CHAPTER 5

REVIEW OF INDIRECT LIQUEFACTION[1]

5.1 INTRODUCTION AND SUMMARY

5.1.1 Introduction

Indirect liquefaction encompasses a wide range of catalytic processes to convert coal-derived synthesis gas to liquid fuels, and can be categorized into two principal areas: (1) conversion of synthesis gas to light hydrocarbon fuels (gasoline and light paraffins) via Fischer-Tropsch synthesis, and (2) conversion of synthesis gas to oxygenates such as methanol, higher alcohols, and ethers.

An excellent in-depth review of the status of indirect liquefaction technologies and their research needs may be found in the 1987 DOE-sponsored COGARN study report entitled "Coal Gasification: Direct Application and Synthesis of Chemicals and Fuels, A Research Needs Assessment" (1). The COGARN report should be consulted for complete descriptions of indirect liquefaction technologies and their backgrounds. This report will be referenced in the current review where appropriate.

Another recent review document by IEA entitled "Catalysts for Fuels from Syngas: New Directions for Research (IEACR/09)," authored by G.A. Mills, should also be consulted (2). In this IEA document, which emphasizes catalysis research, research priorities were divided into three categories: (1) research for near-term, (2) research for mid-term, and (3) research for long-term applications.

---

[1] This chapter was written by Irving Wender, University of Pittsburgh, and Kamil Klier, Lehigh University.

In this current review emphasis is placed on the recent advancements in synthesis of oxygenates, since this is a relatively new emerging technology. For the synthesis of light hydrocarbon fuels, a summary of the most significant progress will be presented. An attempt will be made to incorporate or report on developments that have occurred or are undergoing change since the 1987 COGARN report.

5.1.2 Summary

Indirect liquefaction encompasses a variety of catalytic technologies to convert synthesis gas to (1) light hydrocarbon fuels and (2) oxygenates. Commercial technologies exist for both hydrocarbon fuel and oxygenates production, although only the SASOL plant in South Africa uses coal to make the synthesis gas for fuel and chemical production. In the U.S., plants have been built to produce ammonia and other chemicals via coal-derived synthesis gas. The distinguishing features of synthesis gas derived from coal are the low H_2/CO ratio and various catalyst contaminants in coal gas.

Coal-derived synthesis gas with a low H_2/CO ratio often requires shifting via the water gas shift reaction to achieve the higher ratios necessary for F-T or oxygenate syntheses. A sulfur-tolerant shift catalyst would greatly reduce the cost of synthesis gas clean-up and lead to improved process economics for indirect liquefaction processes. The panel made the development of such catalysts a high-priority recommendation (No. I6).

For light hydrocarbon synthesis the oil slurry F-T process has recently been shown to yield high synthesis-gas conversion with the advantages of accepting low-H_2/CO coal-derived synthesis gas. Extensive research on three-phase slurry reactors for optimum performance of catalytic reactors is ongoing.

Another initiative in F-T process research is to maximize the yield of middle distillates and wax, while minimizing the production of light gases. The wax is then cracked to marketable fuel products. Continued work in this area was recommended by the panel with special emphasis on developing catalysts having high selectivity to long-chain hydrocarbons suitable for cracking to naphtha and distillate fuels (No. I5). If this high wax yield is achieved in a slurry reactor, separation of wax products from the catalyst and catalyst recovery and recycle will have to be addressed as part of the overall process.

Continued research is also needed in improving F-T synthesis catalysts to attain high activity with controlled and reproducible properties. Based on its assessment of current F-T catalysts and the potential for developing improved catalysts, the panel recommended that new advances in materials science be applied to catalyst preparation for F-T synthesis reactions (No. I1). These new techniques include production of novel supports and new ways of developing the active surface as well as new methods of catalyst characterization. In general, these new techniques appear to offer major opportunities for the scientific design of greatly improved catalysts -- catalysts which would not be achieved by traditional trial-and-error methods. As related recommendations, the panel also recommended that supported organometallic complexes be analyzed for application to F-T syntheses (No. I2) and that the factors leading to deactivation of F-T catalyst be determined (No. I8).

Technologies to produce oxygenates, with emphasis on new methanol technology, higher-alcohol synthesis, and production of ethers, have received a great deal of attention in recent years. This interest in oxygenates production will continue to increase as these compounds penetrate the transportation fuel market as additives, either neat or as precursors to other clean-burning octane-enhancers. Thus, many of the panel's recommendations were directed toward alcohol or ether production in the areas of new catalysts, new processes, and studies of kinetics and catalysis.

For methanol synthesis, new developments are being made in the liquid-phase methanol process by Air Products and Chemicals and the gas-solid-solid trickle flow reactor by Shell. Progress is continuing on new heterogeneous and homogeneous catalysts for methanol synthesis, although additional studies on reaction kinetics are needed. The low H_2/CO ratio and the catalyst contamination problems associated with impurities in coal-derived gas point to the need for testing an integrated gasification/indirect liquefaction system. Such testing is currently being done at the LaPorte liquid-phase methanol PDU, which is the only unit in the DOE's indirect liquefaction program of sufficient size and integration which can be used to investigate complete system performance. The panel felt that new catalysts are needed having good activity with syngas streams but without requiring the extensive expensive cleanup needed for current catalysts (No. I7).

Progress is being made on developing higher-alcohol synthesis (HAS) processes. These developments include recent work related to (1) the SEHT (MAS) process, (2) the IFP (substifuel) process, (3) the DOW HAS process, (4) the Lurgi OCTAMIX process, and (5) the Lehigh University (LU) HAS process. Review of this work points to the need to develop better synthesis catalysts and new processes. In particular, new routes are needed to produce ethanol from synthesis gas with greater selectivity, minimizing the hydrocarbon yield (Recommendation No. I3).

Improvements must also be made in methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME) technologies. The panel also saw potential for finding new catalyzed paths to produce octane-enhancing ethers and made this a high-priority recommendation (No. I4).

The major focus of the panel's recommendations in indirect liquefaction is catalysts -- new materials, methods of characterization, structure, deactivation, kinetics, and mechanisms. This focus may be somewhat narrow, but it stems from a program in which little process development is being performed. (The Liquid-Phase Methanol program is the notable exception.)

In addition, indirect liquefaction is the second reaction of a two-stage reaction sequence that starts with coal gasification. DOE has placed gasification in a separate program, leaving only syngas reactions as part of the liquefaction program. Since gasification constitutes at least 70 percent of the total cost, improvements in syngas conversion technology may have relatively little impact on overall economics. Furthermore, such improvements may be contingent on process changes upstream of the syngas reactor.

5.2 CONVERSION OF SYNTHESIS GAS TO LIQUID HYDROCARBON FUELS[2]

5.2.1 Fischer-Tropsch Reactions, Chemistry, and Mechanisms

A broad view of the Fischer-Tropsch synthesis (FTS) mechanism is that it is a simple polymerization reaction, the monomer being a C_1 species derived from CO. This polymerization follows a molecular-weight distribution described mathematically by two groups independently: Anderson and the Bureau of Mines groups (3) and Manes (4), and the polymer chemists, Schulz (5) and Flory (6).

The description of the FTS product distribution is usually referred to as the Anderson-Schulz-Flory (ASF) distribution. The ASF equation is now well known and constantly used. This F-T distribution has also been described by Madon (7) and Dry (8). The ASF equation is usually written as:

$$\log \frac{Wn}{n} = n\log x + \log \frac{(1-x)^2}{x}$$

Wn is the mass fraction, n is the carbon number, and x is the probability of chain growth. The equation predicts the highest selectivities attainable by an F-T synthesis with an optimized process and catalyst:

Product	Maximum Selectivity, Wt.%
Methane	100
Ethylene	30
Light Olefins (C_2-C_4)	50
Gasoline (C_5-C_{11})	48

---

[2] This section was written by Irving Wender, University of Pittsburgh.

These predictions hold whether the products are hydrocarbons (paraffins and olefins) or hydrocarbons plus alcohols.

A linear plot of log Wn/n indicates that the data are indeed consistent with a chain growth mechanism. The chain growth probability, x, can be calculated either from the slope, log x, or from the intercept, log $[(1-x)^2/x]$.

5.2.2 F-T Synthesis Catalysts

Catalysts with a small value of x produce a high fraction of methane; thus a selective methanation catalyst would have an x value approaching zero. At the other extreme, a high x value indicates the production of heavier components. As will be discussed, the latest FTS work is aimed at producing high-molecular-weight products (and thus very little CH_4) and then cracking these materials to produce lower hydrocarbons.

There have been many attempts to "beat" the ASF prediction so that one could produce gasoline and diesel or middle distillate range products in yields that exceed those allowed by ASF polymerization. While there have been many indications that the particle size of the metal catalyst or the pore structure of the support may cause deviations from the ASF prediction, none of these has proven valid under further scrutiny. Deviation from the ASF distribution, at least on a practical industrial scale, has been the result of the conversion of primary FTS products by secondary reactions.

The only commercial use of the FTS is at SASOL in South Africa. Cheap iron catalysts prepared by fusing iron oxides such as millscale oxides are used. In practice, either an alkali salt or one or more non-reducible oxides are added to the catalyst. The literature on the use of iron catalysts is enormous. However, because of the wide range of experimental differences in catalyst preparation, pretreatment, reaction conditions, and product analysis, it is virtually impossible to make direct comparisons of much of the data.

The SASOL plants furnish more than 40 percent of that country's requirements for fuels and chemicals. Data on the existing SASOL plants are listed below:

Plant	Start Date	Coal t/d	Liquids bbl/d	Cost $Billion
SASOL-1	1935	6,600	6,000	-------
SASOL-2	1981	30,000	40,000	2.9
SASOL-3	1982	30,000	40,000	3.8

An approximate distribution of products from SASOL-2 follows:

Product	Tons/Year
Motor fuels	1,650,000
Ethylene	204,000
Chemicals	94,000
Tar Products	204,000
Ammonia (as N)	110,000
Sulfur	99,000
Total Saleable Products	2,361,000

SASOL is now planning to use its same process to produce synthetic oil from offshore natural gas (9). In May 1988 a government corporation selected a mining corporation to build a gas liquefaction project to explore the newly-discovered Mossal Bay offshore gas field. This project will be broken down into two parts, Mossgas plans to process natural gas and gas liquids directly into gasoline, diesel oil, and other higher-boiling liquids. Mossref -- short for Mossel Bay refinery -- will produce synthetic crude and chemicals from the remaining methane. However, contracts have not as yet been let for the needed bank of SASOL Synthol reactors.

There are thousands of journal publications and patents on investigation of other F-T catalysts, chiefly cobalt, ruthenium, nickel, rhodium, and molybdenum (the last as a sulfide). Researchers have claimed high yields of particular products or types of products, often in differential reactors under particular conditions. Dry (10) (personal communication) has been asked why SASOL cannot reproduce these results. Obviously, since SASOL's process is tied to a cheap throwaway iron catalyst employed in integral reactors, it is not possible for SASOL to reproduce the often desirable products via processes that appear in various publications.

5.2.3 Fischer-Tropsch Processes Not Yet in Commercial Operation

The title for this section is taken directly from the 1987 COGARN report (1). Modern gasifiers make synthesis gases with low (0.6-0.7) H_2/CO ratios. Iron is a good water gas shift (WGS) catalyst while neither cobalt nor ruthenium is active. In the absence of WGS activity, the oxygen in CO is rejected as water so that a synthesis gas with an H_2/CO ratio of two is needed to produce olefins or alcohols; for paraffins an H_2/CO ratio somewhat larger than two is required. With good WGS catalysts the oxygen in CO is mostly rejected as CO_2. When water is formed in the F-T reaction, it can react with CO to form more H_2 so that low-H_2/CO-ratio synthesis gas (SG) can be used with these catalysts.

Attempts to produce C_2-C_4 hydrocarbons in the F-T reaction have not resulted in conversions that exceed those predicted by the ASF equation. This result, coupled with low H_2/CO gas ratios produced by current or developing coal gasification processes, has led to F-T syntheses that produce high-molecular-weight/low-methane products. The long-chain products are then used to produce lower hydrocarbons by cracking, as well as gasoline and diesel fuels (1).

Most of the current work uses slurry F-T reactors. Koelbel and Ralek (11) have published an excellent review of the development of slurry F-T work up to the 1970s. Major developments of slurry F-T processes since 1980 have been done at the Mobil Research and Development Corporation, with some funding from DOE (12, 13). The work was done in association with the concept of upgrading a total vaporous F-T reactor effluent over a ZSM-5 catalyst. This concept is reported in the 1987 COGARN coal gasification research needs report (1), which described two modes of operation: (1) a gasoline or low-wax mode of operation and (2) a gasoline and diesel or high-wax mode of operation.

In 1985, Shell announced its SMDS (Shell Middle-Distillate Synthesis) process for the production of kerosene and gas oil from natural gas (14). It is a two-stage process based on the development of a catalyst which converts synthesis gas into long-chain hydrocarbon waxes, which are hydroconverted and fractionated into naphtha for gasoline, kerosene for jet fuel, and gas oil for diesel. The thermal efficiency from natural gas is 60 percent. The synthesis gas made from natural gas would have a high H_2/CO ratio. Little CO_2 is produced so that the proprietary F-T catalyst has little or no WGS activity. A fixed-bed (Arge-type) reactor will be used for the F-T reaction and a trickle flow reactor for hydrocracking. The catalyst almost certainly is partly or largely cobalt with iron or ruthenium likely present. Product carbon number distributions obtained with these catalysts have x values from 0.7 to over 0.9 (15). The calculated distributions of C_1 - C_{10} and C_{10} - C_{20} products from the SMDS concept are 64 and 36 respectively for $x = 0.8$, and 20 and 80 for $x = 0.95$(2).

In related work UOP (16) characterized F-T wax and its potential for upgrading. Obviously, high wax formation in the FTS will minimize methane formation. Utilization of catalysts designed for high wax/low methane, coupled with new catalyst technology for selective cracking of the wax, is a very promising route to desired products via F-T technology.

The COGARN coal gasification report discusses the Gulf-Badger process for converting natural gas to liquid hydrocarbons via methane steam reforming followed by an F-T reaction. Again, an Arge-type reactor is used. The proprietary catalyst, probably cobalt with some ruthenium, has little or no WGS activity. Typical process conditions of 210°C, 250 psig, $H_2/CO = 1.5-2$, space velocity of 500-1000 1/hr, with a CO conversion of 40-60 mol percent plus product selectivities are listed in the COGARN report. STATOIL of Norway is involved in a similar process.

Dow has developed molybdenum catalysts with a sulfur tolerance up to about 20 ppm. The catalyst system is selective for the synthesis of C_2-C_4 hydrocarbons, especially when promoted with 0.5-4 weight percent potassium.

5.2.4 Fischer-Tropsch Synthesis in the Slurry Phase

Using a precipitated iron catalyst, the slurry F-T reactor, which operates with a finely divided catalyst suspended in an oil reactor medium, has been shown to yield high single-pass syngas conversion with low (0.6) H_2/CO ratios. Koelbel and Ralek (11) and Frohning et al. (17) have reviewed slurry-phase F-T processing more recently. Kikuchi (18) developed ultrafine particles of Fe-Co-Ni or Fe for liquid-phase F-T synthesis. There have been extensive studies of three-phase slurry reactors for optimum performance of catalytic reactors (2, 19).

5.2.5 Conversion of Methanol to Gasoline with Zeolite-Containing Catalysts

This work was discussed in detail in the COGARN report on gasification for the synthesis of fuels and chemicals, and the reader is directed to this report (1).

The Mobil Research and Development Corporation developed the methanol-to-gasoline (MTG) process, one of the very few synthetic fuel technologies that has been commercialized since the 1973 oil embargo. The process is based on the use of zeolites of the ZSM-5 class (20,21) discovered by Argauer and Landolt (22).

The MTG process may be represented as:

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} (CH_3)_2O \xrightarrow{-H_2O} -C_2\text{-}C_5 \text{ olefins}$$

$$C_2\text{-}C_5 \longrightarrow \begin{array}{l}\text{Olefins, Paraffins,}\\ \text{Naphthenes, Aromatics,}\\ C_6\text{+ Olefins}\end{array}$$

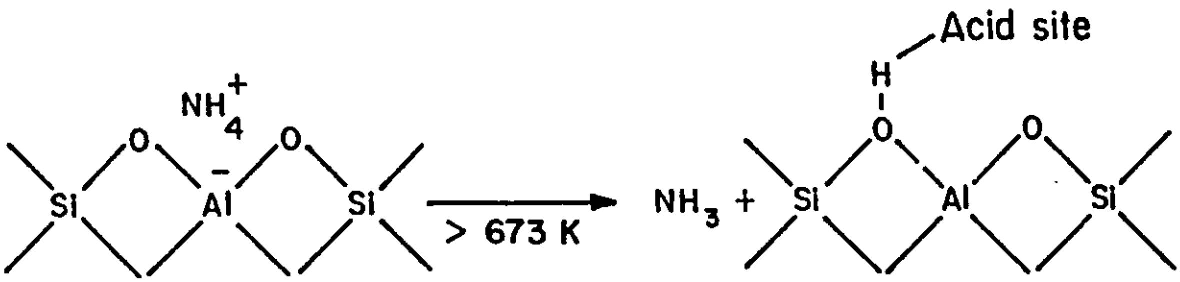
The mechanism may involve the formation of ethylene as the primary product, but there is much debate on this subject. Several mechanistic pathways have been proposed.

Because of the shape-selective pore structure of the ZSM-5 zeolite, the hydrocarbons produced are predominantly in the gasoline range. The paraffins consist mostly of isoparaffins, and a large yield of aromatics is obtained. The total product is in the C_5-C_{10} range so that it has a high octane number. The aromatics are highly substituted by methyl groups due to the alkylation of the aromatics by methanol and dimethyl ether (DME).

A discussion of zeolites, natural and synthetic, is given in Reference 1. They are porous crystalline solids which have well-defined pore systems and large surface areas. The most common zeolites are tectosilicates (<u>23</u>) (T is usually Si or Al, but other atoms may be present) such that each of the four oxygen atoms is shared with another tetrahedron.

Weisz (<u>24</u>) has discussed the thinking that lead to the synthesis of highly siliceous zeolites such as ZSM-5. This zeolite has high structural stability, thermally and particularly toward hydrolytic attack during chemical processing. The Mobil workers were able to form aluminosilicate frameworks in which both Al and Si were the principal building units. SiO_2 was the main constituent with occasional, almost randomly positioned Al substitutions; this leaves the Al sites available in a dilute, isolated state in the zeolite, a condition which seems to confer high acidity to the Al sites. In amorphous silica-alumina, such as that found in clays, only a small fraction of the Al atoms are sufficiently active.

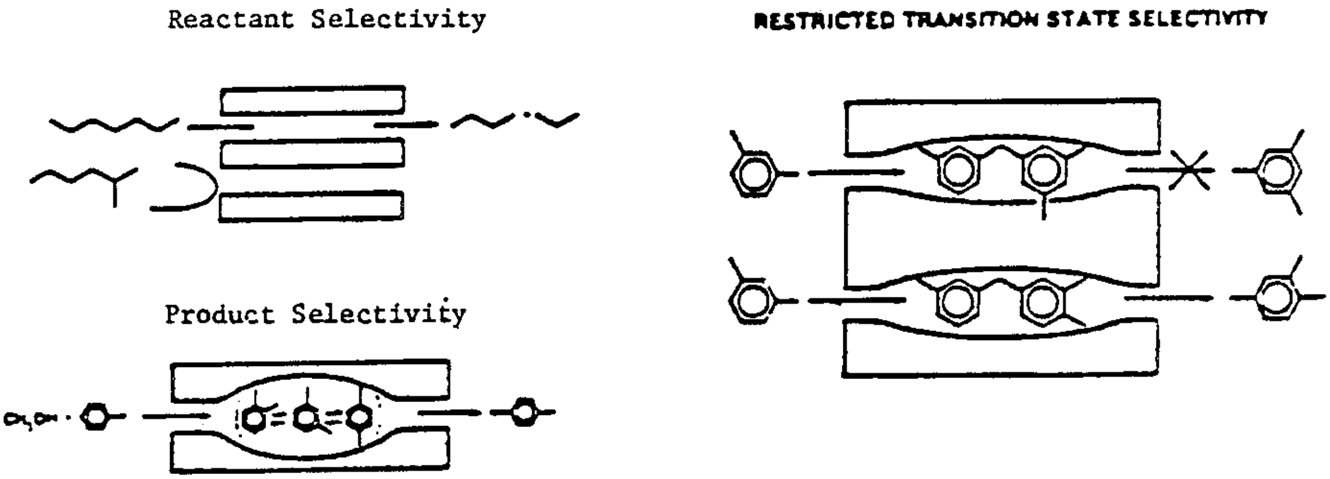
The acidity of zeolites is the fundamental basis of their catalytic activity. This holds for the MTG process for the conversion of methanol to gasoline; the catalyst is used in the HZSM-5 form. Acidity, shape selectivity, and structural stability of the catalyst combine to make the MTG process a success.



Acidity of Zeolites

Csicsery (25) has pointed out three categories of shape-selective catalysts. These are reactant selectivity, product selectivity, and restricted transition state selectivity (Figure 5-1). The interior surface of the zeolite is the principal source of catalytic activity although reactions may take place on the external surface.

The synthesis of ZSM-5 led to the discovery, by Chang and Silvestri (26), of the MTG process. It also led to an enormous amount of research on its use in chemical processing. Because of its molecular shape and size (Figure 5-2), ZSM-5 does not generate appreciable amounts of aromatics larger than C_5-C_{10}, thus avoiding generation of coke precursors which would quickly deactivate the catalyst.



Reactant Selectivity

Product Selectivity

RESTRICTED TRANSITION STATE SELECTIVITY

Figure 5-1. Types of Zeolite Selectivity

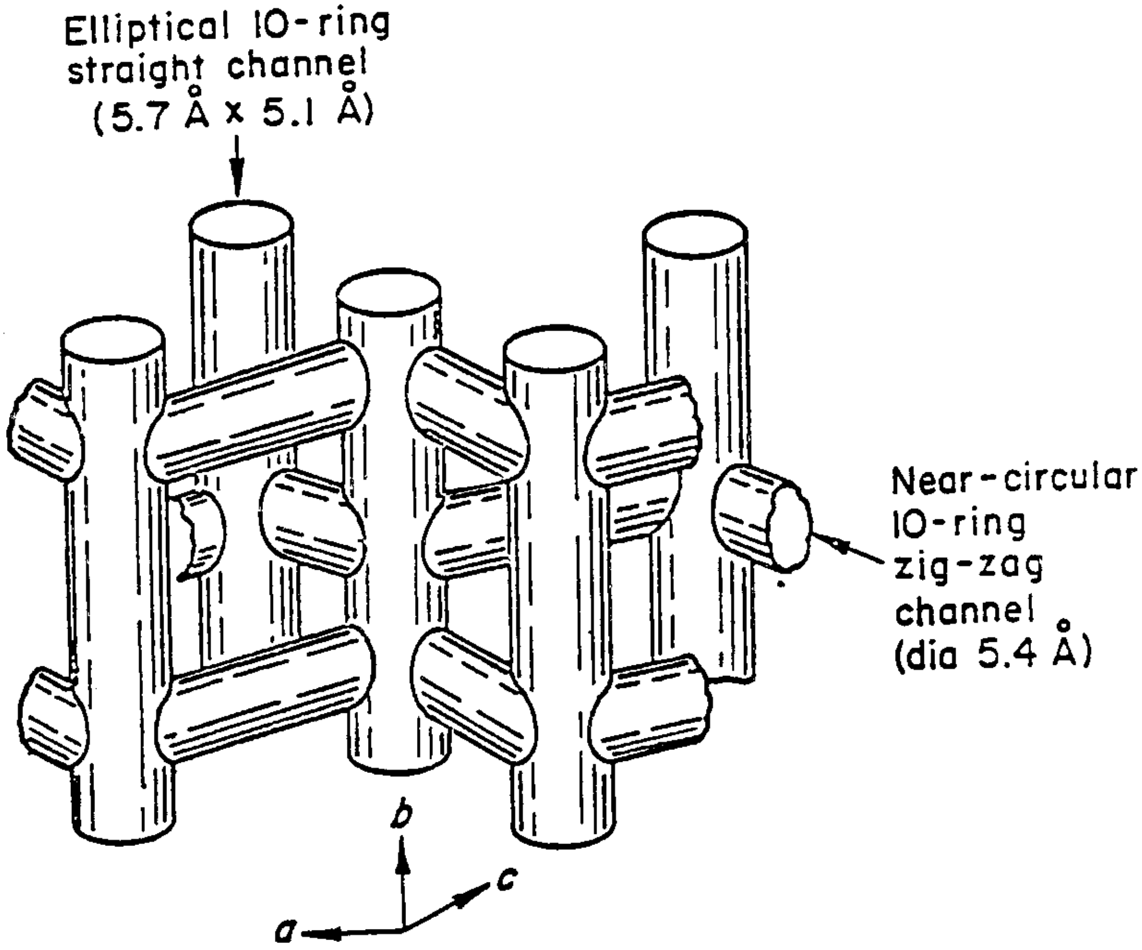


Figure 5-2. Framework Structure of ZSM-5

The MTG process first converts synthesis gas (SG) to methanol; in a second step the alcohol is nearly quantitatively converted to high-octane gasoline over the ZSM-5 molecular sieve. The MTG technology was developed under the joint technical direction and financial sponsorship (30/70) of Mobil and the U.S. DOE (27). The MTG process has been tested in a fixed-bed mode at the Mobil laboratories and in a fluid-bed mode in a 100-BPD unit in West Germany (28). In Table 5-1 Haag et al. (1) have compared process conditions and product yields from the two MTG systems.

New Zealand, desiring to become more self-sufficient in liquid transportation fuels, had the choice of adopting the F-T process or the Mobil MTG process. They chose the fixed-bed version of the MTG process over the fluid-bed, chiefly because of the simpler engineering and easier scale-up. The fixed-bed version had only been tested previously in a four-barrel-a-day unit. The choice of the MTG process over a Fischer-Tropsch route involved thinking along the following lines:

- The selectivity of the MTG process is much greater.
- The MTG process gives little or no CH_4, in contrast to the F-T process.
- The MTG process yielded extensive aromatics formation, conducive to a high-octane rating of the gasoline.
- The MTG catalysts have long lives and may be regenerated in situ. The F-T catalyst, millscale, is cheap and adequate; while its composition changes during its life, it is a throw-away catalyst.
- The MTG route is more efficient (57 percent to SASOL's 48 percent).
- The MTG process has lower investment costs with fewer upgrading steps.

New Zealand now produces about 14,000 BPD of 92-93 octane gasoline via the MTG process; this is one-third of their requirements. The SG needed for the manufacture of methanol is obtained from offshore gas fields. New Zealand has extensive deposits of coal and could eventually use coal as their source of SG.

Table 5-1. Typical Process Conditions and Product Yields for MTG Processes

Conditions	Fixed-bed Reactor	Fluid-bed Reactor
MeOH/Water charge, w/w	83/17	83/17
Dehydration reactor inlet T, °C	316	-
Dehydration reactor outlet T, °C	404	-
Conversion reactor inlet T, °C	360	413
Conversion reactor T, °C	415	413
Pressure, kPa	2170	275
Recycle ratio, mol/mol charge	9.0	-
Space velocity, WHSV	2.0	1.0
Yields (wt% of MeOH charged)		
MeOH + dimethyl ether	0.0	0.2
Hydrocarbons	43.4	43.5
Water	56.0	56.0
CO, CO_2	0.4	0.1
Coke, other	0.2	0.2
	100.0	100.0
Hydrocarbon product (wt%)		
Light gas	1.4	5.6
Propane	5.5	5.9
Propylene	0.2	5.0
Isobutane	8.6	14.5
n-Butane	3.3	1.7
Butenes	1.1	7.3
C_{5+} gasoline	79.9	60.0
	100.0	100.0
Gasoline (including alkylate),		
RVP-62kPa (9psi)	85.0	88.0
LPG	13.6	6.4
Fuel gas	1.4	5.6
	100.0	100.0
Gasoline octane (R+O) (Research octane number, lead-free)	93.0	97.0

Source: Reference 1.

There is now an enormous literature on ZSM-5, a good deal of it on understanding the scientific aspects of the MTG reaction chemistry. There is also much literature on developing improved catalysts to maximize olefin or aromatic production, and using ZSM-5 to upgrade products from the F-T process, and developing a hybrid slurry F-T/MTG process (26). Other ions have been added to replace Al in the ZSM-5 crystal framework.

The Topsoe Integrated Gasoline Synthesis process (TIGAS) (27) uses combined steam reforming and autothermal reforming for SG production with a multifunctional catalyst system to produce an oxygenates mixture rather than only methanol. When the MTG process is integrated into this synthesis of oxygenates, operating conditions are relatively mild.

Lurgi, alternatively, has developed a direct heat exchange MTG reactor (29).