Production (CO-Rich Feed)	All-Methanol Product (Balanced Feed)
H ₂	35.0 Mole %	55.0 Mole %
CO	51.0	19.0
CO ₂	13.0	5.0
CO ₄	--	3.0
Inerts	1.0	18.0
	100.0%	100.0%
H ₂ /CO	0.69	2.89

TABLE 2. MTG Process - Typical Yields from Methanol
in Fixed Bed Reactor System (7)

Yields, wt. percent of methanol charged

Methanol	0.00
Hydrocarbons	43.66
Water	56.15
CO, CO ₂	0.04
Coke, oxygenates	0.15
Total	100.00

Yields, wt. percent of hydrocarbon product

Gasoline (including alkylate*)	85.0
LPG	13.6
Fuel gas	1.4
Total	100.0

- * 93 unleaded RO no. Without alkylate gasoline is 80.0%. Alkylate is process derived from propylene, butenes and isobutane. Reactor inlet temperature 316°C; pressure 2.17 MPa (314 psia).

TABLE 3. Mobil Liquid Phase Fischer-Tropsch
Summary of Data from Low-Wax Operation*

Yields, wt. percent product

C ₁	7.5
C ₂ /C ₂ =	1.6/3.0
C ₃ /C ₃ =	2.0/8.0
C ₄ /C ₄ =	2.1/6.6
C ₄ oxygenates	5.1
C ₅ -C ₁₁	39.4 (2.5)**
C ₁₂ -C ₁₈	14.3 (0.8)**
C ₁₉ -C ₂₃	2.9 (0.04)**
C ₂₃ ⁺ wax	7.5
Total	100.0

* Bubble column reactor, 260°C 1.52 MPa, H₂/CO = 0.67, Fe/Cu/K catalyst, 2.75 NL syngas/gFe/hr, 86 mole % syngas conversion, 800 g hydrocarbons/g Fe catalyst life.

** Numbers in parenthesis are oxygenates.

TABLE 4. Comparative Costs for Fischer-Tropsch
Synthesis (4)

Unit product cost*, market basis, all liquid output

<u>Case</u>	<u>Relative Cost</u>
Sasol (dry Lurgi/Synthol)	1.00
Modified Sasol (BGC Lurgi/Synthol)	0.83
Liquid Phase Fischer-Tropsch (BGC Lurgi/Kolbel)	0.69
Liquid Phase Fischer-Tropsch (BGC/Mobil)**	0.73

* All liquid hydrocarbon fuels valued the same.

** Upgrading of Fischer-Tropsch liquids to marketable fuels based on ZSM-5 catalyst.

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