NREL/TP-421-5150 • UC Category: 245 • DE93010025

Status and Future Opportunities for Conversion of Synthesis Gas to Liquid Energy Fuels: Final Report

G. Mills
Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware

NREL technical monitors:
R. Overend and R. Bain

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
Operated by Midwest Research Institute
for the U.S. Department of Energy
under Contract No. DE-AC02-83CH10093

Prepared under subcontract number HZ 1-11208-1

May 1993

MASTER

[illegible]

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A09

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issue of the following publications which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

Acknowledgments

Appreciation is expressed to Dr. Ralph P. Overend and Dr. Richard L. Bain of the National Renewable Energy Laboratory (NREL) for valuable technical guidance, to René Texeira (NREL) for expert editing, and to Paulette A. Warren, also of NREL, for efficient administrative support.

Special thanks are extended to those who contributed by sharing ideas during site visits and discussions at meetings and to those who commented constructively on this report in draft form.

Appreciation is due to the many individuals whose names are recognized in the references for their contribution of scientific and engineering information. It is they who are the real authors. It is my hope that this report will assist in advancing catalytic science and technology of syngas for energy purposes by bringing to the attention of researchers information they did not previously know and by assisting those making research choices through delineating possible advantageous opportunities.

G. Alex Mills, Senior Scientist
Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware

Contents

Contents (Continued)

Page

Contents (Concluded)

List of Figures

List of Figures (Continued)

List of Figures (Concluded)

List of Tables

List of Tables (Concluded)

Acronyms

ARCO	Atlantic Richfield
ASF	Anderson Shulz Flory (equation)
BON	blending octane number
CAAA	Clean Air Act Amendments of 1990
CFB	circulating fluid bed
CGCC	coal gasification combined cycle
CSTR	continuous stirred tank reactor
DIPE	disopropyl ether
DME	dimethyl ether
DOE	Department of Energy (U.S.)
EPRI	Electric Power Research Institute
ETBE	ethyl tertiary butyl ether
FFB	fixed-fluidized bed
FFV	flexible fuel vehicle
FT	Fischer-Tropsch (process)
GSTFR	gas solid trickle flow reactor
HCS	hydrocarbon synthesis
IBA	isobutyl alcohol
IGCC	integrated gasification combined cycle
IPA	isopropyl alcohol
LPDME	liquid phase dimethyl ether
LPMEOH	methanol (process)
MITI	Ministry of International Trade and Industry
MOGD	Mobil olefins to gasoline and distillates
MTBE	methyl tertiary butyl ether
MTG	methanol to gasoline (process)
MTO	methanol to olefins
ORR	oxygen retention reversal
RSIPR	reactor system with interstage product removal
RVP	Reid vapor pressure
SASOL	South African Coal, Oil, and Gas Corporation Ltd.
SBA	sec-butyl alcohol
SMDS	Shell Middle Distillate Synthesis
TAME	tertiary amyl ether
TBA	tertiary butyl alcohol
TIGAS	Topsøe integrated gasoline synthesis
TPR	temperature programmed reduction
TVA	Tennessee Valley Authority
UHV	ultrahigh vacuum

Executive Summary

Status

E.1 Overview

The manufacture of liquid energy fuels from syngas (a mixture of H_2 and CO, usually containing CO_2) is of growing importance and enormous potential because

- Abundant U.S. supplies of coal, gas, and biomass can be used to provide the needed syngas.

- The liquid fuels produced, oxygenates or hydrocarbons, can help lessen environmental pollution. Indeed, oxygenates are required to a significant extent by the Clean Air Act Amendments (CAAA) of 1990.

- Such liquid synfuels make possible high engine efficiencies because they have high octane or cetane ratings.

- There is new, significantly improved technology for converting syngas to liquid fuels and promising opportunities for further improvements. This is the subject of this report.

The purpose of this report is to provide an account and evaluative assessment of advances in the technology for producing liquid energy fuels from syngas and to suggest opportunities for future research deemed promising for practical processes.

Much of the improved technology for selective synthesis of desired fuels from syngas has resulted from advances in catalytic chemistry. However, novel process engineering has been particularly important recently, utilizing known catalysts in new configurations to create new catalytic processes.

This report is an update of the 1988 study *Catalysts for Fuels from Syngas: New Directions for Research* (Mills 1988), which is included as Appendix A. Technology for manufacture of syngas is not part of this study.

The manufacture of liquid synfuels is capital intensive. Thus, in evaluating advances in fuels technology, focus is on the potential for improved economics, particularly on lowering plant investment costs. A second important criteria is the potential for environmental benefits.

Improved technology and special needs, some political and some environmental, have led to a variety of recent commercial installations of liquid hydrocarbon fuels from syngas. The novel MTG (methanol-to-gasoline) process began operation in New Zealand in 1985. A new type of Fischer-Tropsch unit, a fixed-fluidized-bed unit, was installed by South African Coal, Oil, and Gas Corporation, Ltd. (SASOL) in South Africa in 1989. The largest synfuels plant built to date is being started up in Mossel Bay, South Africa, using SASOL synthesis technology. In 1993, the SMDS (Shell Middle Distillate Synthesis) plant will begin operation in Malaysia. A small plant near Denver, CO, has started operations, producing diesel fuel based on slurry-phase catalytic conversion of syngas made from landfill gas.

Insofar as oxygenate fuels from syngas are concerned, gasoline blends containing mixed alcohols, manufactured from syngas, were marketed in Italy for a period of time in the 1980s. In the United States, the Tennessee-Eastman plant has been recently expanded, manufacturing products that include methanol, using syngas made from coal. The growth in use of methyl tertiary butyl ether (MTBE), manufactured from methanol and isobutene, has been phenomenal. Production reached 6 million gallons per day in the United States in 1992 (gasoline usage is 300 million gallons per day).

The use of oxygenates in fuels is greatly influenced by the CAAA of 1990. Forty-four cities require that gasoline contain 2.7% oxygen (equivalent to 15 vol % MTBE) in the winter months beginning in 1992. In these cities the carbon monoxide in the air exceeds the amount deemed allowable for health reasons. Further, in 1995 nine cities not in compliance with air standards will require that gasoline contain 2% oxygen year-round. There are other future requirements for clean fuel fleets.

It should be noted that gasoline reformulation has been voluntarily instituted to some degree by the petroleum industry. Reformulated gasoline contains some oxygenates.

Our discussion will be concerned with two types of hydrocarbon fuels and three types of oxygenate fuels that can be synthesized from syngas. Seven alternative reaction pathways are involved (see Figure E-1).

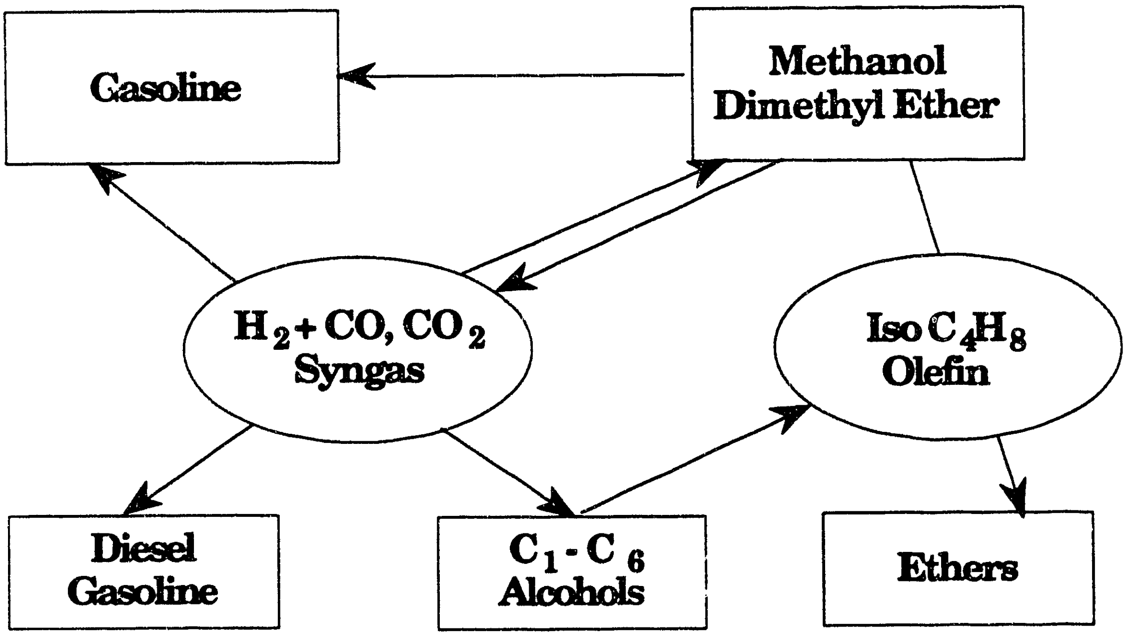


Figure E-1. Liquid fuels from syngas: pathways for their syntheses

E.2 Oxygenate Fuels

Oxygenates generally thought to be most suitable for fuels are shown in Table E-1.

Table E-1. Oxygenates Most Suitable for Fuels

	Blending RVP[1]	Blending Octane	Btu/Gal 1000s
Methanol	31	116	65
Ethanol	17	113	77
MTBE	8	110	109
ETBE[2]	4	110	117
TAME[3]	2	103	112
t-Butanol	9	100	101
Isobutanol	5	102	95
Gasoline		87	125

[1] RVP = Reid vapor pressure
[2] ETBE = ethyl tertiary butyl ether
[3] TAME = tertiary amyl methyl ether

Other oxygenates under consideration as blending agents include diisopropyl ether and dimethylcarbonate.

E.2.1 Methanol Manufacture

Blends of gasoline and low levels of methanol have been tested extensively. Higher molecular weight alcohols are usually included in the blend to help prevent phase separation, which can occur when small amounts of water are inadvertently present. At present, blends containing low levels of methanol are not well regarded as commercially desirable by the public and industry.

In contrast, fuel M85, 85% methanol and 15% gasoline, provides excellent performance in vehicles designed for this fuel. M85 is being marketed in California and other U.S. locations. In addition, flexible fuel vehicles (FFVs) are being manufactured. FFVs can use gasoline or methanol or blends of any intermediate composition.

Technology that will permit a higher conversion per pass of syngas will improve the economics of methanol production. In current methods for methanol manufacture, conversion of syngas per pass is limited by thermodynamics to 25% and in practice is about 10%. Expensive recycle is required. Several encouraging concepts for higher conversion rates per pass are being investigated.

E.2.1.1 More Effective Heat Removal

If heat could be removed more effectively from the reactor, temperature rises could be prevented, creating hot spots that decrease methanol conversion levels and shorten catalyst life.

- A slurry catalyst system, liquid phase methanol or LPMEOH process, has been developed and operational parameters established both in the laboratory and in a 10-ton-per-day pilot unit. Demonstrations on a larger scale are being proposed.

- Utilization of a fluidized bed catalytic reactor for heat removal has been explored with some success.

E.2.1.2 Methanol Removal From Reactor to Achieve Higher Conversion

Conversion of syngas to methanol is limited under industrial conditions by thermodynamic considerations. However, the following schemes are proposed for methanol removal from the reactor, which would increase conversion and decrease or eliminate the need for expensive recycle of unreacted syngas.

(1) Gas solid trickle flow reactor
(2) Reactor system with interstage product removal
(3) Condensing methanol principle.

E.2.1.3 Novel Catalysts for Methanol Synthesis

These novel catalysts can be used at 150°–180°C instead of the usual 250°–300°C. These catalysts would permit higher conversion of syngas because of more favorable thermodynamic limitations at lower temperatures. Also, operation at lower pressure in less expensive equipment would be possible. Additionally, the possibility is offered that the expensive oxygen plant would not be required. Syngas made in an air-blown gasifier would be used and the nitrogen separated more easily from the liquid methanol product rather than from gaseous oxygen.

Unusually high-activity catalysts have been discovered. These are based on metal alloys, $KOCH_3$ (methyl formate route), and supported metals platinum group metals such as Pd and Rh.

Although these catalysts have promise, each has practical problems. It is here that fundamental research can provide critical information and ideas.

E.2.2 Coproduction of Methanol and Electricity

Several plants are being installed to generate syngas from coal for use in generation of electricity in integrated gasification combined cycle (IGCC) operation. It is proposed that it would be economically beneficial to combine the generation of electricity and the manufacture of methanol. Methanol would be manufactured from syngas in off-peak electrical periods when syngas is available. Methanol synthesis technology that can accommodate CO-rich gas and that can "load follow" efficiently is needed. One option being proposed is a "once-through" configuration, in which the syngas passes through the methanol synthesis reactor and on to the electrical plant.

E.2.3 Coproduction of Methanol and Dimethyl Ether

Higher syngas conversion per pass can be achieved by providing a catalytic system that produces a mixture of methanol and dimethyl ether (DME) in a single reactor. This is a chemical method of removing methanol from the reaction system. DME is synthesized by the sequential reaction:

$$2\,CO + 4\,H_2 \rightarrow 2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O\ .$$

Depending on the catalyst and conditions, CO_2 may be produced instead of H_2O. A combination of a methanol synthesis and a methanol dehydration catalyst is employed. DME has a number of applications for fuels and manufacture of fuels and chemicals. The development of mixed MeOH and DME manufacture is regarded as an important new technology.

E.2.4 Increased Energy Efficiency in Methanol Use

If waste heat from an engine exhaust is used to provide the energy to convert methanol back to syngas, an endothermic reaction, the heating value of the syngas is larger than that of the methanol from which it is derived. A gain in energy efficiency of as much as 20% is possible.

E.2.5 Mixed Alcohols

There was much enthusiasm during the 1980s for the production of mixed alcohols for use as octane-enhancing components in gasoline blends. The following special catalysts were developed: (1) alkali modified copper methanol synthesis catalysts, (2) Co or Ni modified copper methanol synthesis catalysts, (3) MoSx-based catalysts, and (4) supported platinum-group metals (Pd, Rh). A comprehensive technology base was developed and trial commercial production was initiated in Italy. An extensive series of pilot unit tests were conducted in Japan using French/Japanese technology. Processes are available for license. However, at present mixed alcohols are not regarded as commercially promising because they cost more to manufacture than methanol, and most importantly, the need for a octane-enhancing blending agent is being filled with MTBE, which is regarded as having better all-round properties.

However, there is interest in and opportunities for individual higher alcohols, particularly ethanol and isobutanol.

E.2.6 Ethanol

Ethanol is regarded as a desirable fuel both alone and in blends. Promising research results for selective ethanol synthesis have been obtained by

• Homologation of methanol	$CH_3OH + CO + 2H_2 \rightarrow CH_3CH_2OH + H_2O$
• Biocatalysis	enzymes
• Isomerization of DME	$CH_3OCH_3 \rightarrow CH_3CH_2OH$.

E.2.7 Isobutanol

It is proposed that isobutanol can be suitable as a blending agent in competition with MTBE. Alternatively, isobutanol is also desired for manufacture of isobutylene needed for reaction with methanol to produce MTBE. Although the isobutanol content of mixed alcohols is high, (for example, 70% of C_4 alcohols) the overall selectivity from syngas to isobutanol by known technology is not high.

It is encouraging that, in syngas conversion, the thermodynamically allowable isobutanol is very high. Secondly, it has been found that recycle of methanol in mixed alcohol synthesis increases higher alcohol formation by homologation of lower alcohols.

E.2.8 Methyl Tertiary Butyl Ether

MTBE was first introduced in gasoline blends in Italy in 1973. Its growth has been phenomenal, reaching 6 million gallons per day in the United States (gasoline use is 300 million gallons per day). Synthesized by the reaction

$$CH_3OH + \text{iso } C_4H_8 \rightarrow CH_3OC(CH_3)_3 \text{ ,}$$

MTBE is partly derived from syngas: 36% by weight of MTBE is provided by methanol. Plants to manufacture TAME are also being installed.

One interesting technical innovation in ether synthesis is the use of "catalytic distillation" to carry out the above reaction with the advantage that the reaction is driven almost 100% to the ether.

There has been concern that there would be insufficient isobutene for MTBE needs. However, the need is being met by dehydrogenation of isobutane and by new cracking catalysts, which produce higher than usual amounts of isobutene. Also, as pointed out above, isobutanol can be produced from syngas and dehydrated to isobutene.

E.3 Hydrocarbon Fuels

E.3.1 Fixed-fluidized-bed Fischer-Tropsch (FT) Synthesis Reactor

The FT process has long been employed for production of gasoline from syngas, notably in Germany in World War II and in South Africa (SASOL) beginning in 1954. Recently, important new and improved technology has emerged, unexpectedly perhaps, since FT is such a long and well-researched process.

SASOL announced in 1989 that a fixed-fluidized-bed catalytic synthesis reactor had been installed. They report that this cuts the cost of the synthesis plant section in half relative to the previous entrained-fluid-bed reactors. Improved plant operability is also reported. SASOL has also indicated that a slurry-phase reactor system will be operated in 1993.

E.3.2 Synthesis to Wax, Hydrocrack to Diesel and Gasoline

Royal Dutch/Shell, Amsterdam, is constructing a 14,000-barrel-per-day (bpd) plant in Malaysia at a cost of $660 million. A novel combination of catalytic processes is employed in the SMDS process. Syngas from natural gas is converted to high molecular weight waxy hydrocarbons. It appears certain that a cobalt catalyst will be used, operated under conditions that provide for conversion to high molecular weight hydrocarbons (high alpha value [ASF]) in the synthesis process. A key feature is that the production of low molecular weight hydrocarbons, particularly methane, is avoided. The waxy product is selectively hydrocracked, using modern hydrocracking catalysts, to produce high-quality diesel fuel, valuable waxes, and gasoline.

Exxon has been active in developing a new process for synthesis of hydrocarbon fuels from syngas. Almost nothing has appeared in the technical literature. However, Exxon has said to stockholders that its divisions are "collaborating on advanced proprietary technology for on-site conversion of natural gas to liquid products." A demonstration unit is now in operation and excellent progress is being made in obtaining critical data for scaleup to commercial size. An investment of more than $100 million has been made over a 10-year period and more than 100 patents have been obtained. It appears that this is also a variation in the FT-type process. It is reported that a new fluid-bed gas-reforming process has been developed. Exxon has reported that the syngas is converted to an intermediate product. This may consist of C_{5+} hydrocarbons that are isomerized and/or hydrocracked to produce a gasoline that has a suitable octane rating, as well as other products, such as diesel fuel.

E.3.3 Slurry Phase FT

One of the most exciting developments in FT technology is the slurry phase conversion of syngas to hydrocarbon fuels. Originally investigated in Germany by Koelbel following World War II, recent engineering and economic evaluations have given great impetus to the possible advantages of slurry phase FT. A major improvement is the capability to carry conversion per pass nearly to completion, thus avoiding major recycle costs. It has been recognized that information obtained on a larger scale unit is needed. An important test was carried out in August 1992 in the La Porte unit sponsored by the U.S. Department of Energy (DOE) and a number of national and international industrial partners.

A slurry phase FT operation is being conducted on a very small scale in a plant operated by the Fuel Resources Development Company near Denver, CO. An iron-based catalyst is used and the diesel fuel product has been reported to have excellent properties.

E.3.4 Methanol-to-Gasoline and Related Processes

The Mobil MTG process, developed cooperatively with DOE, has been in successful operation in New Zealand for 6 years. Also with support from DOE, a fluid-bed version of MTG has been demonstrated on a semi-commercial scale in Weseling, Germany. Further, related processes called MTO (methanol to olefins) and MOGD (Mobil olefins to gasoline and distillates) have been developed.

Improvements have been made to the MTG process since its installation in fixed-bed form. The TIGAS (Topsøe) variation provides for plant savings by process integration. The experience gained with these processes has shown that several additional improvements can be achieved. The process can be optimized to make it more economical by engineering the best technology combinations of MTG, MOGD, and TIGAS for particular applications. One such application might be for removal of the greenhouse gas CO_2 and its conversion to a useful fuel.

E.4 Chemistry of Syngas Catalysis

The development of improved catalysts and processes has, to a great degree, been made possible by advances in understanding the chemistry of syngas catalysis reactions. Advanced instrumental characterization of catalyst surface structures has been particularly important, as well as reaction mechanism studies using isotopic labeling and kinetic research. It is now clearly established, perhaps unexpectedly, that over $Cu\text{-}ZnO/Al_2O_3$ catalysts and industrial conditions for methanol synthesis, hydrogenation of CO_2 predominates over CO hydrogenation and copper metal is the active catalytic component. CO is converted to CO_2 by the water gas shift reaction. The reaction steps of the water gas shift reaction are independent of those in methanol synthesis. It is believed that methanol formation proceeds through reaction of CO_2 to formate and methoxy intermediates. It has been established that higher alcohol formation over alkali-containing catalysts is a kinetically controlled chain growth mechanism superimposed on a thermodynamic background. Experimental and theoretical calculations support the mechanism in which chain growth in oxygenate synthesis is via aldol addition with oxygen retention reversal.

For hydrocarbon synthesis, a quantitative understanding has been developed of product carbon distribution numbers in FT synthesis over both iron- and cobalt-based catalysts. This knowledge, coupled with kinetic data, has been vital in the development of new processes for diesel and gasoline manufacture. Likewise, experiments on heat and mass transport are being used in critical development of greatly improved slurry-phase catalytic processes.

Exploratory research on innovative catalytic concepts is a powerful tool for making major improvements. Exciting advances have been made in novel catalysts from metal alloys, alkoxide activation of CO and supported rhodium catalysts, and expert system concepts (artificial intelligence) for catalyst design.

E.5 Economics

The cost of production of synthetic fuels is much more dependent on plant investment costs than on raw materials costs. This is illustrated in the following generalized estimate for producing synfuels from coal. The figures may be taken as cents per gallon of fuel, totaling 100 cents per gallon.

Coal	23	
Operation	5	
Maintenance, insurance, etc.	26	(both capital related),
Profit	23	
Taxes	23	
Total	100	

Capital-related charges, including taxes, equal 72; raw materials equal 23.

It is now being recognized that the value of a fuel can be strongly dependent on environmental criteria, which alter fuel economics. Higher environmental performance justifies higher prices. Thus, while the current price of gasoline at the refinery is 65 cents per gallon, MTBE with 87% as large a heat of combustion sells at 100 cents per gallon.

It can be considered that fuel prices are determined by the following values: heat of combustion, octane or diesel rating, and environmental properties. Thus the price of MTBE is determined to be 57, 20, and 23, respectively, for a total of 100. Thus, 23 cents a gallon is justified by environmental benefits.

It should be mentioned that if carbon dioxide emissions are taxed in the future, (an idea being discussed in Europe at about $10/barrel of oil), there could be a significant economic benefit to fuels from biomass. Overall, fuels from biomass are not considered to add to CO_2 pollution.

Experienced engineers have made many detailed economic estimates for the manufacture of synfuels. Considerable variations in estimates occur partly because costs of plant construction and of raw materials are quite site-specific. However, it is clear that, under usual industrial conditions, synfuel manufacturing costs are greater than those for gasoline made from petroleum at current petroleum prices. It is also clear that special considerations can justify synfuel manufacture. These special considerations may be to ensure a secure fuel supply, to receive special credit for coproduction of chemicals or electricity, or to benefit from environmental improvements.

How much can improved syngas conversion reduce fuel manufacture costs? The syngas conversion section of a methanol plant represents only 22% of plant investment. However, improvements can have an amplification effect where

- More valuable products are produced
- Overall plant costs are decreased; for example, where cheaper syngas manufacture is made possible (air-blown syngas), eliminating the oxygen plant.

Perhaps the most striking are the estimates that have been made for the production of diesel and gasoline from syngas using modern gasifiers coupled with slurry FT. In going from the SASOL operation involving Lurgi gasifier and fixed-bed catalytic synthesis to a modern gasifier and slurry FT, the energy efficiency is increased from 44% to 59%. The selling price of the diesel and gasoline is decreased from $55 per barrel to $42 per barrel! The $42 per barrel price for gasoline and diesel makes slurry FT as low or lower than direct liquefaction of coal for the same gasoline and diesel products (not crude oil) made by direct liquefaction of coal.

Future Research Opportunities

E.6 Potential

Liquid oxygenate and hydrocarbon fuels manufactured from syngas have high performance characteristics. Their use provides efficient engine performance and environmental benefits.

There is the potential for substantially increased use of MTBE and other oxygenates in gasoline blends. There are opportunities for manufacture of ethanol or isobutanol from syngas and their use in blends, depending on whether future technology can decrease costs of their manufacture from syngas.

Fuels consisting entirely or mostly of oxygenates also have much potential. In the long term, of the oxygenates, methanol appears to be the fuel of choice in vehicles designed for its use. However, if methanol, now being marketed as M85, proves unacceptable because of its poisonous character, ethanol may become the preferred alcohol fuel.

Important new technology for manufacture of hydrocarbon diesel fuel from syngas provides opportunities for this type of fuel. Diesel fuel performs with high efficiency in well-established engines. The diesel from syngas has an excellent cetane rating and is reported to be environmentally superior to conventional diesel fuel.

The main barrier to synfuels from syngas is their cost relative to gasoline made from petroleum at today's prices. As described in this report, there is the potential to lower the cost of liquid synfuels from syngas by new and improved catalytic synthesis technology, which can

- Lower the cost of manufacture by 10%–30%, particularly by lowering plant investment costs
- Justify higher-than-gasoline price by 10%–15% by providing improved engine performance
- Justify higher-than-gasoline price by 35% by providing environmental benefits (MTBE is an example)
- Improve the economics of synfuel manufacture by providing for high price coproducts: chemicals or electricity
- Provide for liquid synfuels from biomass that are not subject to future tax on CO_2 emissions. This could be a $10 per barrel advantage over fuels from petroleum.

To accomplish these objectives, a combination of research approaches is needed: fundamental science and innovative and exploratory chemistry, as well as engineering/developmental research. New ideas could open up unexpected opportunities. A modest improvement in a near-commercial process could serve an important function of crossing the threshold in making it commercially viable.

Specific research opportunities are summarized in Table E-2 and E-3 in terms of technical objectives, potential benefits, and research concepts/approaches to achieve objectives. The nature and status of accomplishments and problems to be overcome are reviewed in the detailed report.

E.7 Integral Syngas Production/Fuel Synthesis

There is an opportunity to combine catalytic syngas production with fuel synthesis with large potential savings. The desired overall reaction is

$$CH_x + H_2O \rightarrow CH_3OH + CO_2 .$$

The concept is combination catalysts that promote steam reforming and methanol synthesis.

E.8 Fundamental Catalytic Science and Engineering

Modern processes for selective synthesis of high-performance fuels from syngas have benefited greatly from advances in fundamental catalytic science and engineering. The knowledge of kinetics and thermodynamics and determination of reaction mechanisms has contributed greatly to improved technology of modern processes. There are critical opportunities to more clearly delineate critical catalyst structure/performance relationships. There is much promise that the new instrumentation and research techniques for fundamental catalytic surface science characterizations will lead to the design of even more selective catalysts that are not otherwise achievable.

Table E-2. Research Opportunities for Oxygenates

Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Methanol	
• Achieve nearly complete conversion of syngas in a single pass	• Avoid cost of separation and recycle	• More efficient heat removal from reactor; removal of methanol from reactor; high-activity catalysts operating at low temperature
• Provide efficient coproduction of methanol and dimethyl ether	• Cheaper plant; provide valuable new fuel	• Combination catalysts; slurry-phase catalysts
• Provide efficient methanol synthesis in combination with coproduction of electricity	• Utilize plant full time; choose optimum electricity/methanol mix; environmental benefits	• Once-through operation; engineer processes adapted to load-following and variable production demands
	Ethanol	
• Develop catalysts that will provide selective conversion of syngas to ethanol	• Lower cost ethanol; use for ETBE	• Isomerization of dimethyl ether; homologation of methanol; biocatalysis
	Isobutanol[1]	
• Discover technology that will provide selective conversion of syngas to isobutanol	• Possible preferred competitor to MTBE	• Recycle lower alcohols; alkali (Cs) modified catalysts
	Ethers[2]	
• Make isobutylene from syngas	• Avoids need for petroleum for manufacture of MTBE	• Convert syngas in a single step by combination catalysts

Table E-2. Research Opportunities for Oxygenates (Concluded)

	Methanol	
Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Syngas Fuel	
• Convert methanol to syngas	• Increases useable Btu by utilizing waste heat for converting methanol to syngas with a higher Btu content	• Catalysts that operate over a wide temperature range

[1] Improved synthesis of isobutanol could be important for its conversion to isobutylene for manufacture of MTBE and ETBE.

[2] *Efficient processes, including catalytic distillation,* have been developed for conversion of alcohols and iso-olefins to ethers. Thus, research opportunities for improved alcohol synthesis are most pertinent in improving ether technology.

Table E-3. Research Opportunities for Hydrocarbons

Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Synthesis of Wax and Hydrocracking[1]	
• Improve selectivity to desired gasoline and diesel fractions	• More economical production of higher quality fuels	• Catalysts based on molecular sieves; improved multimetal cobalt catalysts; reactor engineering and process integration
	Slurry Phase Fischer-Tropsch[2]	
• Improved and optimized catalysts for this new type of catalytic processing	• Make this process economically competitive	• Catalysts designed for controlled suspension/settling; catalysts that facilitate separation from heavy hydrocarbon products; reaction engineering and process integration

[1] Recent research and development results have opened up new opportunities for converting syngas to an intermediate hydrocarbon product that is then hydroprocessed to high-quality fuels.

[2] Recent engineering and economic estimates have provided great encouragement for FT synthesis that is carried out using a slurry catalyst system. Operability tests on a larger scale have been recommended as crucial; an important test was recently carried out.

Status

1.0 Introduction

The manufacture and utilization of synthesis gas—a mixture of H_2 and CO that usually contains CO_2—is rapidly growing in importance as a source of liquid energy fuels and as a clean fuel for electricity generation.

Several factors are expediting the move in this direction. First, syngas can be made from abundant U.S. supplies of coal, gas, and biomass. This provides the advantage of choice of feedstocks and, in particular, avoids reliance on importation of expensive, uncertain, foreign petroleum.

Second, synfuels from syngas can help lessen environmental pollution. Fuels from syngas are sulfur free. Furthermore, the inclusion of oxygenates in gasoline blends acts to lessen levels of atmospheric carbon monoxide and ozone. Indeed, oxygenates are required to a considerable extent by the Clean Air Act Amendments (CAAA) of 1990.

Third, fuels of widely varied composition can be selectively synthesized. These can be hydrocarbon or oxygenate fuels that have high engine performance characteristics. Specifically, fuels of higher octane (gasoline) or cetane (diesel) values, which provide for higher energy efficiencies, can be manufactured.

Fourth, a major factor in advancing the viability of synfuels from syngas is the advent of new, significantly improved catalytic technology for their manufacture and use. This improved catalytic technology is the subject of this report.

This report is designed to provide an account and evaluative assessment of advances in technology for production of liquid energy fuels from syngas and to suggest specific opportunities for future research deemed promising in bringing such technology to commercialization. Technology for manufacture of syngas is not included in this study.

In direct liquefaction, the starting material, generally coal, is contacted with hydrogen under pressure in the presence of a catalyst to produce a liquid that is then extensively refined. The hydrocarbon liquid fuels from direct liquefaction are highly aromatic, reflecting the characteristics of the parent coal.

The manufacture of liquid fuels via syngas is often referred to as indirect liquefaction because two separate, successive steps are involved. First, coal, gas, or biomass is converted to syngas. Second, the syngas is converted over a catalyst to a liquid fuel. In contrast to direct liquefaction, hydrocarbons from indirect liquefaction are paraffinic in nature. The growing concern and increasing restrictions on aromatic in gasoline favor indirect liquefaction fuels that do not contain aromatics. In addition, hydrocarbon fuels from indirect liquefaction are sulfur free.

As an alternative to production of hydrocarbon fuels, indirect liquefaction can be used to produce oxygenates. Incorporation of oxygenates in gasoline is environmentally beneficial and is in fact required to a significant degree by the CAAA of 1990.

Of greatest importance to advanced technology for synfuels manufacture is the almost miraculous variety of catalysts available, each of which imparts individual selectivity to product formation during CO hydrogenation. For example, nickel catalysts guide conversion virtually 100% to methane, whereas copper-based catalysts can direct conversion almost 100% to methanol. The variety of catalysts and the reactions they catalyze is illustrated in Table 1. An increasing number of catalysts is being discovered, some with multifunctional capabilities. Additionally, the scientific understanding of catalyst structure/functional relationships is advancing rapidly, which holds promise for the creation of intentionally designed catalysts with higher activity and selectivity capabilities.

A further important point is that catalytic engineering is contributing greatly to the success of new, practical catalytic systems. Such improved reactor systems provide better control of essential heat and mass transfer. More important, virtually new processes have been created by novel process combinations that utilize a previously established knowledge of catalytic kinetics.

In evaluating advances in synfuels technology, criteria for improved technology will focus on the potential to improve the economics of manufacture, particularly by lowering plant costs; to produce fuels that have environmental benefits in manufacture and use; and to provide higher selectivity to higher priced products. This includes chemicals and fuels that have better engine performance characteristics.

Attention is drawn to the interaction of advances in syngas technology in different energy application areas. Specifically, several large commercial installations have been initiated in the United States and abroad for syngas manufacture from coal and utilization of the syngas for generation of electricity, using an integrated gasification combined cycle (IGCC) technology. This is of two-fold significance. First,

Table 1. The Role of Catalysts in Alternative Fuels Technology[a]

Product	Reaction	Catalyst
Syngas	$CH_4 + H_2O \rightarrow H_2 + CO + CO_2$	Ni
Methanol	Syngas $\rightarrow CH_3OH$	$Cu\text{-}ZnO/Al_2O_3$
Higher Alcohols	Syngas $\rightarrow C_nH_{2n+1}OH$	$Cu\text{-}ZnO\text{-}K/Al_2O_3$; $Cu\text{-}Co/Cr_2O_3$; $K\text{-}MoS_2$; $Rh\text{-}Mo/Al_2O_3$
Gasoline (FT)	Syngas $\rightarrow C_nH_{2n+2}$	Fe, K
Hydrogen (shift)	Syngas + $H_2O \rightarrow H_2 + CO_2$	$Fe_2O_3\text{-}Cr_2O_3$; Cu-Zn oxides
Ethanol	Sugar, starch $\rightarrow C_2H_5OH$	Enzymes
IPA, SBA	Olefin + $H_2O \rightarrow$ ROH	H_3PO_4/SiO_2
MTBE, ETBE, TAME	Olefin + alcohol → ether	Acid resin
Isobutylene	TBA $\rightarrow$ i $C_4H_8 + H_2O$	H_3PO_4/SiO_2
Isobutylene	$C_4H_{10} \rightarrow$ i $C_4H_8 + H_2$	Cr_2O_3/Al_2O_3
Gasoline (MTG)	$CH_3OH \rightarrow C_nH_m$ including aromatics	ZSM-5 zeolite
Environmental protection (exhaust converter)	CO, HC, $NO_x \rightarrow CO_2$, H_2O, N_2	Pt, Pd, Rh/Al_2O_3

[a]MTG = methanol-to-gasoline process, IPA = isopropyl alcohol, SBA = sec-butyl alcohol, MTBE = methyl tertiary butyl ether, TAME = tertiary amyl methyl ether, TBA = tertiary butyl alcohol.

industrial experience often leads to technology improvements—in this case, syngas manufacture. Second, it permits possible improved economics through a combination of generation of electricity and manufacture of liquid fuels, particularly methanol.

This report is an update of a previous report—*Catalysts for Fuels from Syngas—New Directions for Research* (Mills 1988). In the earlier report, included here as an appendix, a concerted effort was made to identify novel catalytic concepts, exploratory research testing and scientific advances. Since that time, significant advances have been made in technology for syngas manufacture and utilization. These advances are a primary subject of this report.

Several industrial plants have been installed recently, or are being installed, to manufacture liquid fuels from syngas. It seems that, with the exception of ZSM-5 catalysts, these new installations are based not on novel catalytic chemistry but on catalytic engineering. That is, the processes used in these new plants utilize previously known types of catalysts in advantageous combinations and novel configurations. The fruits of previous research are being harvested. An example of such developments is the selective conversion of syngas to higher molecular weight hydrocarbons using a cobalt catalyst, followed by modern selective hydrocracking to premium liquid fuels. Another example is the use of slurry-phase catalytic reactor systems for more economical synthesis of methanol or liquid hydrocarbons.

A further point of major importance to both hydrocarbon and oxygenate fuels is the impact of the CAAA of 1990. Forty-four cities require that gasoline contain 2.7% oxygen (equivalent to 15 vol % MTBE) in the winter months beginning in 1992. In these cities the carbon monoxide in the air exceeds the amount deemed allowable for health reasons. Further, by 1995 in nine cities not in compliance with air standards, gasoline is to contain 2% oxygen year-round. There are other later requirements for clean fuel fleets. In an understatement, the administration has said "The CAAAs of 1990 were not intended to be an energy policy, but because of their major impact on the energy industry, they will have significant effect on energy use." The CAAA is revolutionizing the petroleum refining industry.

It seems certain that the combination of the technical advances being made, the depletion of petroleum and gas reserves, and balance of trade issues are bringing us close to the time when synfuels manufacture is justified. Indeed, already special circumstances have provided justification for synfuels manufacture here and abroad. In the United States, almost 6 million gallons per day of MTBE are being used. This is a significant fraction of the 300 million gallons per day of gasoline that are used in the United States. It is noted that methanol made from syngas contributes 36% by weight to MTBE manufacture.

The various liquid fuels from syngas and reaction steps to create them from syngas were illustrated in Figure E-1. Two types of hydrocarbon fuels and three oxygenate fuels are identified. Seven chemical reaction pathways lead to the syntheses of these fuels. Of course, there are many more individual chemical reactions involved. This figure serves as the basis for the organization of the report, beginning with oxygenates, then hydrocarbons, followed by sections on science of syngas catalysis and on synfuels economics, and finally a presentation of future research opportunities.

2.0 Oxyfuels

2.1 Overview

Oxygenates that are generally considered to be suitable candidates for fuel use are shown in Table 2. An idea of the relationship between molecular structure/octane values is given in Table 3. A wide variety of alcohols and ethers is represented, each with particular fuel manufacture characteristics. Key fuels properties are energy content (heat released on combustion) and blending octane number (Unzelman 1989a, 1989b; Spindelbalker and Schmidt 1986; Ecklund and Mills 1989). However, other properties are important, such as blending vapor pressure, because evaporative regulations are becoming more stringent (Figure 1).

Alcohols have long been used as transportation fuels, either alone or in gasoline blends to extend gasoline supplies, to enhance octane rating and so improve engine performance, and to decrease pollution (of recent major concern) (Ecklund 1992).

Ethanol is manufactured by fermentating sugar from sugarcane in Brazil and from corn in the United States. In Brazil, three million cars are powered by E96 (96% ethanol, 4% water) and twice as many cars by gasoline blends containing up to 20% ethanol. In the United States, a blend of 10% ethanol from biomass and gasoline is termed gasohol. Ethanol use in gasohol reached 2.3 million gallons (55,400 barrels per day or bpd) per day in 1987, about the present day level. Gasoline usage is 300 million gallons per day in the United States.

Table 2. Properties of Fuel Oxygenates

Oxygenate	Blending RVP	Blending Octane No.	Btu/gal 1000s	BP°C[a]	U.S. Production millions gal/day
Methanol	31	116	65	65	3.0
Ethanol	17	113	77	79	3.5
Isopropanol	14	109	95	82	0.6
t-Butanol	9	100	101	83	
Isobutanol	5	102	95	108	
Mixed alcohols		106		range	
MTBE	8	109	109	55	6.1
ETBE	4	110	117	73	
TAME	2	103	112	86	
Di-isopropyl Ether	5	104		69	
Dimethyl Carbonate		104			
Gasoline		87	125		300

[a] BP = boiling point °C

Table 3. Typical Octane Blending Values of Alcohols and Ethers (adapted from Courty et al. 1990)

R'	RO-	CH_3O-	C_2H_5O-	iC_3H_7O-	tC_4H_9O-	C_1-C_6 Alcohols
	RON	123-134	120-130	121	105-110	120-121
H		Methanol	Ethanol	IPA	TBA	
	MON	98-100	96-100	~96	93-95	97-98
	RON	113-117	~117	~105		
tC_4H_9		MTBE	ETBE			
	MON	95-101	~101	~96		
	RON	112-114				
tC_5H_{11}		TAME				
	MON	96-100				
	RON			~110		
iC_3H_7				DIPE		
	MON			~99		
	RON	~93				
tC_6H_{13}		t-Hexyl ME				
	MON	~85				

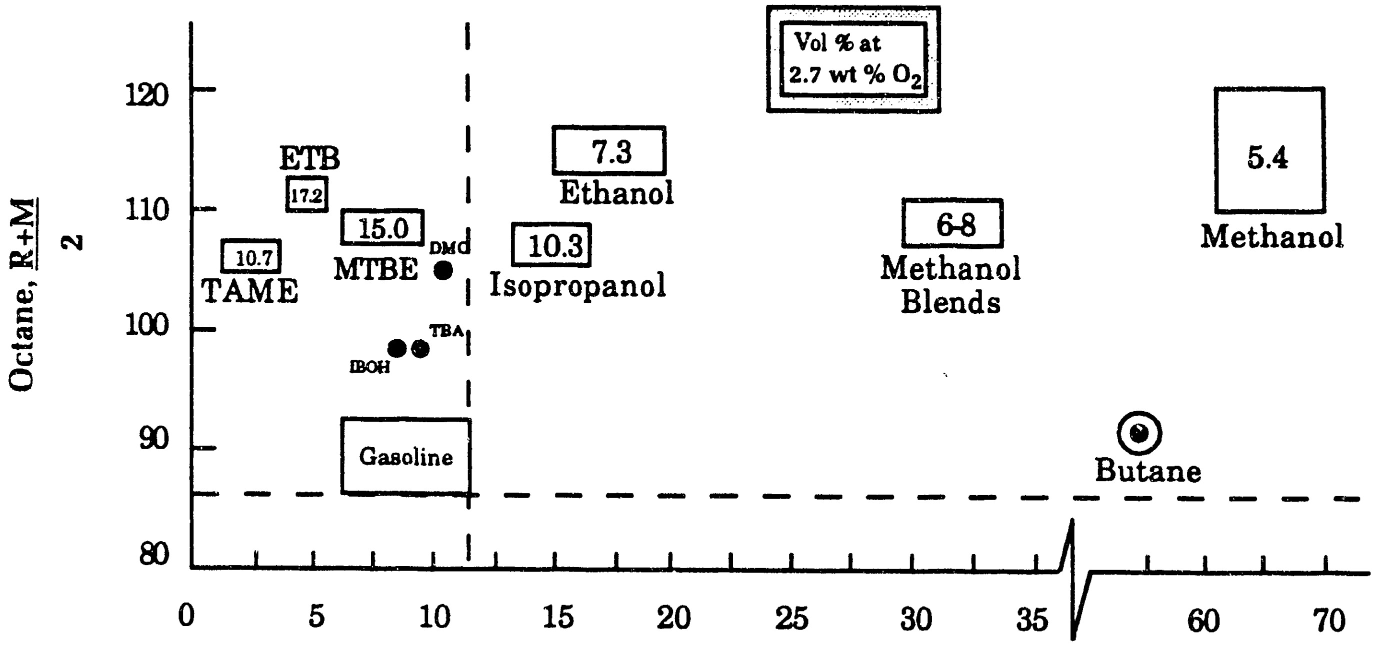


Figure 1. Blending properties of various oxygenates (Chem Systems 1992)

Alcohols used as transportation fuels, other than ethanol, are manufactured from syngas (Courty and Chaumette 1987). Methanol-gasoline blends of relatively low levels of methanol (5%–10%) have been tested extensively worldwide. Blends of gasoline and methanol plus higher molecular weight alcohols, which are added to assist in solubilizing methanol, have been used extensively. In 1982, Atlantic Richfield (ARCO) pipelined more than 35 million barrels of Oxinol™ blends (methanol/tertiary butyl alcohol) in its Pennsylvania/New York pipeline, which served more than 20 terminals (now discontinued). Methanol/gasoline blends are subject to phase separation brought on by the inadvertent addition of small amounts of water. Concern about possible deleterious effects of methanol on engines and fuel systems in autos not designed for methanol use has also been a negative factor for methanol acceptance.

However, methanol blends of high (85%-100%) methanol levels have had much success in vehicles designed for their use. Methanol is the fuel of choice for race cars because of increased power that can be obtained compared to a similar gasoline-fueled engine. M85 fuel, 85% methanol/15% gasoline, is being marketed to the public by a number of petroleum companies, particularly in California, to test the validity of perceived improved environmental benefits and engine performance qualities. In addition, flexible fuel vehicles (FFVs) have been tested extensively and their mass production is near. These vehicles can utilize either gasoline, methanol, or blends of any intermediate composition.

2.1.1 Ethanol

Japan and other countries continue to be interested in the selective manufacture of ethanol from syngas. Research continues directed to the homologation of methanol, that is, the addition of CO and H_2 to methanol according to the reaction

$$CH_3OH + CO + H_2 \rightarrow CH_3CH_2OH \ .$$

There is also interest in enzymatic conversion of syngas to ethanol.

A new possibility is suggested, namely the isomerization of dimethyl ether (DME) to ethanol according to the reaction

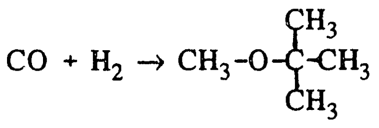
$$CH_3OCH_3 \rightarrow CH_3CH_2OH \ .$$

DME can be manufactured efficiently from syngas.

2.1.2 Isobutanol

There is special interest in isobutanol; it is proposed that isobutanol could compete with MTBE as a blending agent.

A further interest in isobutanol comes from the fact that it can be dehydrated to form isobutylene, needed for reaction with methanol to manufacture MTBE. It is interesting that MTBE can be manufactured entirely from syngas. Methanol and isobutanol are synthesized first and, as discussed later, are converted to MTBE providing the following overall reaction:



$$CO + H_2 \rightarrow CH_3\text{-}O\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{-}CH_3$$

2.1.3 Mixed Higher Alcohols

The technology for manufacture of mixed alcohols, namely C_1–C_5 alcohols, has been well developed. Commercial processes have been developed by Snamprogetti/Topsøe (Paggini et al. 1986), Lurgi (Goehna and Koenig 1989); Dow (Murchison et al. 1988), and IFP/Idemitsu (Courty et al. 1990). Gasoline blends containing C_1–C_5 alcohols were marketed as Superfuel E in Italy in the late 1980s (Morandi et al. 1988). Additionally, extensive semiworks experimental runs for mixed alcohol production were carried out by Idemitsu Kosan in Japan in cooperation with the Institut du Petrole of France (Courty et al. 1990).

Extensive research has established that catalysts containing alkali, particularly cesium, have the ability to catalyze the formation of relatively high amounts of isoalcohols, particularly isobutanol (Klier et al. 1992a). A large-scale test is planned 1993 in the LaPorte, TX, Air Products plant with DOE support, using a slurry-phase Cs-containing catalyst. It will be interesting to see if this test includes recycling of lower alcohols, since as discussed above, this study concludes that there is little interest in mixed alcohols that include C_1–C_3 alcohols.

The consensus is growing that mixed alcohols are not promising commercial blending agents because (1) they contain lower alcohols that are perceived to make such blends subject to phase separation, (2) they are more expensive to manufacture than methanol, and (3) the primary reason—MTBE has a better overall combination of qualities.

2.1.4 MTBE

MTBE is an indirect but straightforward method of introducing methanol into gasoline blends. The petroleum industry has long known MTBE as an octane enhancer. Gasoline blends containing MTBE were first marketed in Italy in 1973. The greatly increased use of MTBE has been augmented by a combination of favorable factors: its compatibility with gasoline (it is said to be "fungible"); its high blending octane number (109); its established efficient manufacture from methanol and isobutylene, the need for octane enhancement occasioned by the removal of lead from gasoline; perceived problems with blends containing methanol; and the requirement of the CAAA for use of fuels containing 2.7% oxygen in metropolitan areas that have not attained low enough levels of CO or ozone deemed essential for health. Commercial growth of MTBE manufacture has been phenomenal (Piel 1991; Haigwood 1991) (see Figure 2).

The status of technology for manufacture of oxygenates will now be examined. In particular, the potential value of recent improvements and opportunities for future research will be addressed.

2.2 Methanol Manufacture

There is extensive literature on the technology of methanol synthesis, including recent authoritative reviews by Supp and Quinkler (1984), Bart and Sneeden (1987), Lee (1990), Chinchen et al. (1990), Hoehlein et al. (1991), Trimm and Wainwright (1990), and Catalytica (1991). Utilization of methanol in spark and diesel engines has been extensively reviewed in the Ninth International Alcohol Fuel Symposium in Italy (1991). Social considerations deriving from methanol fuel have also been presented (International Energy Agency 1990a, 1990b; U.S. National Research Council 1990; Sperling and DeLuchi 1989; Gushee 1989).

Although the chemistry of methanol manufacture is simple ($CO + 2H_2 \rightarrow CH_3OH$), several process steps are required as shown in the process diagram for a modern plant for methanol production from natural gas (Figure 3).

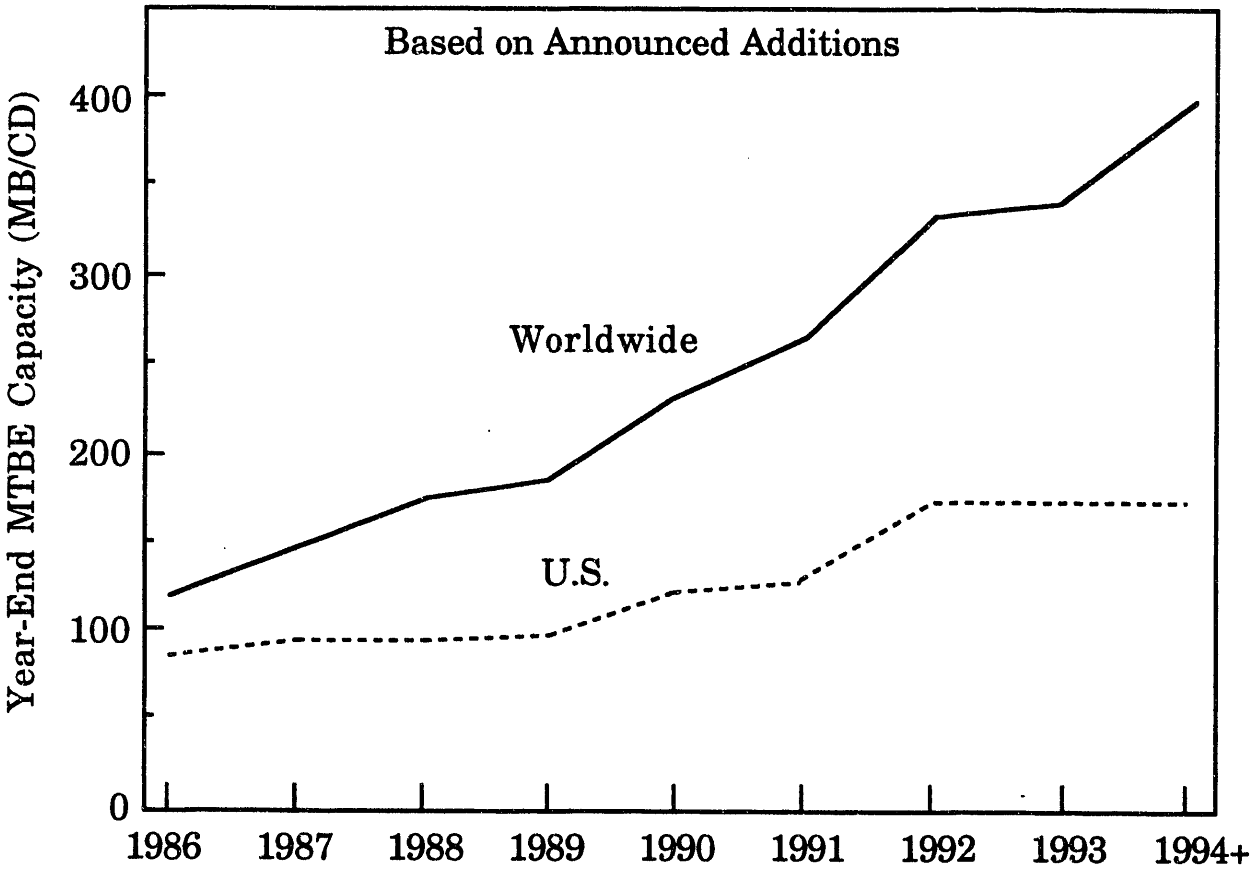


Figure 2. Worldwide production capacity for MTBE—MB/CD is thousand barrels per calendar day

Syngas conversion to methanol per pass in present commercial operation is limited to 25% or less by thermodynamic restrictions, even with modern catalysts and plant design. Costly recycle is required. A primary objective of improved technology for methanol manufacture is therefore to provide means for higher conversion of syngas per pass. This is being sought by

- More effective heat removal to keep reaction temperatures as low as possible (methanol synthesis is highly exothermic)
- Methanol removal during reaction to shift equilibrium to higher methanol conversion per pass
- More active (novel) catalysts able to operate at lower temperatures and so increase thermodynamically allowed methanol levels.

2.2.1 More Effective Heat Removal

Heat removal from catalytic reaction zones in modern plants is achieved either by indirect heat exchange by having catalysts packed in tubes surrounded by boiling water, or by the use of multiple, sequential catalyst beds with interstage quenching.

2.2.1.1 Slurry Catalyst Operation for Heat Control. A different concept for heat removal and temperature control is the use of a slurry catalyst system, utilizing catalyst particles suspended in an inert liquid (Bukur et al. 1990). This has been termed the liquid phase methanol process (LPMEOH). The liquid acts as a heat sink and keeps down temperature increases by making efficient heat exchange

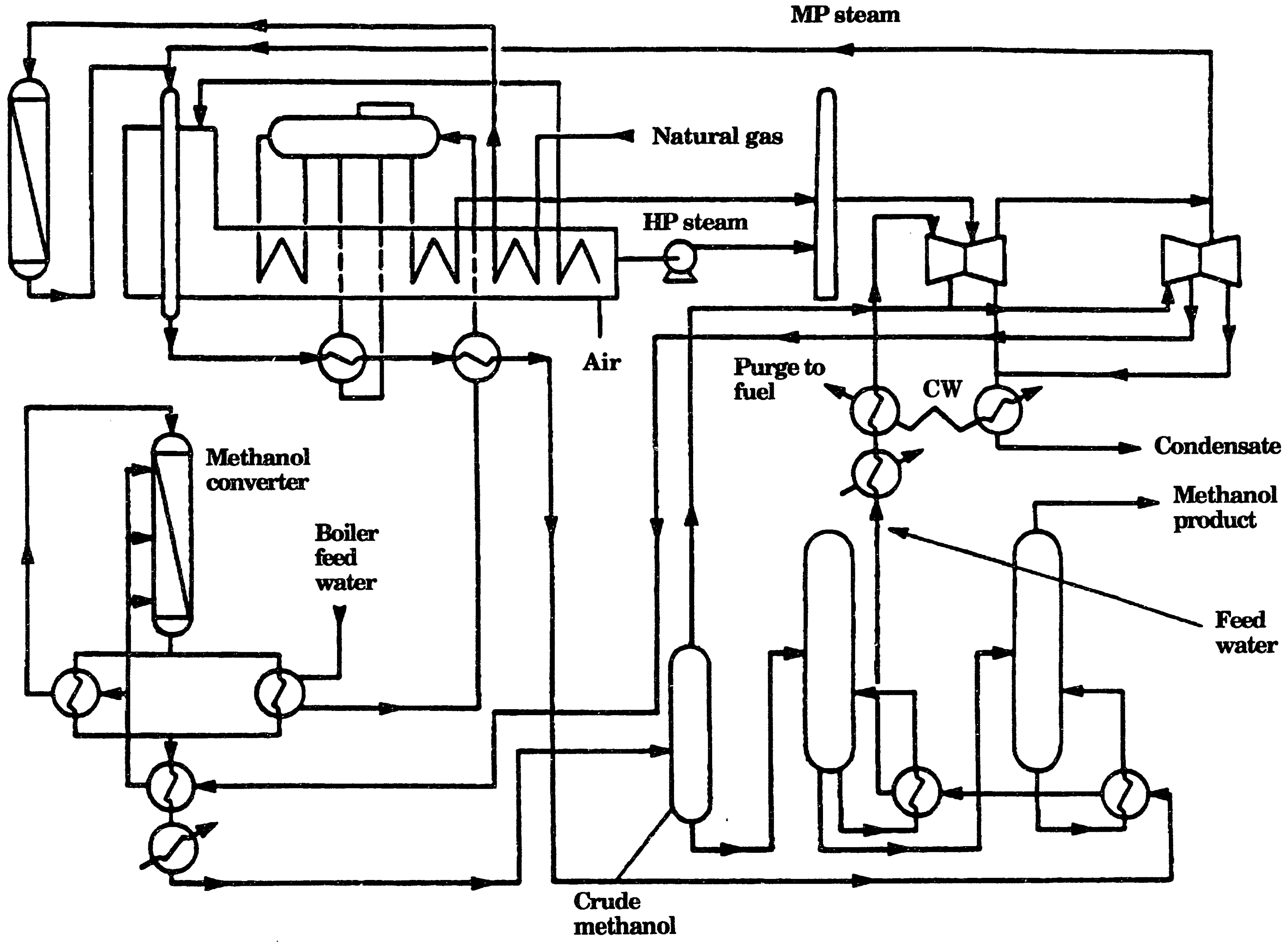


Figure 3. **Diagram of a modern plant for methanol production from natural gas** (Reprinted with permission from Chinchen et al., Copyright 1990, American Chemical Society)

possible. Building on initial work by Chem Systems, Air Products has carried out a 10-year laboratory research and pilot plant program costing $25 million, cost-shared by DOE and the Electric Power Research Institute (EPRI) (Underwood et al. 1991; Brown et al. 1990). Some 7,000 hours of experimental and demonstration operation were carried out in a 10 ton per day plant in La Porte, TX. A wide spectrum of operational conditions was examined. This work has established the technology base for operation:

- Characteristics required of a 1- to 10-µm catalyst for the synthesis reaction and suspension
- In-situ catalyst activation
- Demonstration that this system can simultaneously carry out methanol synthesis and water gas shift reactions and so utilize a cheaper syngas made by a modern gasifier with a H_2/CO ratio as low as 0.5
- Improved original plant design, including better gas distribution configurations and heat removal using more efficient internal heat exchange design
- Better operational procedures, which resulted in extended catalyst life.

Plant outputs higher than design were achieved over extended operational periods.

Proposals are under discussion for demonstration of the LPMEOH process in the Cool Water, CA, plant and other locations. One proposal in cooperation with EPRI contemplates combining the process with generation of electricity using coal gasification combined cycle (CGCC) technology.

Estimates of improvements provided by the LPMEOH process have been favorable by Chem Systems (Nizamoff 1989) and marginal by Bechtel (Fox et al. 1990).

2.2.1.2 Fluidized Bed or Superconverter for Heat Control. Fluidized reactors have been used commercially for many highly exothermic reactions because they permit high heat transfer and consequently near-isothermal operation. Higher process efficiencies as a result of higher per-pass conversions have been reported using a fluidized bed (Trimm and Wainwright 1990). Another design reported is the "superconverter," which features a 20-meter-long double-wall reactor. It was reported that this was being tested in a unit that has full-scale dimensions.

2.2.2 Methanol Removal to Achieve Higher Conversion

As mentioned, a major improvement in methanol synthesis manufacture can be achieved by lowering thermodynamic limitations on methanol conversion (Figure 4). This may be achieved by removal of methanol as it is formed, so shifting the reaction to further methanol formation.

2.2.2.1 GSTFR, RSIPR. A novel approach has been tried in two forms. The first design is named gas solid trickle flow reactor (GSTFR) (Westerterp and Kuczynski 1986). In this scheme, the product methanol is removed from the reactant zone by selective adsorption on a porous solid powder (an amorphous silica-alumina cracking catalyst), which trickle flows over (through) a fixed bed containing pellets of conventional methanol synthesis catalyst and Rashig ring packing. By removing the methanol from the reaction, methanol yields of 100% can be achieved. An alternative approach to product separation, by the same group at Twente University, is by the use of the reactor system with interstage product removal (RSIPR) (Westerterp et al. 1988; Kuczynski et al. 1987). This reactor scheme is based on conventional fixed multibeds with selective methanol removal between each bed.

2.2.2.2 Solvent Methanol Process (SMP). This concept of "beating the equilibrium" (Berty et al. 1990) involves a high boiling, inert solvent that is introduced into the reactor, which contains a fixed catalyst bed. The solvent flows concurrent with the synthesis gas stream. The solvent selectively absorbs methanol as soon as it is formed over the catalyst bed, causing the methanol activity to remain low and

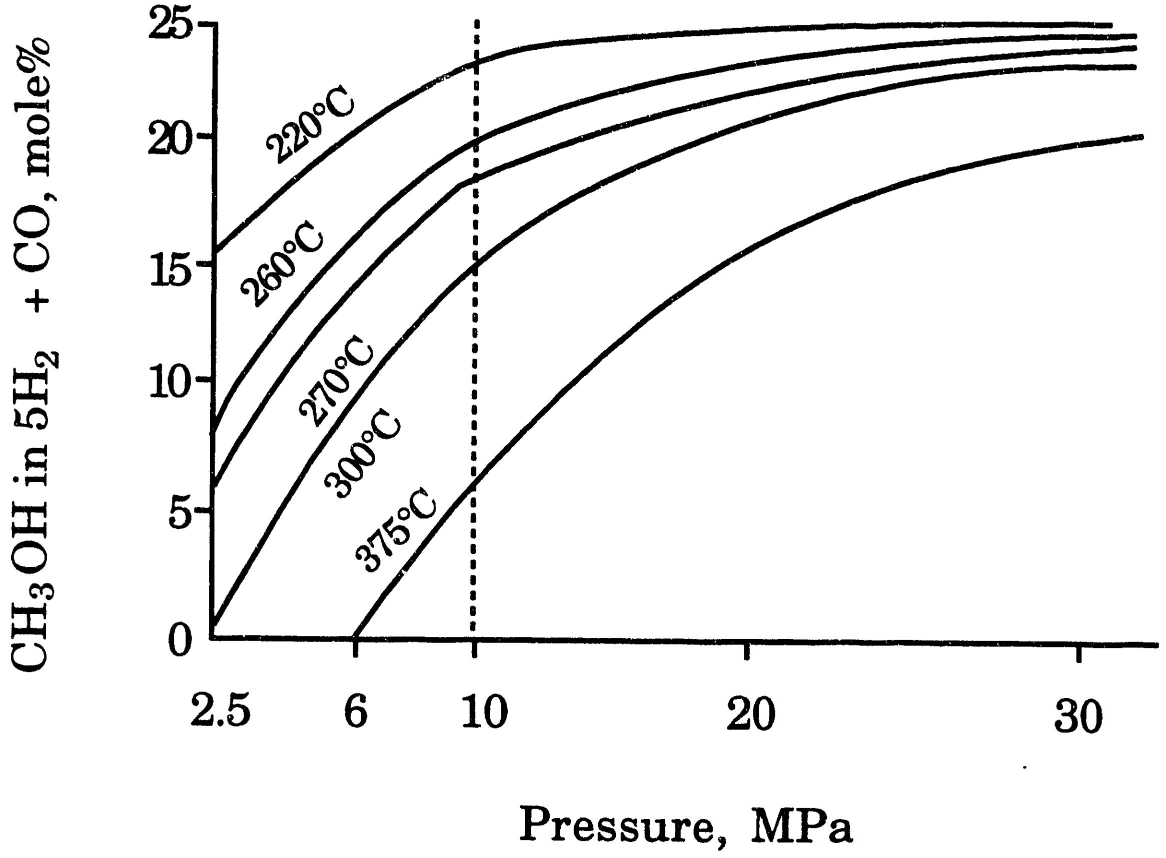


Figure 4. Methanol equilibrium as a function of pressure and temperature

enabling an equilibrium shift toward the product. Feed conversion can be enhanced and gas recycle can be virtually eliminated. Operability was demonstrated. Best results were reported using tetraglyme as solvent.

2.2.2.3 Condensing Methanol Principle. Recent advances in methane reforming have made it possible to generate a synthesis gas, $H_2/CO = 2$, (stoichiometric for methanol synthesis), with a low CO_2 (2%) content at a reasonable cost. Thermodynamic calculations were made (Hansen and Joensen 1991) to determine equilibria for methanol synthesis, shift equilibria, and methanol dew points for various pressures and temperatures (Figure 5). Laboratory experiments were carried out in isothermal reactors; results are shown in Figure 6. The conversions measured at 230° and 240°C were in excellent agreement with those predicted for gas phase equilibria. However, at 220°C and below, it was found unexpectedly that conversion levels were so high that condensation must have occurred and in fact the dew point line had been crossed. More surprisingly, at 200°, 210°, and 220°C the conversions were *above* the levels that gas phase thermodynamics actually predict.

The observations were explained by the highly non-ideal properties of the liquid phase condensing on the catalyst. In further experiments it was determined that it was possible to operate completely without a gas purge from the reactor at a conversion of $CO + CO_2$ of 97%. Pilot plant tests were conducted over a period of several months, which demonstrated that the thermodynamic "barrier" had been broken because condensation occurred in the exit section of the reactor.

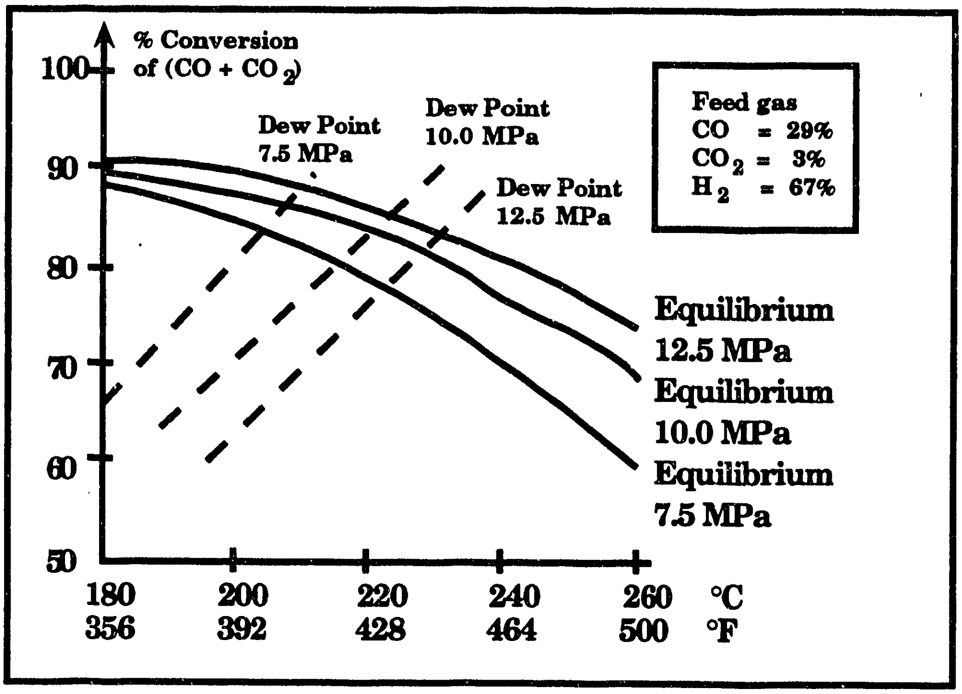


Figure 5. **Methanol + shift equilibria and dew points** (Reprinted with permission from Hansen and Joensen 1991, Elsevier Science Publishers)

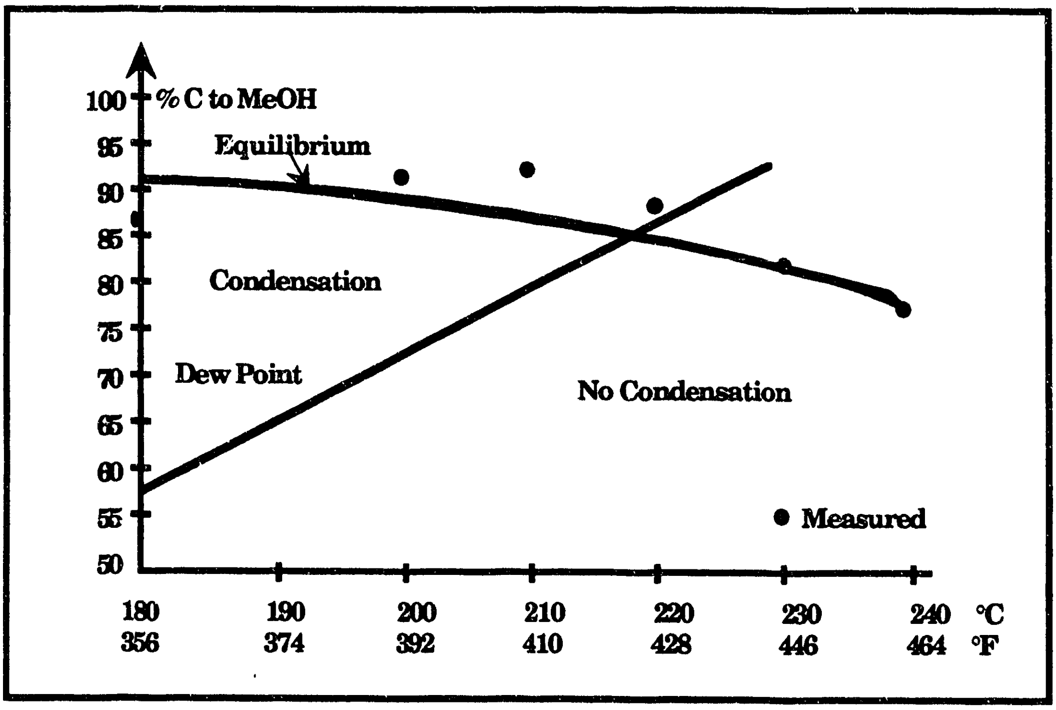


Figure 6. **Once-through conversion of CO and CO$_2$. 9.6 MPa; CO = 30%; CO$_2$ = 2%** (Reprinted with permission from Hansen and Joensen 1991, Elsevier Science Publishers)

2.2.3 Novel Catalysts for Methanol Synthesis

Several non-conventional catalyst types have attracted attention because of their high activity for methanol synthesis. These include (1) catalysts from alloy precursors, (2) supported platinum group metals, (3) alkoxide to activate CO-forming methyl formate and hydrogenation of the formate to methanol, and (4) biocatalysis. Reviews of novel catalysts have been provided previously by Mills (1988) and a very informative update has appeared by Trimm and Wainwright (1990).

2.2.3.1 Alloys: Raney. The Raney method has been utilized for catalyst preparation, dissolving aluminum from $CuAl_2$ alloys with or without the presence of dissolved zinc (Trimm and Wainwright 1990). Catalysts prepared in this way have high activity and selectivity for methanol synthesis. Research focused on leaching conditions. It was found that catalysts could be greatly improved by low-temperature leaching in caustic solutions that contain near-saturation levels of sodium zincate (see Table 4).

Curry-Hyde et al. (1991) reported on the performance of a new Raney Cu-ZnO-Al_2O_3 methanol synthesis catalyst, produced by leaching a Cu-Al-Zn alloy pellets in a sodium rich sodium hydroxide solution. They conclude that, compared with industrial coprecipitated catalysts, the use of the Raney catalyst could significantly reduce the costs of methanol production. The rate of production of methanol at 220°C was up to 70% higher than those obtained over commercial catalysts using similar reaction conditions.

2.2.3.2 Alloys: Cu–Rare Earths. Binary copper-thorium alloys were prepared followed by oxidizing the thorium to thoria, then reducing the copper oxide formed to copper metal. The catalyst was active for methanol synthesis over a range of conditions (Baglin et al. 1981; Daly 1984).

Table 4. Methanol Yields over Catalysts Suitable for Use in Conventional Converters, Syngas to Methanol (Trimm and Wainwright 1990)

Catalyst	Syngas H_2:CO:CO_2	Temperature (K)	Pressure (MPa)	GHSY (h^{-1})	Yield (kg/l/h
Raney I[a]	91:5:4	493	4.5	36,000	1.1
Raney II[b]	91:5:4	493	4.5	36,000	0.6
$ThCu_{3.6}$	16:1:0	513	6.0	31,000	0.83
$ThCu_{3.6}$	16:1:0	493	6.0	31,000	0.42
$CeCu_2$	1:1:0	513	5.0	72,000	2.42[c]
$ZrCu_{3.3}$	2:1:0	507	6.0	3,990	0.24
CAT X[d]	91:5:4	493	4.5	36,000	0.60

[a] Cu-Al-Zn alloy leached in 6.1 M NaOH/0.62M Na-Zincate at 303 K
[b] Cu-Al_2 alloy leached in 6.1 M NaOH/0.62 M Nz-Zincate at 303 K
[c] Calculated on the basis of a bulk density of 3.9 kg l^{-1}
[d] Commercial coprecipitated Cu-Zn-Al_2O_3 catalyst

Catalysts derived from rare earth/copper intermetallic alloy precursors have been found (Owen et al. 1987) to exhibit extraordinarily high activity for CO hydrogenation to methanol (Table 4). Typical precursor alloys were also prepared by melting Cu and Ce or La. Methanol synthesis over Cu/La catalysts was observed at temperatures as low as 100°C. Detailed studies showed that the formation of certain intermediate hydride phases is critical to formation of the active catalyst (Owen et al. 1987). The highest steady-state activity was obtained for catalysts from CuCe alloys. Greatest activity was obtained when the Ce was only partially oxidized to CeO_2. Unfortunately, it was observed that these catalysts are irreversibly deactivated when exposed to low concentrations of CO_2.

2.2.3.3 Supported Platinum Group VIII Metals. Interest in this type of catalyst was aroused by the report by Poutsma et al. (1978) that catalysts containing Pd can produce sizable amounts of methanol when operated under conditions where methanol is thermodynamically stable. Of the platinum group metals, rhodium catalysts have received the most attention. Supported rhodium catalysts containing large amounts of molybdenum are particular active. (See later report, Section 2.5.4.) Although selectivity to alcohols is enhanced by molybdenum addition—to about 60% to alcohols and 40% to hydrocarbons—at 250°C, this selectivity is not attractive commercially. However, it has been pointed out that there is an opportunity to improve selectivity by utilizing the differences between energies of activation for alcohol formation, 18.6 kcal/mole, and hydrocarbon formation, 31.2 kcal/mole (Bhore et al. 1990). The wide E_{act} difference results in a more rapid decrease in formation of hydrocarbons relative to oxygenates as reaction temperature is decreased. Selectivity to oxygenates is increased. The relative rates for selectivity to oxygenates, r_o, and to hydrocarbons, r_h, are expressed by the relationship:

$$\frac{t_0}{r_h} = \frac{\text{selectivity to oxygenates}}{\text{selectivity to hydrocarbons}} = D \cdot e^{\frac{-(E_0-E_h)}{RT}} .$$

D is a constant whose value was established experimentally (Bhore et al. 1990). The following selectivities to oxygenates are those calculated and found for various temperatures using the activation energies cited above.

Temp. °C	273	250	225	200	180	160	140
Calculated %	50	61	75	85	91	95	98
Found %		65	73	86			

Although much previous research with rhodium catalysts has focused on mixed alcohols, it is suggested that the approach discussed above points the way for research to develop a methanol catalyst that can operate advantageously at low temperature (Comotti et al. 1991; Bhore et al. 1990). A more active catalyst is needed. There are a number of concept suggestions for catalyst synthesis, which are discussed in Section 2.6.

2.2.3.4 Methyl Formate. One interesting concept that dates back to 1919 (Christiansen 1919) is the conversion of an alcohol to a formate by carbonylation of methanol to formate and subsequent hydrogenation of the formate to two alcohol molecules:

$$CO + ROH \rightarrow HCO_2R \quad HCO_2R + 2H_2 \rightarrow ROH + CH_3OH .$$

The catalyst for carbonylation is an alcoholate such as $KOCH_3$, formed by reacting an alkali metal, K, with the starting alcohol. The reaction to synthesize formate is carried out in homogeneous solution containing $KOCH_3$ at 80°C and 3 MPa. Then the hydrogenation reaction is conducted in the liquid phase (slurry) or gas-phase (fixed bed of catalyst) 180°C and 3 MPa using a copper chromite catalyst (Tonner et al. 1983; Rao 1990). A severe if not fatal problem has been that the alkali methoxide reacts with and is deactivated by CO_2, which is generally found in syngas. Moreover, the methoxide reacts with and is deactivated by water, formed to some extent as a reaction byproduct.

The methyl formate route has recently received new attention with reports that, if the carbonylation and hydrogenation reactions are carried out simultaneously in the presence of both catalysts, small amounts (1%) of water or of 1% CO_2 can be tolerated (Liu et al. 1988, 1989; Palekar et al. 1990). Research at the University of Pittsburgh and elsewhere is being conducted to determine the tolerance of the dual catalyst system.

2.2.3.5 Brookhaven Homogeneous Catalytic Process. A novel process is claimed to enable the production of methanol at much lower temperatures and pressures than conventional methanol synthesis (Sapienza et al. 1986, O'Hare et al. 1986; Slegier et al. 1984). The catalyst is described as a complex reducing agent with the structure $NaH\text{-}RONa\text{-}M(OAc)_2$, where M is a metal such as Ni with a strong hydrogenating activity and R is an alkyl group such as tertiary amyl. The preferred carbonyl is $Mo(CO)_6$, although Ni(CO)4 is also used. An important suggestion is that the process be operated using a synthesis gas manufactured by partial oxidation using air, so the expense of an oxygen plant is avoided. The nitrogen is separated from methanol rather than from oxygen.

A cost evaluation has been carried out (see Section 5). It has been reported that this process is being investigated further by Amoco.

2.2.3.6 Biocatalysis. The conversion of syngas to liquid fuels offers an unusual opportunity to selectively synthesize liquid oxygenates, particularly higher alcohols such as ethanol (Klasson et al. 1992).

2.3 Coproduction of Methanol and Electricity

The manufacture of syngas from coal or from biomass and the use of the syngas for generation of electricity has important technical and environmental advantages. The clean syngas is highly suitable for use in high-efficiency gas turbines. The syngas can be purified to a degree not practical by stack gas cleanup of combustion gases. IGCC technology has been successfully demonstrated at the commercial scale by Dow at Plaquemine, LA, and by Shell at Deerpark, TX, and is planned in Cool Water, CA.

Using modern coal gasifiers, several IGCC plants are being installed in the United States. In the Netherlands a 250-MW_e plant is being built using a Shell Oil gasifier. Commercial experience usually assists in improving technology and so can be expected to improve the use of modern gasifiers for syngas production.

It has been proposed that it would be advantageous to coproduce electricity and methanol. An advantage would accrue by operating the gasifier at capacity all the time and, when electricity needs are low, to manufacture methanol with part of the syngas. This methanol can be marketed or used for "peak shaving" generation of electricity.

Advanced studies are being carried out for EPRI by Houston Power and Lighting Co.; Interfact, Inc.; Stone and Webster Engineering; and Shell Oil Co. (Kern et al. 1991; Bauman and Epstein 1991). One of the main objectives of this study is to design a standard IGCC plant that is integrated to both electricity and methanol production. Included is base load to cycling operation: full electricity to full methanol production.

An additional technological proposal is to operate methanol synthesis more economically by a "once through" technique. The syngas is passed over a methanol synthesis catalyst, the methanol is removed, and the unreacted syngas is used for generation of electricity.

It is interesting that plants for the generation of syngas are being installed in the United States but plants for the conversion of syngas to transportation fuels are not. Certainly environmental regulations are a main driving force for the electric utility companies. It may be that the utilities, traditionally very conservative, rather than the usually enterprising petroleum companies, will begin the manufacture of liquid fuels from coal.

2.4 Coproduction of Methanol and Dimethyl Ether

Coproduction of methanol and dimethyl ether offers an opportunity for increasing syngas conversion per pass. Higher conversion of syngas per pass may be achieved by removal of some methanol by chemical conversion, in the synthesis reactor, by its conversion to DME.

Much interest has been generated by novel technology being developed for the conversion of syngas to a mixture of methanol and dimethyl ether in a single reactor in which the following reaction sequence proceeds:

$$2CO + 4H_2 \rightarrow 2CH_3OH \text{ methanol synthesis catalyst}$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \text{ dehydration catalyst .}$$

A combination of two types of catalysts is employed to make this reaction sequence possible. One catalyst is a methanol synthesis catalyst; the second is a dehydration catalyst, such as alumina, that has acidic properties.

The water gas shift reaction can also be carried out simultaneously. Then the following reactions proceed:

methanol synthesis	$2CO + 4H_2 = 2CH_3OH$	$\Delta H = -43.2$ kcal
DME synthesis	$CH_3OH = CH_3OCH_3 + H_2O$	$\Delta H = 5.6$
water gas shift	$H_2O + CO = H_2 + CO_2$	$\Delta H = -9.8$
net	$3H_2 + 3CO = CH_3OCH_3 + CO_2$	$H = -58.6$.

The effect of the combination of these reactions results is to essentially avoid unfavorable thermodynamics limitations for methanol synthesis. Methanol, the product of the first reaction step, is consumed in the second reaction, forming DME and water. The water is shifted by the water gas shift reaction, generating carbon dioxide and hydrogen. The latter is a reactant for the methanol synthesis. Thus, one of the products of each step is a reactant for another. This creates a strong driving force for the overall reaction, allowing very high conversion of syngas in a single pass.

The advantage of combining methanol and DME synthesis is illustrated in Figure 7. Carbon equilibrium conversions are shown as a function of pressure with and without inclusion of the DME reaction. Conversion levels similar to those of conventional methanol synthesis may be achieved at far lower

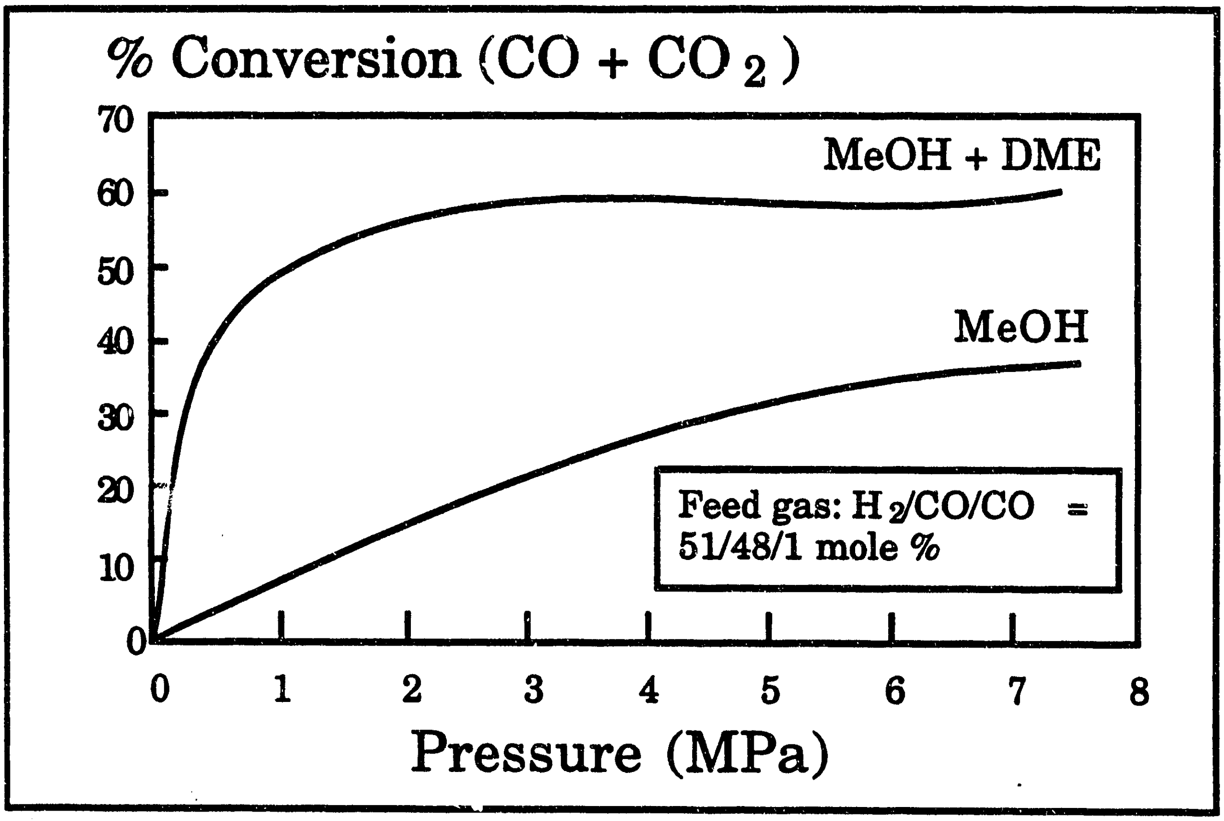


Figure 7. **Equilibrium conversion of syngas versus pressure at 240°C** (Reprinted with permission from Hansen and Joensen 1991, Elsevier Science Publishers)

pressures (lower plant construction cost) when the DME reaction is allowed to proceed. Utilization of DME for energy and chemicals manufacture is discussed later.

A variety of dual functioning catalysts has been tested in the Topsøe laboratory in order to optimize activity and selectivity and to study deactivation phenomena (Hansen et al. 1991). An aging test showed only a modest activity loss during an 1800-hour test period.

The consecutive nature of the reactions involved emphasizes the objective of proper catalyst optimization with respect to concentration of active sites. This is illustrated in Figure 8. Actual and equilibrium conversions are shown as a function of temperature for two catalysts with different site densities.

A pilot plant test was conducted to study the consequence of scaleup with respect to temperature control. Although there was a rapid temperature increase in the bed close to the reactor inlet and temperature rose from 240° to 330°C, virtually no byproducts were formed. It was concluded that the combination production of methanol and DME offers advantages in terms of favorable thermodynamics that allow high conversion per pass, high activity and selectivity achieved by proper catalyst design, long-term stability, and high flexibility.

The slurry catalyst reactor system has been used in carrying out the novel simultaneous synthesis of MeOH and DME from syngas (Brown et al. 1991). Operation of a back-mixed slurry reactor exploits synergisms of the three reactions (synthesis of MeOH, DME, and water gas shift), and moderates the reaction exotherm to permit higher conversion of the syngas to liquid products than could be achieved from the three reactions practiced separately. Process development focused on the use of coal-derived syngas that is rich in CO.

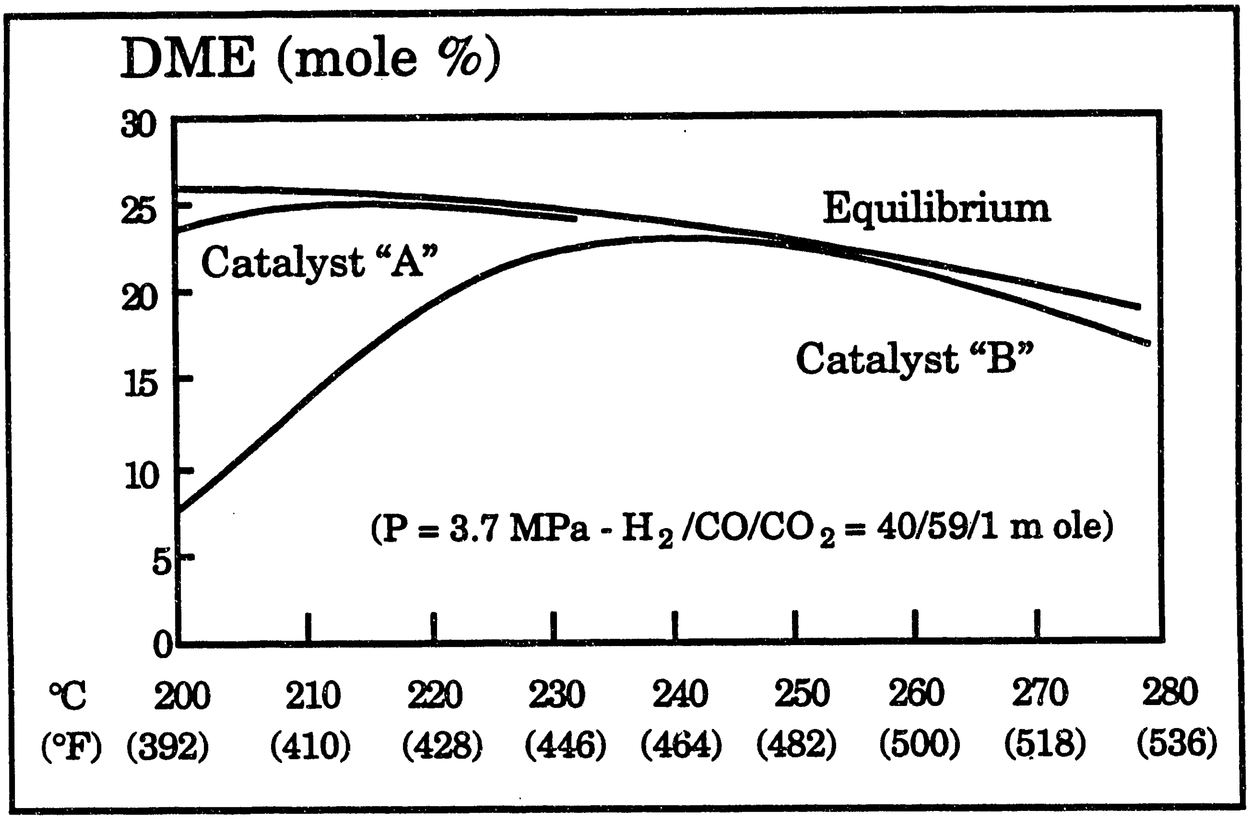


Figure 8. Dimethyl ether syntheses—equilibrium and measured concentrations (Reprinted with permission from Hansen and Joensen 1991, Elsevier Science Publishers)

Three potential commercial modes of operation that produce MeOH/DME were investigated (Figure 9). The first operating mode uses an oxygen-blown coal gasifier with recycle of the syngas. The second scenario is a derivative of the first, in which syngas makes only one pass through the reactor. MeOH and DME are recovered and unreacted gas is fired in a turbine. The "once-through" configuration can be adapted to a CGCC plant. The third scenario is also a once-through process but uses basic oxygen furnace (BOF) off-gas as the feed stream.

The slurry catalyst concept has been demonstrated using combinations of standard catalysts. Productivities of MeOH and DME are shown in Figure 10 as a function of space velocity at 250°C and 750 psig, (5.3 MPa) for combinations of BASF S3-86 catalyst and three different alumina-based catalysts. Because the same amount of methanol catalyst was used in these experiments, catalysts with higher dehydration activity would lead to higher DME productivity at the expense of lower MeOH productivity. Catalyst A shows the best dehydration activity. Other tests demonstrated the effects of varying the methanol synthesis catalyst. A comparison of the use of different methanol catalysts is shown in Figure 11.

A comparison of LPDME and LPMEOH is shown in Figure 12. The CO conversion in liquid phase dimethyl ether (LPDME) is up to twice as high as that in LPMEOH and much higher than the equilibrium conversion achievable in the methanol reaction alone.

A variety of options for commercial operation were analyzed including the use of kinetic models to predict the effect of removal of CO_2.

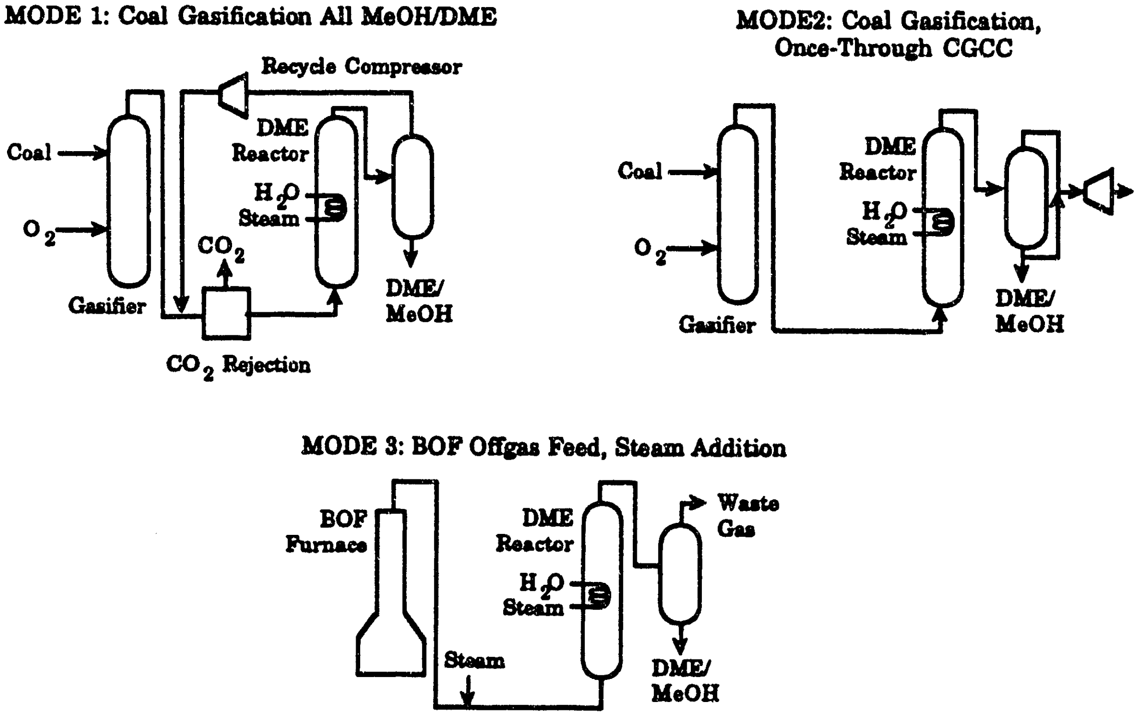
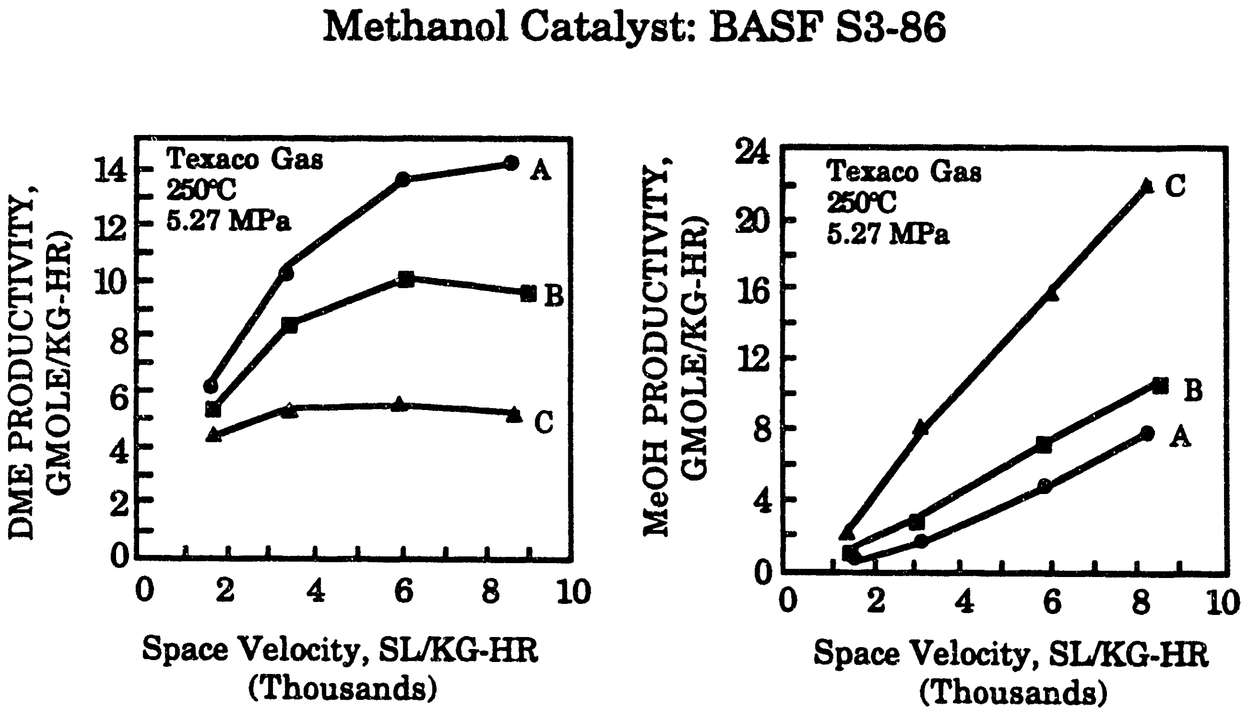


Figure 9. **Three operating modes for the DME process** (Reprinted with permission from Brown et al. 1991, Elsevier Science Publishers)



A. DME Productivity

B. MeOH Productivity

Figure 10. **Effect of different dehydration catalysts** (Reprinted with permission from Brown et al. 1991, Elsevier Science Publishers)

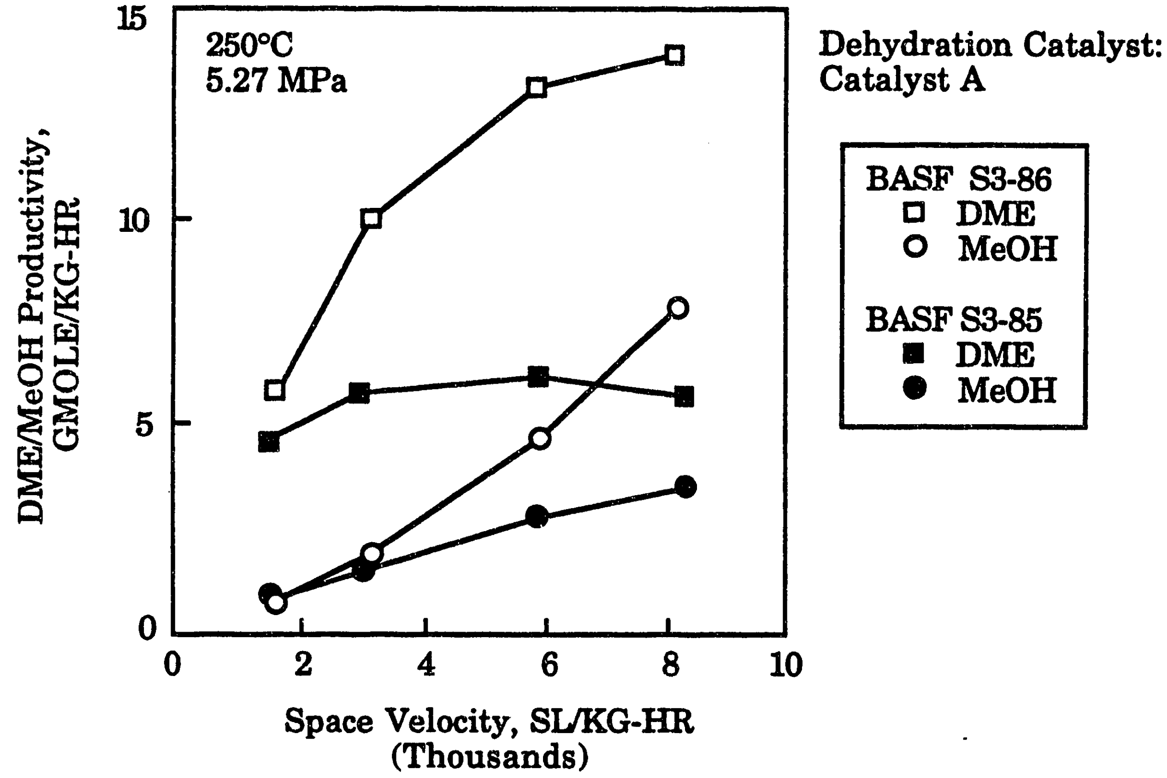


Figure 11. **Effect of different methanol catalysts** (Reprinted with permission from Brown et al. 1991, Elsevier Science Publishers)

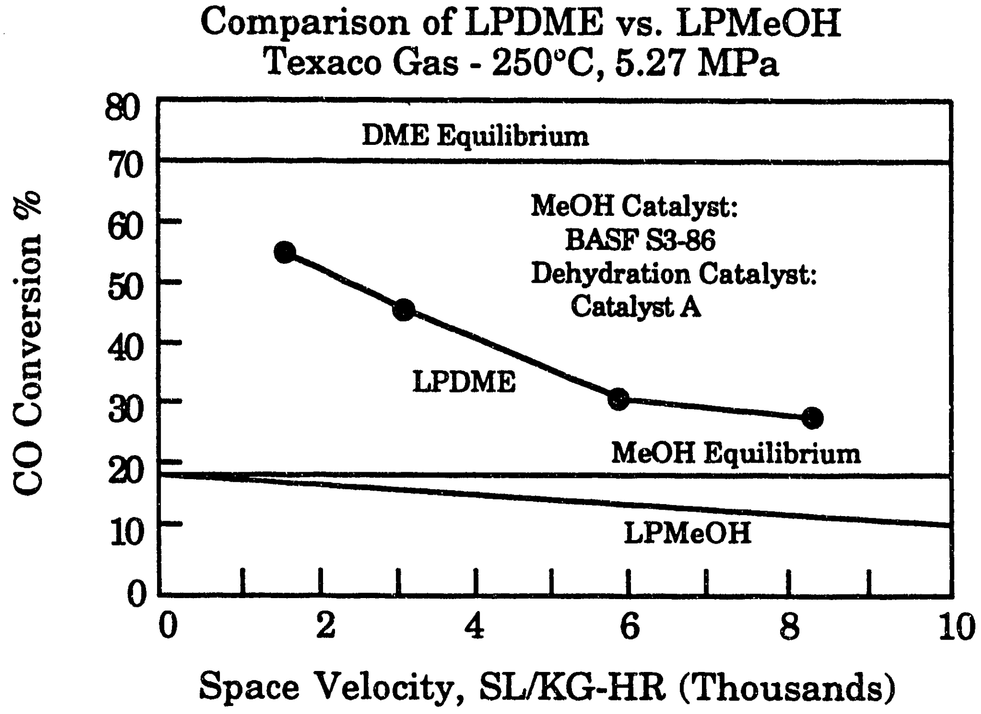


Figure 12. **Comparison of LPDME versus LPMEOH** (Reprinted with permission from Brown et al. 1991, Elsevier Science Publishers)

With DOE support, Air Products carried out a demonstration of the LPDME in the Laporte, TX, unit in April/May 1991.

Several attractive uses for DME have been discussed. DME or DME/MeOH mixtures can be used for generation of electricity in gas turbines. The manufacture and use of DME or DME/MeOH in a CGCC application provides a liquid fuel for peak shaving application. There is interest in use of DME for diesel engines, providing for ignition particularly in cold engines (see above). DME/MeOH is an excellent feed for manufacture of gasoline by the methanol to gasoline (MTG) process.

An attractive portfolio of suggestions for use of DME and DME/MeOH as fuel precursors, fuels, and chemicals has been identified (Brown et al. 1991; Underwood et al. 1991) (see Figure 13). The carbonylation of DME reaction to methyl acetate, and hence the manufacture of acetic acid, is regarded as having high potential.

2.5 Utilization of Methanol

It is beyond the scope of this study to report in detail on engine performance features of fuel oxygenates. It is true, of course, that the status of fuel utilization does have a critical role in the acceptance of oxygenate fuels and therefore interest in fuel synthesis. It is pertinent to point out that the automotive community and government agencies have carried out major programs on the utilization of alternate fuels.

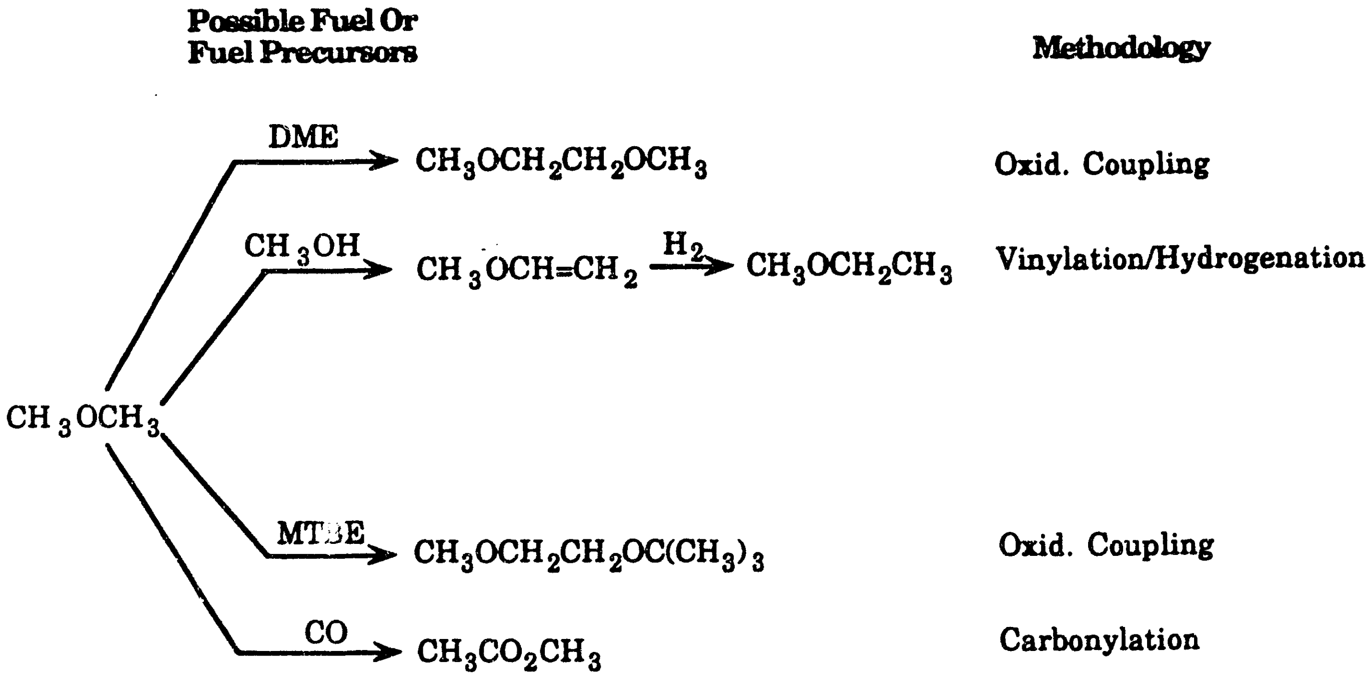


Figure 13. Possible fuel or fuel precursors from DME (Reprinted with permission from Brown et al. 1991, Elsevier Science Publishers)

The current state of knowledge was reported most recently at the IX International Symposium on Alcohol Fuels in Firenze, Italy, in November 1991. Reports were presented on utilization, environmental, and implementation aspects. Authoritative reports were presented by representatives from major U.S., German, and Japanese engine and auto industry representatives. Both neat and blended alcohols were discussed. In general these reports described successful use of alcohols and were concerned with optimizing efficient fuel use, safety, and possible environmental benefits.

Both spark and diesel engines (as well as fuel cells) were described. A particularly important segment of the meeting was the discussions of the use of fuels in diesel engines and technology for providing cold start assistance. In this regard, of interest and relevant to this report is the paper "Dimethyl Ether as an Ignition Source for Heavy-Duty Methanol Engines" by King and Green (1991). The authors found that the use of DME allows compression ignition of neat methanol and DME-assisted combustion showed a drastic reduction in total hydrocarbon exhaust output.

Further, Dippo et al. (1991) in their paper "Design of a Methanol Dehydration Reactor for Cold-starting Methanol-fueled Engines" found that on-board DME generation from methanol may be an attractive method of cold starting methanol-fueled engines.

There is a further concept for improving methanol fuel efficiency. This is the "on-board" catalytic decomposition of methanol to syngas fuel. If waste heat is utilized, there is a gain in efficiency because the heating value of the syngas is greater than that of the methanol from which it was derived (Figure 14). When waste exhaust heat, which is available on board an automobile or in a power plant, is used to

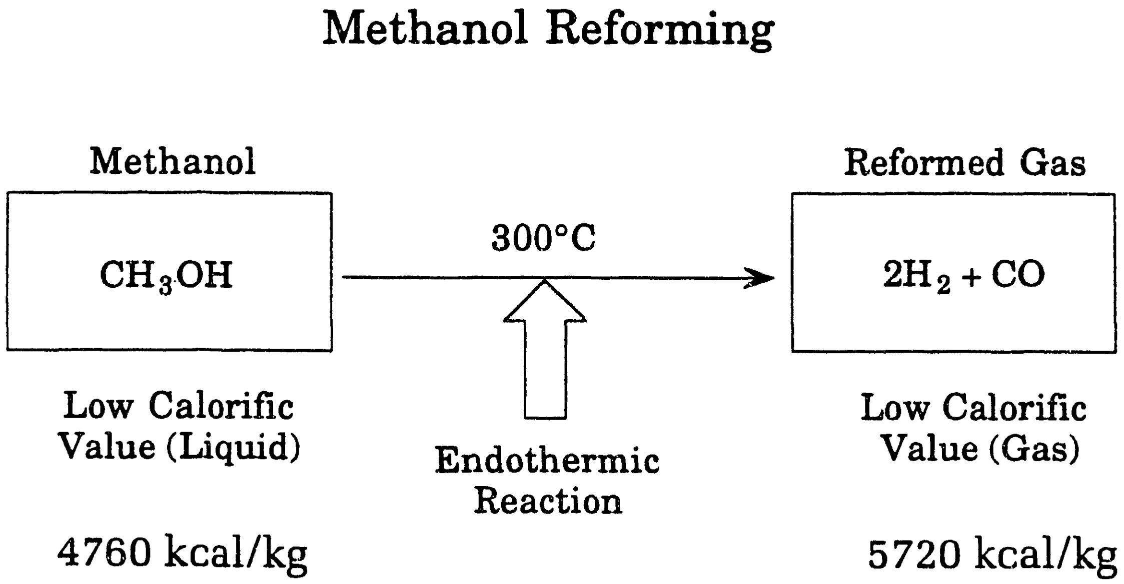


Figure 14. Increase in energy content by reforming methanol

decompose methanol, greater efficiency can be attained: 15% when methanol is steam reformed and 20% when it is dissociated (Yoon et al. 1985).

The use of catalysts to enhance fuel-use efficiency presents opportunities of considerable potential. This is a research area that has been relatively neglected.

2.6 Mixed Alcohols

The synthesis of higher alcohols from syngas has long been known. Fischer and Tropsch observed alcohols in their earliest catalytic research. Mixed alcohols were manufactured in Germany for the period 1927–45 in the so-called Synthol process using an alkalized iron catalyst (not to be confused with the SASOL Synthol process). In the United States, an alkalized Mn-Cr catalyst was used by Du Pont in the 1940s to produce methanol and higher alcohols on a commercial scale for a period of more than 10 years (Stiles et al. 1977, 1991).

Early work has been reviewed by Natta et al. (1957) and Stiles (1977) and in the 1980s by Haag et al. (1987), Wender and Klier (1989), and Mills (1988). Recently, excellent reviews have been provided by Herman (1991), Tronconi et al. (1989), Xaiogding et al. (1987), and by Courty et al. (1990).

Catalytic processes and appropriate catalysts for manufacture of mixed alcohols have been developed and are available for license for commercial production. A diagram for manufacture of alcohols from gas is shown in Figure 15. The status, characteristics and performance features has been summarized by Herman (Table 5) and Courty et al. (Tables 6 and 7).

The composition of fuel alcohols is given in Table 8. The alcohols do not conform to the Anderson Shulz Flory (ASF) distribution pattern. It should be noted that, in contrast to alkali-modified Cu catalysts, the MoS_x (Dow) catalyst produces straight chain alcohols. In the Lurgi product, isobutanol makes up 70% of the C_4 alcohols. It was shown that methanol can be recycled to extinction in the Dow process, increasing ethanol production.

Essentially four types of catalysts have been investigated in the past decade:

- Alkali-modified $Cu\text{-}ZnO/Al_2O_3$ methanol synthesis catalysts
- Fe or Ni modified $Cu\text{-}ZnO/Al_2O_3$ methanol synthesis catalysts
- MoS_x catalysts
- Supported platinum-group catalysts.

2.6.1 Alkali-modified MeOH Catalysts

It has been long known that by adding alkali elements, methanol catalysts can be modified to produce higher alcohols. Reaction conditions may be severe, e.g., > 400°C and 30-40 MPa (Stiles 1977). Products do not follow the ASF distribution pattern. The mixed alcohol product contains methanol, substantial amounts of isobutanol, and some ethanol and propanol (Slaa et al. 1991). From a practical viewpoint, K compounds are used although Cs is known to be more effective (Nunan et al. 1989). This is illustrated in Table 9, which shows that the promotional effect towards C_{2+} alcohols follows the order Cs>Rb>K and that the lower ratio H_2/CO syngas produced the highest yield of the higher alcohols, although the total CO conversion was decreased by decreasing the H_2 content of the syngas.

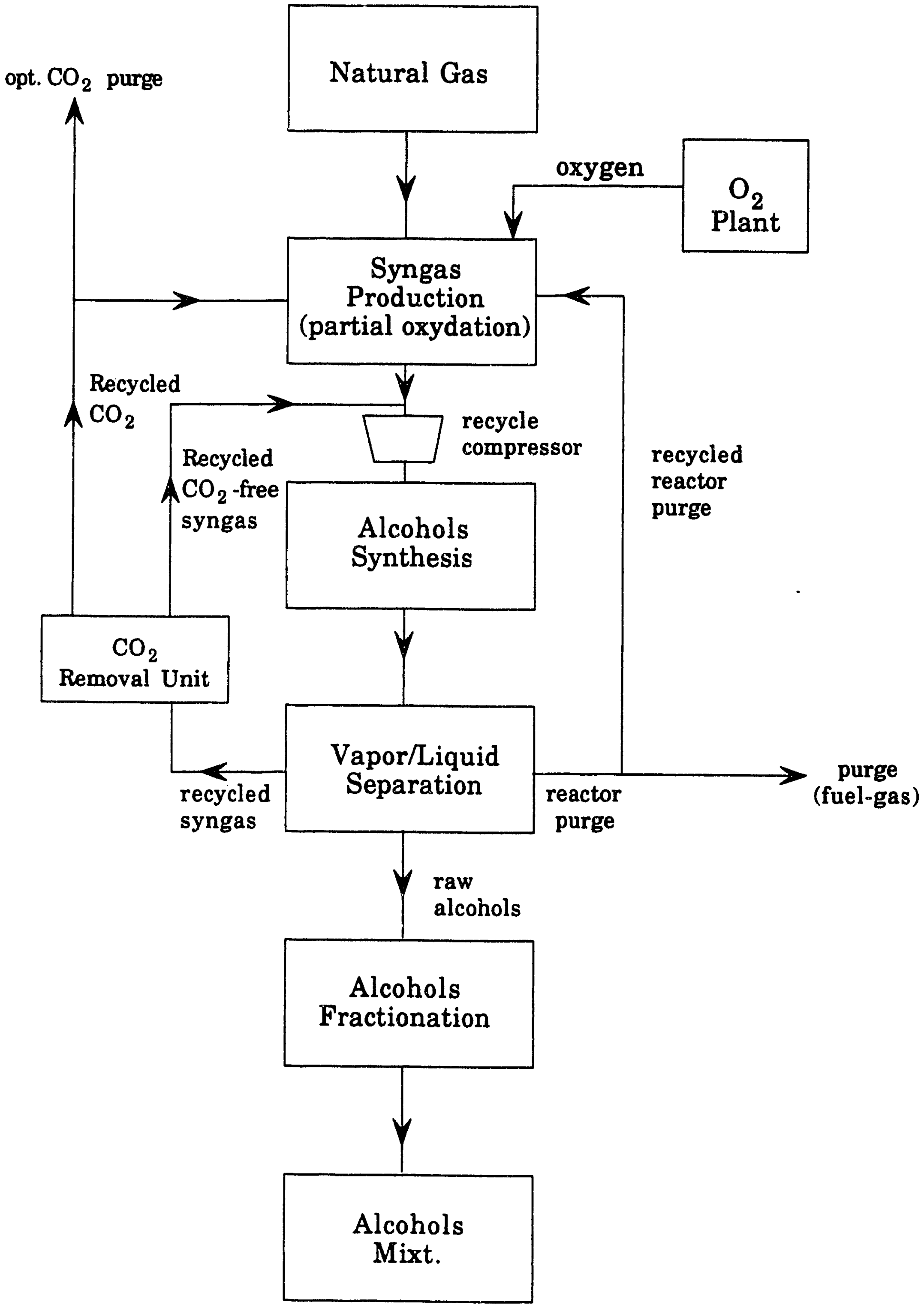


Figure 15. Block diagram of the integrated natural gas to alcohols complex (Courty et al. 1990)

Table 5. Typical operating conditions for higher alcohol synthesis processes (Herman 1991)

Process	Catalyst	Temp. °C	Pressure MPa	H_2/CO Ratio	vol % CO_2 Content	GHSV[a] h^{-1}	% CO Conv.[b]
SEHT[c]	K/Zn/Cr[d]	350–425	9–20	2–3	0–3	3,000–15,000	14
Octamix[e]	K/Cu/Zn/Al	270–300	6–10	0.5–2	0–1	400–6,000	20–60
IFP[f]	K/Cu/Co/Al	260–340	6–20	1–2	2–4	3,000–6,000	12–15
Lu Has[g]	Cs/Cu/Zno, Cs/Cu/ZnO/Cr_2O_3	275–325	5–10	0.45–1	0	3,000–7,000	10–20
Dow	K/MoS_2 or K/Co/MoS_2	255–325	3–20	1	0	3,000–10,000	10–20
Union Carbide	Alkali/MoS_2	300	2–5	1	0	12,000	5
Lu Has-2[g]	Cs/MoS_2	255–300	8.2	1	0	2,000–8,000	5–20

[a] GHSV = Gas hourly space velocity

[b] Exclusive of CO_2

[c] SEHT = Snamprogetti/Enichem/Haldor Topsøe

[d] The catalysts usually contain Cu, e.g., $K_{0.023}Cu_{0.018}ZnCr_{0.33}$

[e] Lurgi and Süd Chemie

[f] IFP = Institut Française du Petrole

[g] Lu Has = Lehigh University Higher Alcohol Synthesis

Table 6. Research and Development Status in 1988 for Syngas to Alcohol Projects (Courty et al. 1990)

	The Catalysts			Range of Operating Conditions					
Company	Key-Elements	Alk-metals	Others	GHSV h^{-1}	T°C	PMPa	H_2/CO	CO_2 removal	State of Development
1 Enichem Snamprogetti Haldor Topsøe	Zn Cr Cu	K Na	Mn-Al Mo Ti La V Ce	3,000-15,000	350+ 420	12-16 (18)	0.5-3	NO	Industr. plant (15,000 t/y Italy)
2 Lurgi	Cu Al Zn	K others	no	2,000-4,000	270 300	7-10	1-1.2	YES (1% synth. loop)	Bench scale
3 IFP and	Cu Co	Na K	AL Cr Zn others	3000-6,000	260-320	6-10	1-2	YES (0.5%-3% synth. loop)	Demonstration unit (20 bbl/day)
Idemitsu-Kosan	Cu Ni	K	Ti Mn Zn Others						
4 Dow Chemicals (Union Carbide)	Mo Co S	K	H_2S	5,000-7,000	290-310	12-14	1.1-1.2	YES	Bench scale (28 liters cat.)
5 C. Chemistry Group (Japan)	Rh Mn + Cu Zn	Li	—	30,000-45,000	260-280	5	1.4	NO	Lab. scale

Table 7. Syngas to Alcohol Performances (Courty et al. 1990)

	Related operating conditions				CO conversion		Mass product	Alcohols	C_2 + ox. compounds (wt %)		Alcohol purity
The catalyst	GHSV (h^{-1})	T°C	P (MPa)	H_2/CO	per pass	total	$t.t^{-1}.h^{-1}$	selectivity at.g.C.	with methanol recycle	without methanol recycle	(wt%)
1 Zn Cr Cu alk. metals others	?	350- 420	12-16					n.d.	—	28-32	98+
2 Cu Al Zn (K) (EP 152648 data)	2000 4000	270 (300)	10	1			n.d.	n.d.	40-50	20	87-95
3 Cu-Co Cu-Ni alk. metals others	3000- 6000	260- 320	6-10	1-2	12-18	90+	0.10 0.15	70-80		35-45 (alcohols)	97.5-99
4 MoS_2 K_2CO_3 Co_9S_8 H_2S (50-10 vpm)	?	260	13	1.1	20- (about)		0.20?	80-85	49	—	<97.4
5 Rh Li Mn Cu Zn	30,000 45,000	260- 280	5	1.4	1.5	—	0.20	80-85	—	100 (EtOH + ACOEt)	n.d.

Table 8. Composition of Fuel Alcohols from Syngas

Alcohol, %	C_1	C_2	C_3	C_4	C_{5+}	Other Oxygenates	Catalyst
MAS (SEHT)	69	3	4	13	9	2	K/Zn/Cr
Substifuel (IFP)	64	25	6	2	2.5	0.5	K/Cu/Co/Al
Octamix (Lurgi)	62	7	4	8	19	—	alkali/Cu/Zn/Cr
HAS (Dow)	26[a]	48	14	3.5	0.5	8	$CoS/MoS_2/K$

[a]Methanol can be recycled to extinction, increasing ethanol %.
Dow = straight chain alcohols
Lurgi = isobutanol is 70% of C_4 alcohols

Table 9. Catalytic Results of Testing Alkali-promoted $CuO/ZnO/Al_2O_3$ Catalysts (Herman 1991)

	Promoter (ppm)				
	K (252)		Rb (5475)	Cs[a] (8505)	
Synthesis Gas	A	B	A	A	B
CO Conversion, %	59.0	31.3	58.5	56.1	29.6
Yields, g/L catal/h					
Total Liquid	895	770	875	860	710
Methanol	823	716	796	774	593
Higher Alcohols	48.3	71.6	56.0	60.2	795
Selectivity Among Higher Alcohols (wt %)					
C_2	31.6	27.3	26.3	23.0	19.9
C_3	20.9	18.9	19.1	16.7	15.8
C_4	21.5	22.1	27.7	29.2	30.5
C_5	10.5	9.5	11.9	13.4	12.5
C_{5+} + Other Org. Compds.	15.6	22.2	15.0	17.7	21.6

[a]Plus 260 ppm K.

2.6.2 Catalyst Modified by Co or Ni

A major R&D program was carried out by the Institut Française du Petrole in cooperation with Idemistsu Kosan of Japan under the RAPAD program sponsored by the Ministry of International Trade and Industry (MITI) of Japan. A copper-cobalt (IFP) and a copper-nickel (IK) catalyst were tested at the laboratory, bench, and demonstration scale. The copper-cobalt catalysts were made of homogeneous spinel-type multimetallic entities modified by incorporating alkali metals.

The program has been reviewed in a comprehensive report (Courty et al. 1990). Pilot plant performances of various catalysts are given in Table 10.

Table 10. Pilot Performances of Various Alcohol Synthesis Catalysts (Courty et al. 1990)

	CuCoZnK (K/Co.0.03)	CuNiZnK (K/Ni.0.4)	CuAlZnRb (Rb/Cu.0.006 at .at^{-1})
Loading Density			1.15
Hydrogen Reduction 1% H_2-N_2	100 to 300°C (60 h)	100 to 240°C (60 h)	100 to 240°C (36 h)
Test Conditions: T°C	280	310	300
P (MPa)	8	6	6
H_2/CO	1.5	1.8	0.35
CO_2%	1.0	1.0	1.3
GHSV (h^{-1})	3,200	3,000	3,000
Aging time (h)	240	527	265
Performances CO conv. (CO_2excl.):	6.5	10.5	13
Mass product. $g \cdot g^{-1} h^{-1}$	0.06	0.09	0.11
Alcohols select.	76.5		63.3
Oxygenates select.		76.2	82.3
C_2+OH wt %	37.4	30.5	25.2
C_2+oxy. wt %	38.2	34.8	38.4
Liquid Product Characteristics:			
CH_3OH	61.5	55.5	60.1
C_2+OH	37.4	34.8	25.2
(Alcohols)	(98.9)	(90.3)	(85.3)
Esters	0.4	5.6	1.1
Other oxy.	0.4	3.2	12.1
Hydrocarbons	0.3	0.9	1.5

Demonstration tests were carried out on the Co and Ni-containing catalysts in a 7,000 barrel per year (bpy) unit in Chiba, Japan. Good and stable performance was experienced at moderate temperatures (305°-310°C) and pressures (6-8 MPa). Two series of car fleet tests with alcohol/gasoline mixtures demonstrated that the alcohols obtained can be used satisfactorily in practice as octane enhancers.

Although the demonstration tests verified the predicted behavior of the catalysts, the economic evaluation, discussed later, is not favorable at present.

2.6.3 Alkali-promoted MoS_x Catalysts

Although MoS_2 is known to hydrogenate CO to hydrocarbons, it was found that alcohol formation can be promoted by operating at decreased temperatures. Alcohol selectivity is increased by incorporating alkali in catalyst formulations.

In 1984 the Dow Company and Union Carbide Corporation separately disclosed novel catalyst systems for production of linear alcohols from syngas. These new systems consist of supported or unsupported alkali-doped MoS_2 or alkali-doped Co/MoS_2. They are not poisoned by sulfur as are copper-based catalysts. Alcohol selectivities of 75%-90% are obtained from $H_2/CO = 1$ syngas; hydrocarbons make up the balance.

Research reports on MoS_2 catalysts from Dow and Carbide and Lehigh and McMasters universities have been thoroughly reviewed by Herman (1991). Additional information developed by British Coal is found in Mills (1988).

The effect of various alkali elements has been investigated. The selectivities and activities of MoS_2, K/MoS_2, and $Co/MoMoS_2$, catalysts are shown in Table 11. It is clear that practically only hydrocarbons are produced over undoped MoS_2 and that the selectivity is dramatically altered toward alcohols upon promotion of the MoS_2 with either K or Cs. The distribution of products fits generally in the ASF relationship although the sum of hydrocarbons and alcohols fits better than either one alone.

Upon addition of cobalt to alkali-doped MoS_2 catalysts, a shift in product selectivity has been noted. It seems clear that the cobalt promotes the homologation of the methanol step, $C_1 \rightarrow C_2$.

The product distribution obtained with a $K_2CO_3/Co/MoS_2$ and a $CsOOCH.MoS_2$ catalyst is shown in Figure 16. It is apparent that the addition of cobalt shifted the selectivity in favor of ethanol as reported by Murchison et al. (1988). A particular point made by Murchison is that homologation of methanol occurs to such an extent that there is great deviation from the ASF distribution pattern. The commercial significance is that methanol, the lowest value alcohol in the mixed alcohol product, can be adjusted via recycle to any desired level, indeed to zero production.

2.6.4 Supported Platinum Group For Higher Alcohols

Because Pd is well known for its ability to hydrogenate CO to CH_4, it was rather a surprise when it was reported (Poutsma et al. 1978) that palladium catalysts produced sizable amounts of methanol when operated at conditions under which methanol is thermodynamically stable. Much attention has been devoted to rhodium-containing catalysts for synthesizing mixed alcohols (Mills 1988). Interest was heightened by the finding that activity and selectivity can be greatly influenced by the support and particularly by added constituents, which act as promoters (Ellgen et al. 1979; Wilson et al. 1981). Early work established the dramatic effect of small amounts of Mn, Mo, W, and Fe on the activity of Rh/SiO_2 catalysts. The oxidation state of Rh was examined and the concept developed that Rh^+ is needed for oxygenate formation. This remains controversial. Multimetallic catalysts have been investigated by Arakawa et al. (1988), who suggested two classes of promoters for Rh/SiO_2: those that increase CO conversion based on acceleration of CO dissociation and those that improve selectivity based on the control of electronic state and ensemble size of Rh particles (Figure 17).

Considerable effort has been put forth to develop bicomponent catalysts for selective formation of ethanol from syngas (Ewald et al. 1991).

In the mid-1980s it was discovered that when relatively large amounts of molybdena or vanadia are incorporated into supported rhodium catalysts that *the activity for CO hydrogenation is increased more than ten-fold and selectivity to oxygenates is augmented considerably* (Jackson et al. 1986; Sudhakar et al. 1988; Bhore et al. 1988, 1990; DeCanio and Storm, 1991; Marengo et al. 1992; Foley et al. 1990; Kip et al. 1987). The effect of molybdena addition is illustrated in Table 12.

Table 11. Product Selectivities over MoS_2 Catalysts (Herman 1991)

Product	Selectivity[a]		
	MoS_2	K/MoS_2	Cs/MoS_2
Hydrocarbons			
C_1	43.64	17.80	17.88
C_2	25.24	3.31	3.73
C_3	16.98	--	1.17
C_4	8.92	--	--
C_5	3.86	--	--
Alcohols			
C_1	0.67	45.15	38.34
C_2	--	26.14	26.85
C_3	--	5.32	8.98
C_4	--	tr	1.43
Esters			
Methyl Formate	--	1.25	0.54
Methyl Acetate	--	1.03	1.07

[a] Selectivity is based on carbon mole selectivity on a CO_2-free basis.
Product selectivities obtained over undoped MoS_2, 0.22 mole K/mole MoS_2 (10.36 wt % = 18.03 mole % KOOCH), and 0.22 mole Cs/mole MoS_2 (20.00 wt % = 18.36 mole % CsOOCH) Catalysts. Testing was carried out at 295°C and 82 MPa with $H_2/CO = 0.96$ synthesis gas at GHSV = 7790 l(STP)/kg catal/h.

As mentioned earlier, there is promise that this type of catalyst can be developed into a practical low-temperature catalyst for methanol manufacture.

2.7 Ethanol

At present, mixed alcohols are not regarded as commercially promising because they cost more to manufacture than methanol and, most importantly, the need for an octane-enhancing oxygenate blending agent is being filled by MTBE, which is regarded as having better all-round properties than mixed alcohols.

However, there is interest in and opportunities for individual higher alcohols, particularly ethanol and isobutanol. Ethanol is regarded as a desirable fuel both alone and in blends. Promising research results for selective synthesis of ethanol from syngas have been obtained by

(1) Homologation of methanol	$CH_3OH + CO + H_2 \rightarrow CH_3CH_2OH$
(2) Biocatalysis	enzymes
(3) Isomerization of DME	$CH_3OCH_3 \rightarrow CH_3CH_2OH$.

The manufacture of ethanol from syngas by a two-step process is known as the Ensol process or the Davy-McKee process (Mills 1988).

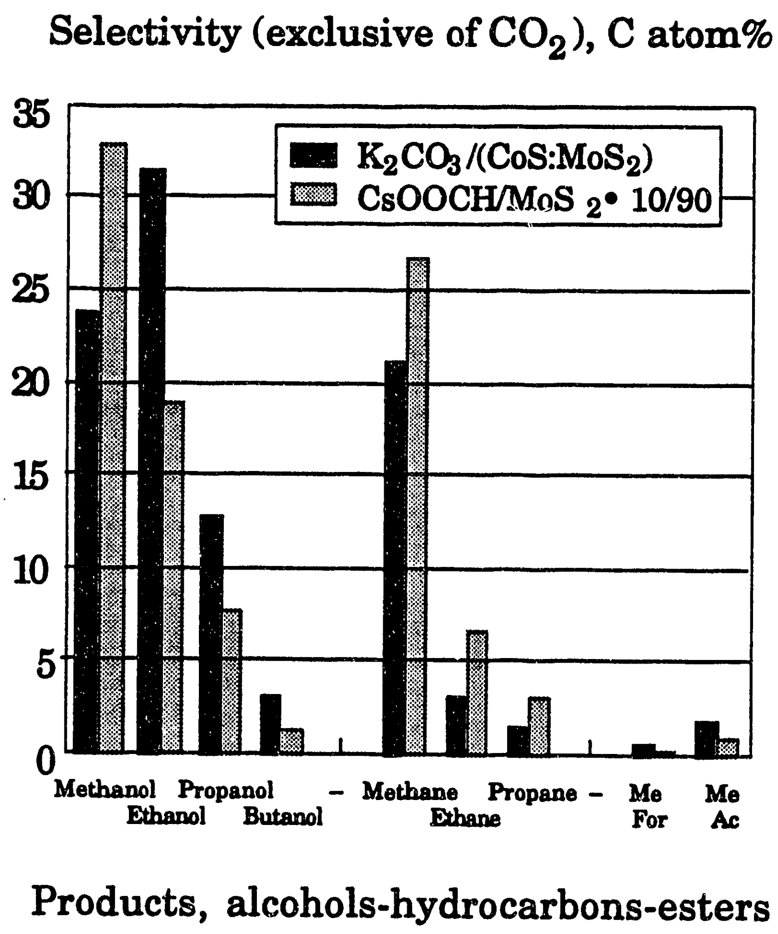


Figure 16. Product distributions MoS_2 catalysts (Reprinted with permission from Herman 1991, Elsevier Science Publishers)
Note: (The product distribution obtained with $H_2/CO = 0.96$ synthesis gas at 8.3 MPa over the $K_2CO_3/(CO/MoS) = 10/90$ wt % catalyst (304°C, GHSV = 1940 L/kg catal/h) and over the $CsOOCH/MoS_2 = 10/90$ wt % catalyst (294°C, GHSV = 7790 L/kg catal/h), where the conversions were 13.1 and 14.1 mole CO/kg catal/h, respectively.)

Numerous attempts have been made to carry out the homologation in a one-step operation but none has been commercialized. Cobalt appears to be the best catalyst in terms of activity and selectivity. A significant discovery was the enhancement in methanol homologation by the addition of iodine. There is an opportunity to improve methanol homologation with better selectivity (Santacesaria and DiSerio 1991).

The enzymatic conversion of syngas to oxygenate fuels presents an opportunity for synthesis of ethanol. A recent report, (Klasson et al. 1992), describes the action of an anaerobic bacterium to be effective in converting CO, CO_2, and H_2 to ethanol at relatively high rates. A continuous stirred tank reactor (CSTR) cell recycle system was shown to be effective in permitting the cell concentrations necessary for high concentrations of ethanol.

With the advent of processes for manufacture of DME from syngas, the suggestion is made to develop technology for catalytic conversion of DME to ethanol. It is evident that ethanol and DME have the same atomic content but different structures. Thermodynamically, the isomerization of DME to ethanol is greatly favored. The free energy of change for isomerization, calculated from free energies of formation, is

$$\Delta G_{298} = -168.5 - (-112.6) = -56 \text{ kilojoules/mole.}$$

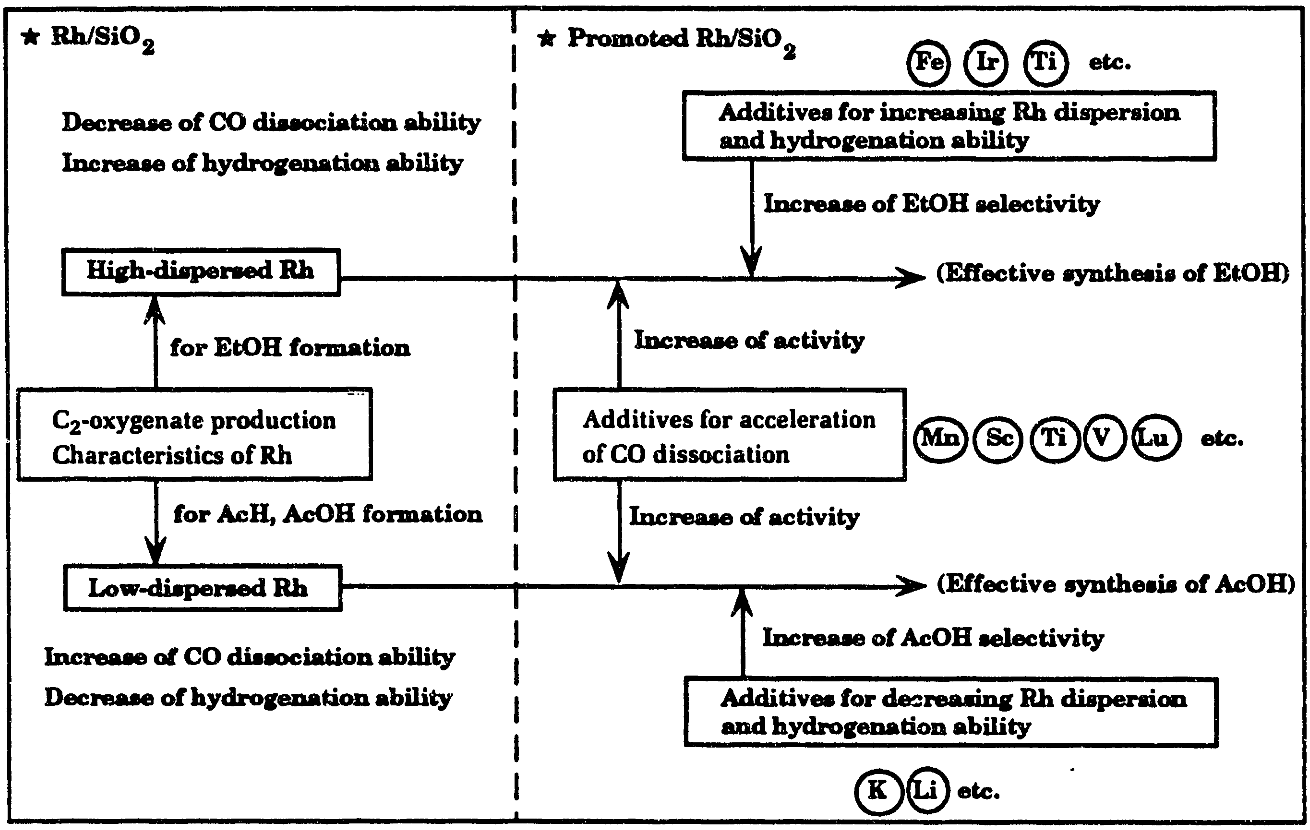


Figure 17. The roles of additives for effective synthesis of EtOH and AcOH (Arakawa et al. 1988)

A multistep process can be visualized: converting syngas to methanol, methanol to ethylene over ZSM-5 catalyst (not very selective), and then hydrating the ethylene. However, a more direct and selective isomerization is desired.

2.8 Isobutanol

Isobutanol is desired as a blending agent in possible competition to MTBE. Alternatively, it is desired for manufacture of isobutylene needed for reaction with methanol for manufacture of MTBE.

It has been noted that there is a remarkable amount of isobutanol in the C_4 alcohol fraction of mixed alcohols; for example, 70% has been reported by Lurgi. However, the overall selectivity of syngas to isobutanol is not high in mixed alcohol synthesis, although Keim and Falter (1989) reported very high selectivity.

There is encouragement in that the thermodynamically allowable isobutanol is very high under certain conditions. The distribution of C_4 alcohol isomers is shown in Figure 18 (Roberts 1992). At ambient temperature, tertiary butyl alcohol is the dominant species thermodynamically; the yields of other isomers are all negligible. As temperature increases, the amount of tertiary butyl alcohol declines rapidly and isobutanol becomes the dominant species at about 450K. This diagram illustrates that erroneous conclusions can be drawn concerning the possible isomers without due consideration of the temperature. It also illustrates the potential for synthesis of tertiary butyl alcohol and isobutyl alcohol.

Table 12. Syngas Conversion by Rh/Mo/Al_2O_3 Catalysts: Effect of Catalyst Composition on Product Distribution (Bhore et al. 1988)

Catalyst	3% Rh	3% Rh/ 7.5% Mo	3% Rh/ 2% Na	15% Mo
Temp. °C	250	250	275	250
GHSV, (H^{-1})	3000	36000	820	3000
CO Conv. %	5.7	5.3	6.1	1.8
of CO Conv. % to CO_2	1	25	7.3	50
of CO converted, % Converted to: (CO_2 free basis)				
Hydrocarbons	72	34	62	100
CH_4	61	26	56	60.9
C_2H_{6C}	4	6	4	29.4
C_3H_6	5	2	1.6	9.7
C_4H_{10}	2	0	0	
Oxygenates	28	66	38.6	0
MeOH	2	16	1.9	
MeOMe	1	26	0	
MeCHO	2	0	9.4	
EtOH	11	7	8.8	
MeOAc	3	1	3.5	
HOAc	0	0	2.5	
EtCHO	0.4	0	2.4	
n-PrOH	2.7	1	0	
MeOEt	3	15	0	
EtOAc	3	0	10.1	
C_1 oxy	5	47	3	
C_2 oxy	21	17	33	
$CH_4 + C_1$ oxy	61+5=66	26+47=73	56+3=59	

It was pointed out by Roberts et al. (1992) that the calculations performed exclude alcohols of C_5 and above in order to keep computational problems within reasonable bounds. However, such higher alcohols are indeed formed and this limitation needs to be remembered in connection with this study.

Attention is drawn to the disappointingly low octane of MIBE, methyl isobutyl ether (Reagan 1992). It seemed an attractive concept to utilize a mixture of methanol and isobutanol, which are coproduced, to synthesize MIBE.

	BRON[1]	BMON[2]	BON
MTBE in unleaded regular gasoline	120.1	96.3	108.2
MIBE in unleaded regular gasoline	60.8	67.0	63.9

[1] Blending Research Octane Number

[2] Blending Motor Octane Number

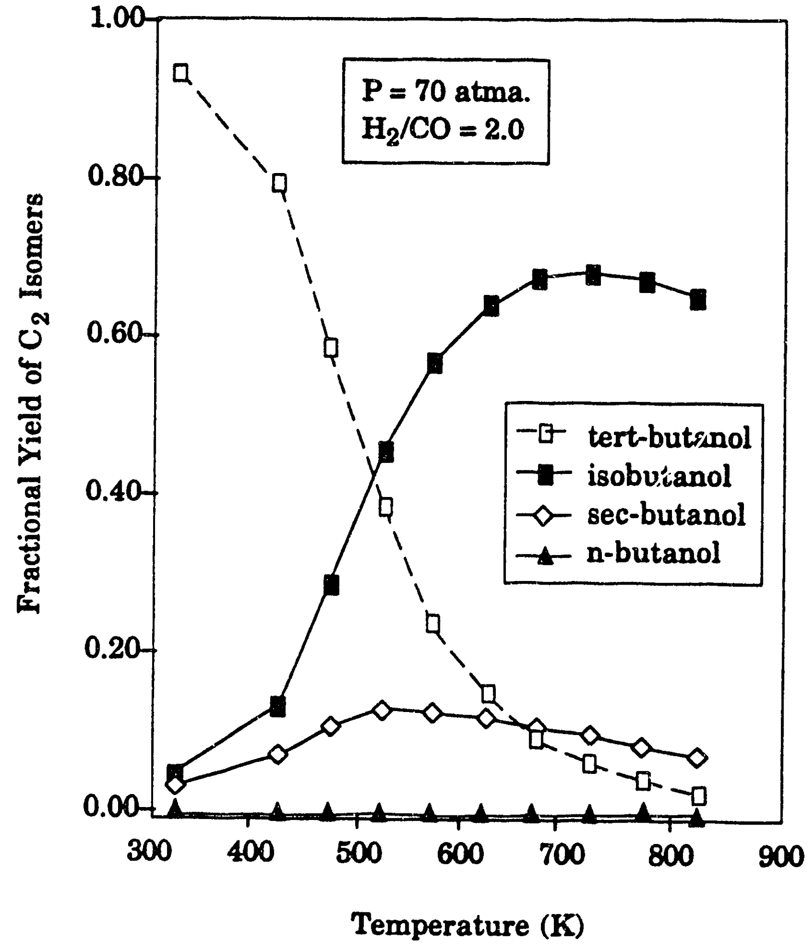


Figure 18. C_4 alcohol isomer distribution as a function of temperature (Reprinted with permission from Roberts 1992, American Chemical Society)

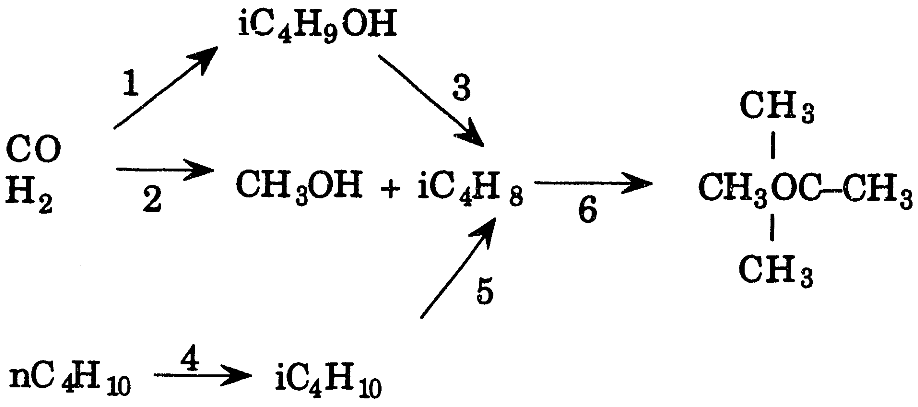
Synthesis of ethers has been reviewed by Brockwell et al. (1991).

Chemical pathways and catalysts for synthesis of MTBE are shown in Figure 19.

At present, fuel ethers are manufactured by reacting alcohol with isoolefin over an acid resin catalyst (Brockwell et al. 1991). Attention is directed to the novel technology for conducting the alcohol + olefin to ether reaction by catalytic distillation (Rock et al. 1992; Lander et al. 1983). This technique provides for more complete reaction by product removal and thereby shifts the reaction to MTBE, if isobutylene is the olefin, or TAME if isoamylene is the ether. Catalytic distillation is carried out in a fractionation tower in which the catalyst forms the packing, so that both catalytic reaction and distillation occur simultaneously (Figure 20).

The question has been raised as to the adequacy of supply of isoolefin. Isoolefin production in normal catalytic cracking is being increased by alteration in cracking conditions and by the introduction of catalysts modified so that more olefins are produced. Further, plants have been installed for production of isobutene by isobutane dehydrogenation.

Furthermore, there is interest in manufacture from syngas via isobutanol synthesis and dehydration and research results are now beginning to appear.



1 Cu-ZnO-Al_2O_3-Alkali

2 Cu-ZnO-Al_2O_3

3 Acid

4 Pt-Cl-Al_2O_3

5 Cr_2O_3-Al_2O_3

6 Acid Resin

Figure 19. Chemical pathways and catalysts for synthesis of MTBE

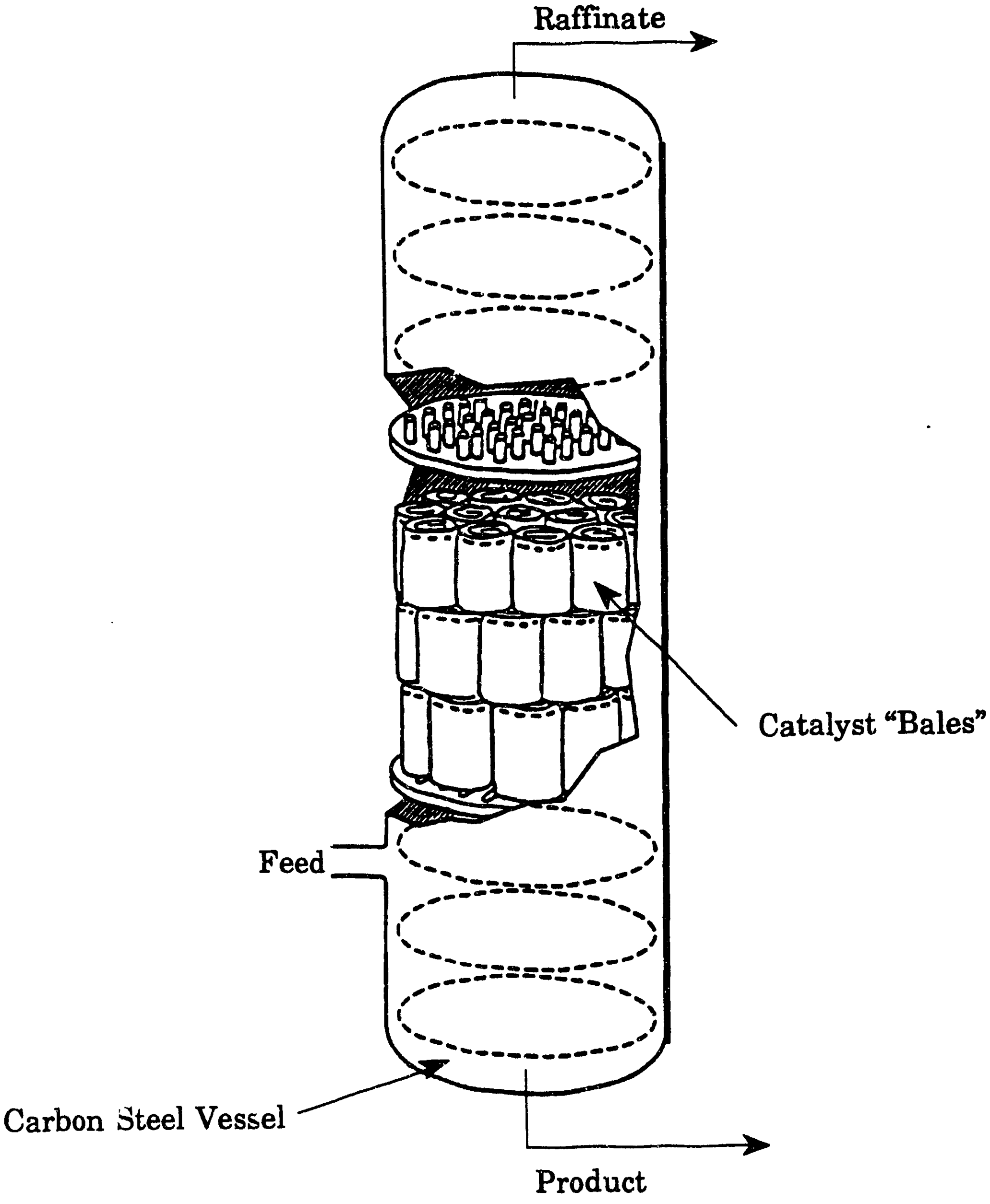


Figure 20. Catalytic distillation column (Rock et al. 1992)

3.0 Hydrocarbon Fuels

3.1 Overview

The catalytic technology for conversion of syngas has been extensively reviewed. Publications by Storch, Anderson, Pichler, and Emmett in the 1950s reflect intensive research in that period. Then during the late 1970s and 1980s reviews on Fischer Tropsch (FT) by Dry (1981), Frohning et al. (1982), Falbe (1980), Anderson (1984), Wender and Klier (1989), and Mills (1988) appeared. MTG by Chang (1983, 1984), Meisel et al. (1976), and Meisel (1988) also appeared. During the last 5 years, progress at SASOL has been reported by Jager et al. (1990) and by Dry (1990) and on MTG by Tabak and Yurchak (1990) and Yurchak and Wong (1991). A particularly comprehensive FT review was given by Bartholomew (1991). Economic evaluations have been provided by Fox (1990, 1992), and Gray et al. (1991).

The history of industrial actual installations of industrial plants for manufacture of hydrocarbon fuels is presented in Table 13.

Much has been learned about the hydrogenation of CO in the last 90 years. Yet with the exception of ZSM-5, the catalysts are essentially those discovered in Germany 50 years ago: Ni for methane; alkalized Fe, Co, or Ru for FT; and those containing ThO_2 for isosynthesis.

Fe is less active for hydrogenation than Co and so produces more olefins and alcohols. Ru is noted for its capability to produce higher molecular weight hydrocarbons. Fe catalysts are active in promoting the water gas shift reaction; neither Co nor Ru are active. Catalysts without water gas shift activity reject oxygen (introduced by CO) as water, so that syngas with a H_2/CO ratio of 2 is required in making olefins or alcohols and a slightly higher ratio than 2 for making paraffins. For catalysts that promote the water gas shift reaction, the oxygen from CO is rejected mainly as CO_2. The water formed in the FT reaction reacts with CO to form additional H_2. Consequently, less expensive syngas with a low H_2/CO ratio, produced in high temperature gasifiers, can be used with these catalysts, with a practical minimum of about 0.6.

Chain growth in FT synthesis has been recognized to be similar to a polymerization process where the distribution of product chain length is a consequence of relative rates of propagation, R_p, and termination, R_t. The weight fraction, W_i, of a product with a carbon number C_i is given by the equation

$$\log(W_i/C_i) = (\log \alpha)C_i + K ,$$

where α is the probability of chain growth = $R_p/(R_p=R_t)$ and K is a constant. This equation, usually known as the ASF equation has as a consequence that, of the hydrocarbons, methane can be made in near-quantitative selectivity. All other products have well-defined maxima allowable selectivities, illustrated in Figure 21 for hydrocarbon synthesis. From a practical viewpoint, in the FT synthesis, there is a wide distribution of chain lengths. For instance, maximum gasoline (C_5–C_{11}) is 47% and maximum diesel (C_{12}–C_{17}) is 40%. A generic problem in conducting catalytic syngas reactions is the formation of too much low-value methane.

3.1.1 Mossgas Project

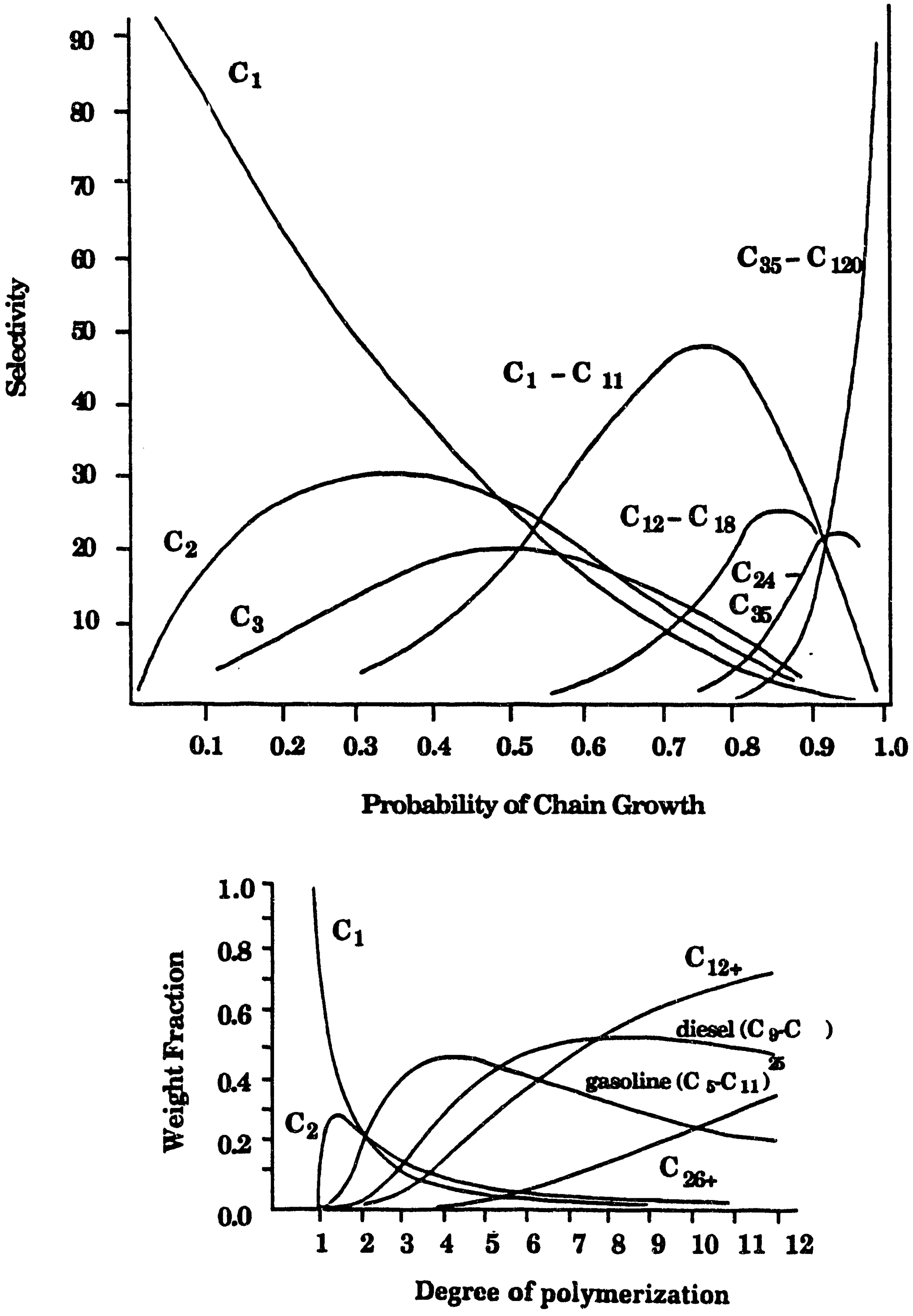
A process designed to produce transportation fuels from off-shore natural gas in South Africa was announced in 1987 (Van Rensburg 1990; Jager et al. 1990). This has been described as the world's largest synthetic fuels project. It is nearing completion. About 85 miles offshore from Mossel Bay, South Africa,

Table 13. Industrial Installations of Hydrocarbon Fuels from Syngas

1902	Methane synthesis over Ni catalysts, Sabatier and Sanderens
1923	Higher hydrocarbons over Fe modified by alkali, FT
1930s–1940s	Nine FT plants installed in Germany, World War II, producing 10,000 bpd fuels (syngas from coal. FT = 15% of fuels used by Germans, Co/ThO$_2$/MgO/SiO$_2$ catalyst. 100/5/8/200. 85% by Bergius direct coal liquefaction)
1950s	Bureau of Mines plant in Louisiana, Missouri, operated briefly Fe catalyst
1950	Brownsville plant in Texas operated briefly. Fixed fluidized bed, Fe-K catalyst. syngas from methane
1950	Slurry-phase FT tested in pilot unit by Koelbel in Germany
1950s	German plants operated on petroleum residua, but shut down because of cheap abundant petroleum
1954	SASOL I, South Africa constructed 8000-bpd plant, using Fe/K catalysts, Arge fixed bed, Synthol circulating fluid bed. Syngas from coal, Lurgi gasifiers
1980	SASOL II, 50,000-bpd plant Synthol technology
1983	SASOL III 50,000-bpd plant Synthol technology
1985	14,000-bpd MTG plant in New Zealand, gas→syngas→methanol→gasoline, molecular sieve ZSM-5 catalyst
1989	SASOL installed fixed fluidized bed
1992	Mossel Bay, large plant using SASOL synthesis technology, syngas from coal
1989–1992	Fuelco installs 50-, then 250-bpd plant using slurry FT, Fe catalyst, syngas from landfill gas, product diesel fuel
1992–1993	Start-up, SMDS 13,000-bpd plant in Malaysia, syngas from methane, products: diesel, kerosene, wax
1993	SASOL, slurry-phase FT reactor

a production platform has been constructed. The gas is 2,500 meters under seabed and under 105 meters of water. An underwater pipeline will transport 200,000 cubic meters per hour of gas and 50 tonnes per hour of gas condensates to a point onshore close to the town of Mossel Bay. Five of the process units, including two oxygen plants (Linde), have been installed. Startup is scheduled for 1992.

The synthesis process being installed is the SASOL circulating fluidized bed. It was stressed that the selection made in 1987 was determined by a deliberately conservative policy to have long established technology and to have technology secure within South Africa. Governmental unwillingness to export technology may have prevented options of the MTG or TIGAS processes.



Yield of selected product fraction with incrossing degree of polymerization.

Figure 21. Chain length selectivity as a function of probability of chain growth

3.2 Fixed Fluidized-bed FT Synthesis Reactor

3.2.1 SASOL

The enormous commitment to FT in South Africa has inspired SASOL to seek improvements and a number of significant advances have been achieved over the past several decades. These have been reported in comprehensive reviews by Dry and Hoogendoorn (1981), Dry (1990), Jager et al. (1990),and Jones et al. (1992) emphasizing the recent use of a new fixed-fluidized bed operation and new emphasis on chemicals production, particularly olefins and waxes.

The overall SASOL plant operation, shown in Figure 22, is a reminder that the total process of indirect liquefaction of coal is a complex series of process operations that include not only syngas manufacture and its FT synthesis but also product upgrading required to meet fuel specifications.

Until recently, SASOL employed two types of FT reactors. The fixed bed, designated Arge, previously operated at 220°C and at 25 bar, but recently at 45 bar, using a precipitated Fe catalyst. The circulating fluidized bed (CFB), known as Synthol, is shown in Figure 23. In operation since 1955, the CFB, operated at 25 bar and 340°C, is employed for gasoline production. Typical product spectra are shown in Table 14. Products of the Synthol are lighter and more olefinic than those of the Arge. Both produce some oxygenates.

Beginning in 1989, a new type of reactor was installed—a fixed-fluidized bed (FFB) (Dry 1990; Jager et al. 1990). Many of the limitations of the CFB reactor are eliminated by the FFB. The FFB consists of a vessel with a gas distributor, a fluidized bed containing the catalyst, cooling coils in the bed, and a system to separate the catalyst from the gaseous product stream. The various SASOL reactors are depicted in Figure 24. The FFB is much smaller than the CFB. Operating experience with the FFB is reported to be good. Catalyst consumption is decreased and improved operability observed. A further advantage is achieved through the use of filters instead of cyclones.

There is new interest in operation of the FT process in a mode that results in production of high molecular hydrocarbons including waxes and diesel fuel. An improvement in the SASOL Arge operation was achieved by operating at increased pressure. It was shown (Dry 1981) that if pressure is increased and the feed flow is increased in proportion that the production per unit volume of reactor space increases in direct proportion to pressure. A new fixed-bed reactor that operates at 45 bar instead of 25 bar was commissioned in 1987 and wax production increased by 50% as predicted.

SASOL (Dry et al. 1981) reported that wax produced in low-temperature FT processes can be cracked to extinction at relatively mild conditions to yield 80% diesel and 15% gasoline. The diesel is more branched than straight-run FT diesel but has a good cetane rating, 65 versus 75 for the straight run. The aromatic content remains at zero so that the fuel is of prime quality. Tests have also been made by UOP using SASOL wax with similar results.

3.3 Synthesis of Wax and Hydrocracking to Diesel and Gasoline

3.3.1 Shell

Shell Oil announced in 1989 that a Shell Middle Distillate Synthesis (SMDS) process plant would be built in Bintulu in Sarawak, Malaysia, to come onstream in 1993. The process consists of three major steps, (Burgt et al. 1985, 1990).

1. Conversion of natural gas to syngas with a H_2/CO ratio of about 2
2. Conversion of syngas in a modernized version of FT using a catalyst having high activity, stability, and selectivity to high molecular weight waxy hydrocarbons
3. Hydrocracking and hydroisomerization to maximum middle distillates (kerosene and diesel) with minimum gas formation.

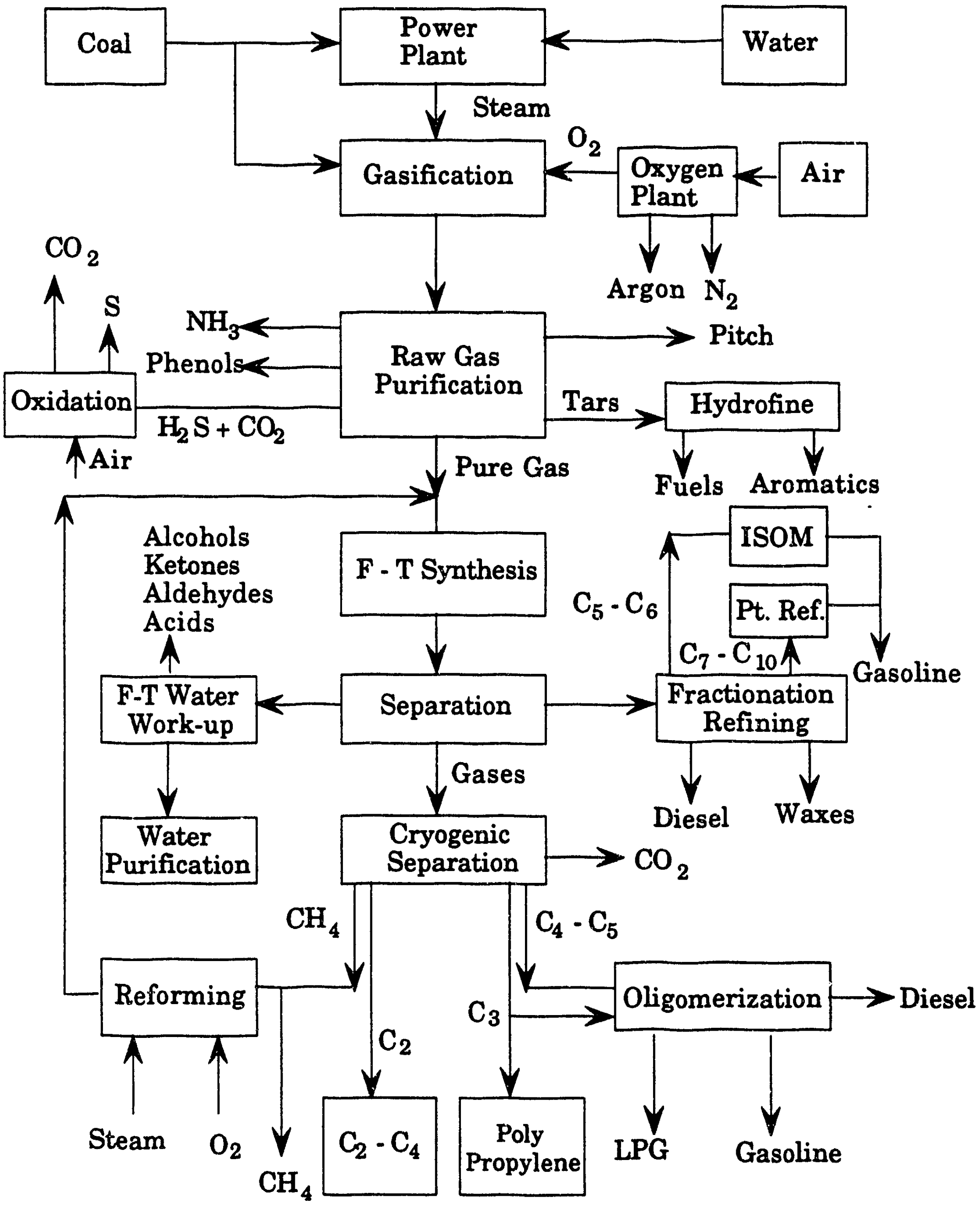


Figure 22. Block diagram for SASOL plant processes (Reprinted with permission from Dry 1990, Elsevier Science Publishers)

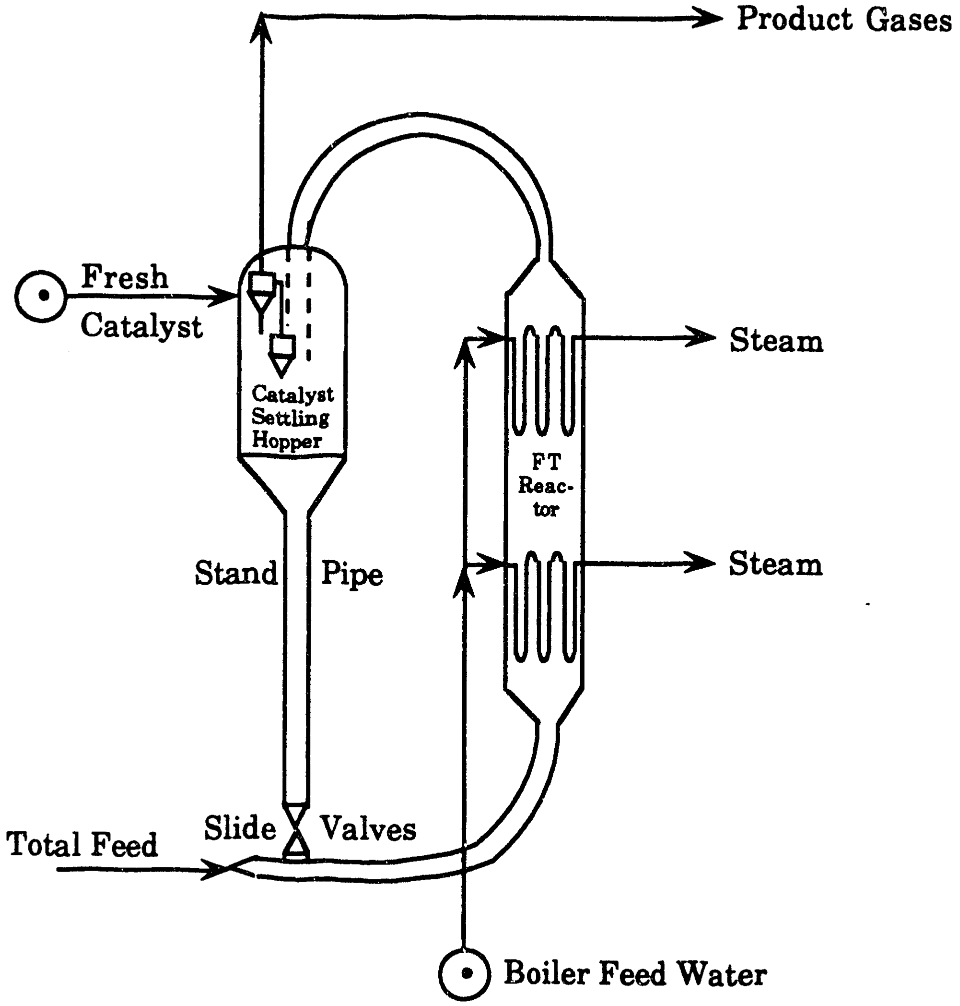


Figure 23. SASOL Synthol CFB (Reprinted with permission from Jager et al. 1990, J.C. Baltzer, A.G. Scientific Publishing Company)

Product distribution follows the ASF pattern.

Classical FT operation is generally operated with an alpha of 0.68 for Fe catalysts and 0.75 for Co. The good fit of the observed carbon number distributions to the ASF model is shown in Figure 25 for typical examples for Fe, Ru, and Co catalysts with alpha values of 0.7 to 0.95.

An important consequence of the sequential chain growth mechanism is that it is theoretically impossible to exclusively synthesize a particular hydrocarbon, except for CH_4, or to synthesize a paraffin fraction of a specified narrow range of chain lengths. However, by providing suitable catalyst and process conditions

Table 14. Product Selectivities of SASOL Commercial Reactors (Jager et al., 1990)

Operating conditions and product selectivity, wt%	SASOL I		SASOL II
	Arge	Synthol	Synthol
Catalyst, alkali promoted Fe	Precipitated	Fused	Fused
Catalyst circulation rate, Mg.h^{-1}	0	8000	—
T, °C	220-255	315	320
p, MPa	2.5-2.6	2.3-2.4	2.2
Fresh feed H_2/CO, molar	1.7-2.5	2.0-3.0	—
Recycle ratio, molar	1.5-2.5	2.0-3.0	—
H_2+CO conversion, mole %	60-68	79-85	—
Fresh feed, km^3/h	20-28	70-125	300-350
Diameter × height, m	3 × 17	2.2 × 36	3 × 75
C_1	5.0	10.0	11.0
$C_2 =$	0.2	4.0	
C_2	2.4	6.0	7.5
$C_3 =$	2.0	12.0	
C_3	2.8	2.0	13.0
C_4	3.0	8.0	
C_4	2.2	1.0	11.0
C_5-C_{12}	22.5	39.0	37.0 (C_5-191°C)
C_{13}-C_{18}	15.0	5.0	11.0 (191-399°C)
C_{19}-C_{21}	6.0	1.0	3.0
C_{22}-C_{30}	17.0	3.0	(399-521°C)
C_{30}	18.0	12.0	0.05 (>521°C)
Nonacid chemicals	3.5	6.0	6.0
Acids	0.4	1.0	—

= indicates olefin

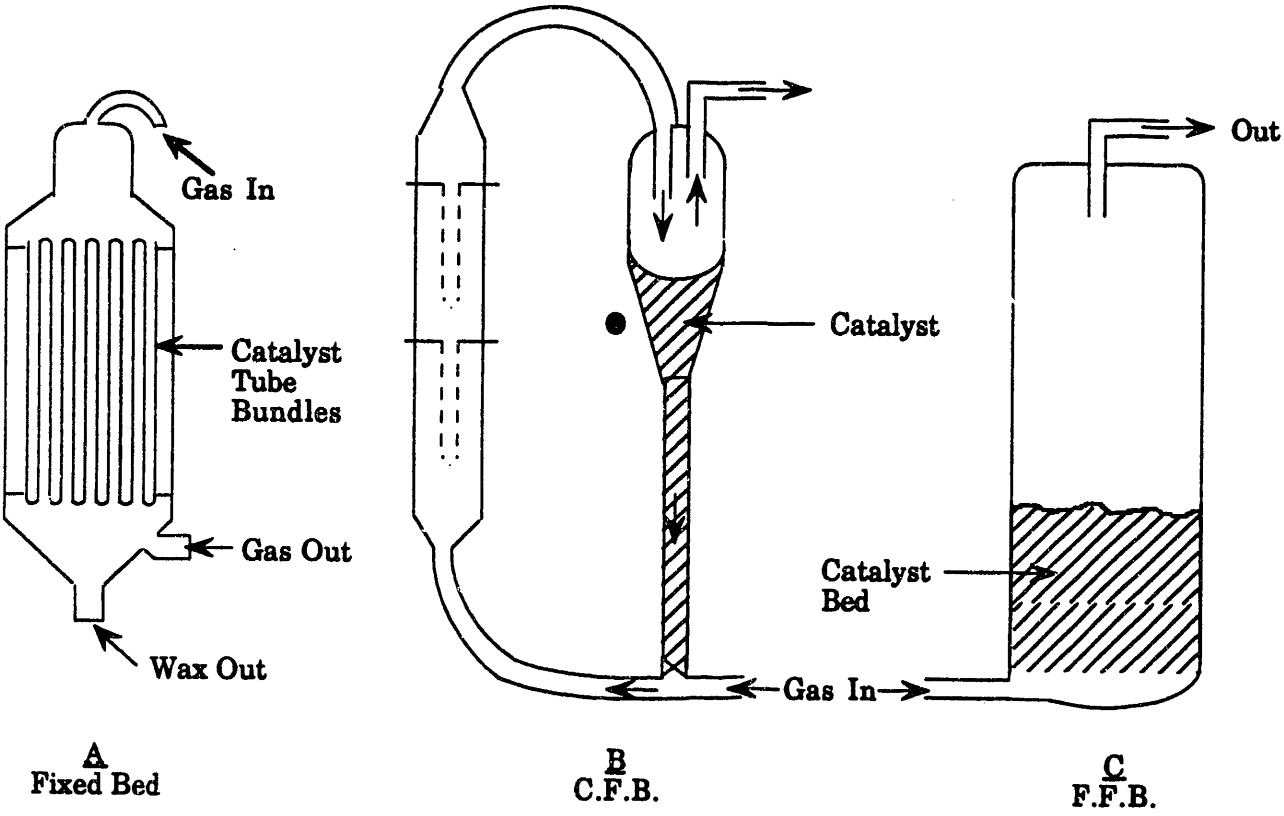


Figure 24. SASOL FT reactors (Dry 1990)

favorable for achieving a desired value of alpha, different product ranges can be manufactured, including those of high molecular weight (Figure 26).

The SMDS process utilizes a multitubular fixed-bed reactor-catalyst system for the FT synthesis. This selection was made after extensive consideration was given to fluidized-bed, ebullating-bed, and slurry reactor options (Sie et al. 1991).

A mathematical relationship was derived giving the maximum alpha value permissible and the limits of operating pressure, temperature, and conversion level to ensure trouble-free fluid-bed operation when producing high molecular weight products. The known commercial FT processes, Hydrocol and Synthol, which operate in a fluidized regime, produce a relatively light product at high temperature and moderate pressure. The conditions for stable fluidized operation are indeed met. It was concluded that fluidized technology is not suitable for the SMDS because of accumulation of condensed products on the catalyst beyond the amount that can be accommodated in the catalyst pores.

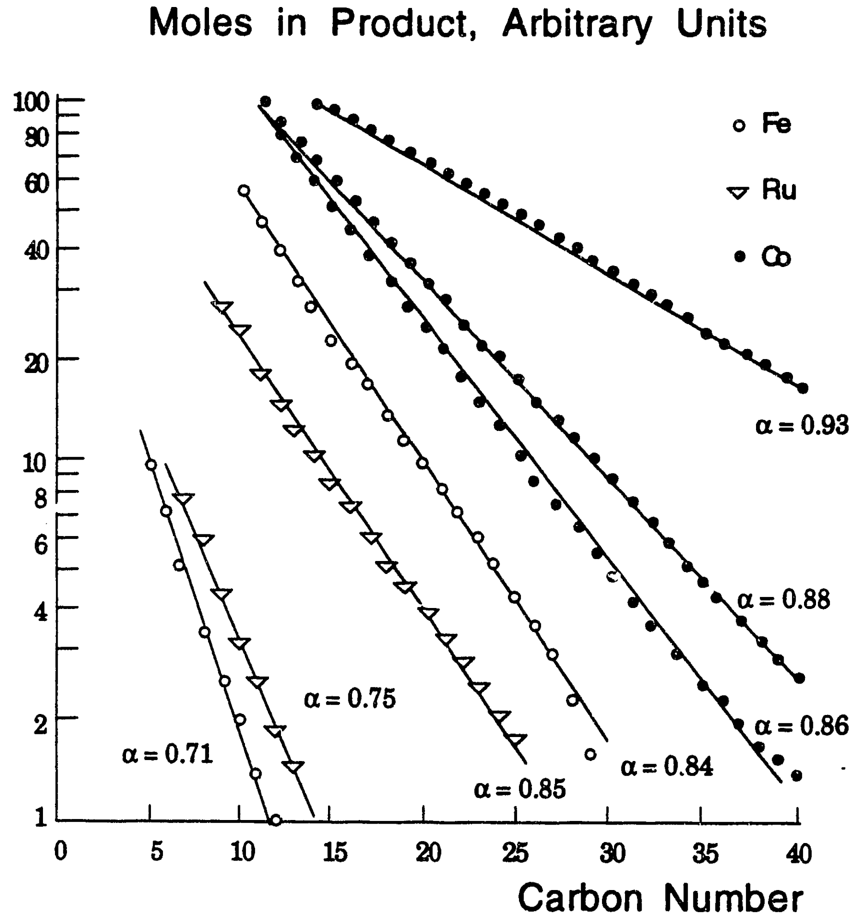


Figure 25. Typical carbon-number distribution, SMDS (Sie et al. 1988)

Consideration was also given to intraparticle diffusion limitations for fixed- and ebullating-bed processes. It was concluded that there is a substantial loss of activity upon increasing particle size from 0.38 to 2.4 millimeters. Further, it appears that the diffusion mechanism that limits the reaction rate in catalyst particles of a diameter greater than 1 millimeter is in essence the diffusion of dissolved gas (CO and H_2) through the liquid-filled pores. This makes it understandable that pore diameter has little or no effect on pore diffusion limitations, in contrast to the situation for a gas-phase reaction under relatively low pressure where Knudsen diffusion is rate determining.

Slurry-phase operation was also considered. Catalyst particle size is important because it determines the maximum allowable concentration in the liquid. Very small particles can only be used in relatively low volume concentrations if unduly high slurry viscosities are to be avoided. Larger particles are acceptable in higher concentrations but may give rise to problems because of their tendency to settle in regions where gas and liquid velocities are inadequate to keep particles fully suspended. Separation of the catalyst from the liquid is also an important factor.

An important factor in a FT slurry process is the mass transfer outside the catalyst particles, in particular the transport of synthesis gas components from the gas bubbles to the liquid. Satterfield and Huff (1980) concluded that significant gas-liquid gas transfer limitations do occur, in particular at higher reaction temperatures.

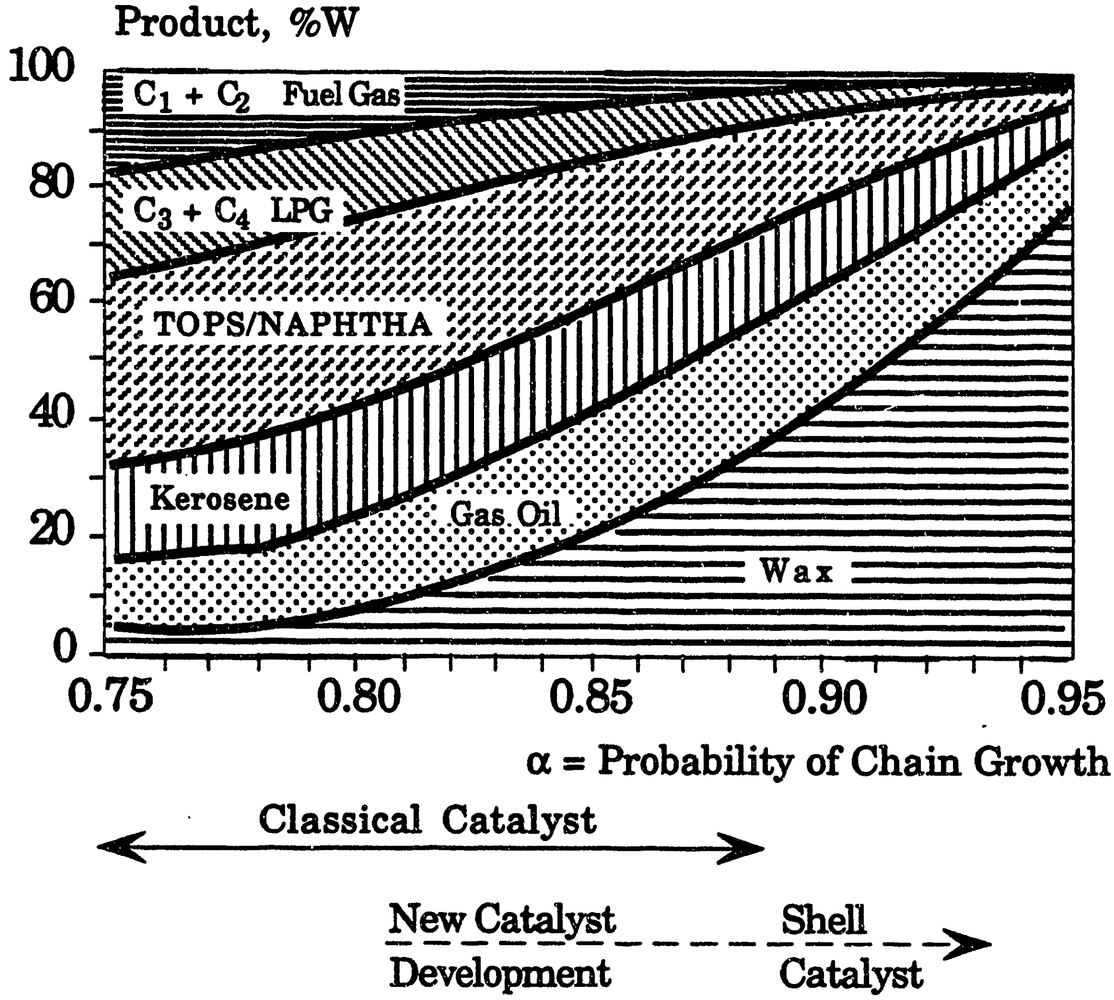


Figure 26. Product distribution for FT synthesis as a function of alpha (van der Burgt et al. 1985)

The slurry phase FT will be discussed further later in this report. In the SMDS process the catalyst is packed in tubes that are cooled by surrounding boiling water. Selection of the multitube mode may have been made in part because of uncertainties in knowledge of slurry-phase operation. Clearly, additional R&D information on slurry is needed.

3.3.1.1 Hydrocracking of Waxes The relative reactivities observed in the hydrocracking of paraffins in the range C_{10}–C_{17} over a bifunctional (acid/metal) catalyst are shown in Figure 27. The reactivity increases dramatically with increasing carbon number of the paraffin.

The carbon number distribution of products obtained by hydrocracking of an FT fraction consisting predominantly of C_{16} is shown in Figure 28. There is very little if any formation of methane or ethane. It is important that there is a strong tendency to break more centrally situated C-C bonds.

Thus there is a length-independent chain-growth process and a chain-length dependent selective cracking process. Calculated products distributions are given in Table 15 for different values of chain-growth probabilities of alpha. It can be seen that selectivities to C_{10}–C_{20} exceeding 70% can be obtained for alpha values of 0.95 or higher. The effectiveness of this combination in producing a carbon-number distribution in the middle range is illustrated in Figure 29, which shows experimentally determined products distributions of a FT liquid product before and after hydroprocessing at two different severities.

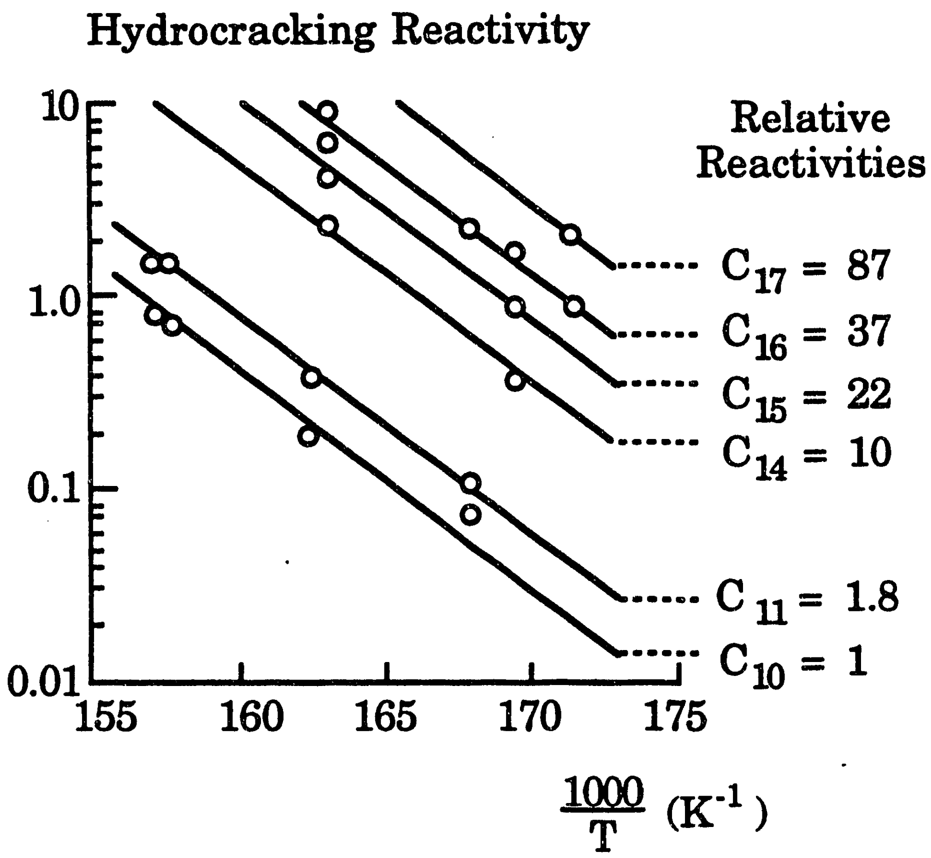


Figure 27. Hydrocracking of synthetic SMDS paraffins of different chain lengths over a dual function catalyst (Reprinted with permission from Sie et al. 1991, Elsevier Science Publishing)

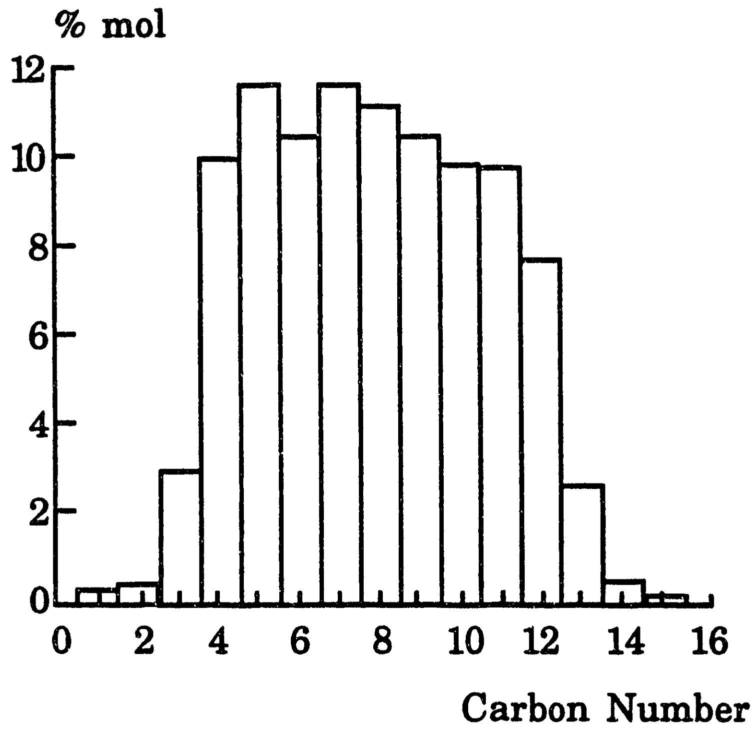


Figure 28. Molar product distribution after cracking an FT fraction (88% wt C16, 12% wt C17) over a dual function catalyst (Reprinted with permission from Sie et al. 1991, Elsevier Science Publishing)

Table 15. Calculated Product Distributions as a Function of the Chain-growth Chance α (Sie et al. 1991)

Growth Chance	AFS Distribution of FT Products			Calculated Distributions of the Two-stage Concept	
	Percent by Weight of			Percent by Weight of	
α	$<C_{10}$	C_{10}–C_{20}	$>C_{20}$	$<C_{10}$	C_{10}–C_{20}
0.80	62.4	31.8	5.8	63.6	36.4
0.85	45.6	38.9	15.5	48.7	51.3
0.90	26.4	37.1	36.5	33.7	36.3
0.95	8.6	19.8	71.7	22.9	77.1
0.98	1.6	4.9	93.5	20.3	79.7
0.99	0.4	1.4	98.2	20.0	80.0

The combination of chain-length-independent synthesis of heavy paraffins and their selective cracking to lighter paraffins is the basis of the SMDS process.

The waxy HPC (heavy paraffin conversion stage) product is hydrocracked and hydroisomerized in a mild trickle-flow process operated typically at 30–50 bar and 300°–350°C.

For syngas production, noncatalytic autothermal partial oxidation is used. Little or no adjustment in the H_2/CO ration is required. There is a net formation of water:

$$CH_4 + 1/2\ O_2 = CO + 2H_2 = \text{-}(CH_2)\text{-} + H_2O\ .$$

There is additional H_2 production by steam reforming of the C_1–C_4 fraction of the FT products. This hydrogen is used for the hydrocracking of the FT products and hydrodesulfurization of the natural gas feed.

The two-stage concept of SMDS process provides considerable flexibility with regard to product range, illustrated in Table 16.

Although a degree of selectivity to desired products is evident, it is also true that there is considerable room for selectivity improvement.

3.3.2 Exxon

The Exxon corporation has announced that its 10-year $100 million gas-to-liquids project is nearing completion, including operation of a demonstration plant at Baton Rouge (Velocci 1991). The Exxon process is a three-step process. First, natural gas is converted to syngas using a unique fluidized-bed reactor system. In step two, hydrocarbon synthesis (HCS) the syngas is converted to an intermediate liquid hydrocarbon product. A high performance catalyst and an advanced reactor system are involved. It is stated that in a major departure from prior industry practice, an advanced reactor and catalyst system has

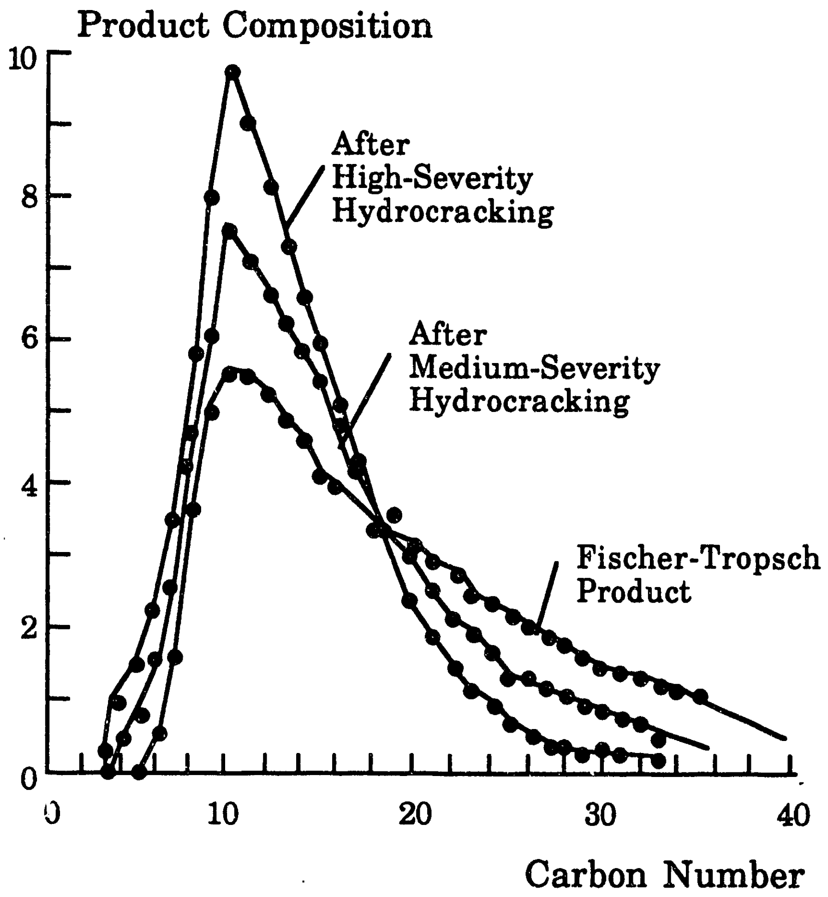


Figure 29. **Carbon number distribution of an FT product before and after selective hydrocracking** (Reprinted with permission from Sie et al. 1991, Elsevier Science Publishing)

Table 16. **Variation in Product Range and Some Leading Properties of SMDS Products** (Sie et al. 1991)

Product		Gas Oil Mode	Kerosene Mode
Tops/naphtha	wt%	15	25
Kerosene	wt%	25	50
Gas oil	wt%	60	25
Property		Gas Oil (Diesel)	Kerosene
Boiling range	°C	250–360	150–250
Density	kg/m^3	780	750
Pour point	°C	-10	
Cetane number		75	
Smoke point	mm		>50
Freezing point	°C		–47

been devised that raised HCS yields and reactor throughput substantially. In the third step, the intermediate hydrocarbon product is upgraded in a step similar to conventional refinery hydroprocessing.

Although little has been published previously other than 100 issued patents, (e.g., Mauldin and Riley 1990; Iglesia et al. 1991, which concern preparation of catalysts in which cobalt is deposited on outer surfaces of particulate supports), related basic research results are beginning to appear on FT synthesis on Co and Ru (Igelesia et al. 1992), reaction-transport selectivity models and the design of FT catalysts (Igelesia et al. 1992), and selectivity control and catalyst design in FT synthesis (Iglesia et al. 1992).

3.3.3 Institut Français du Petrole

The formation of middle distillates from syngas on modified cobalt catalysts (Cu/SiO_2, $Co/Ru/SiO_2$) has been investigated in a fixed-bed and slurry-phase reactor (Chaumette et al. 1992). It was established that obtaining high CO hydrogenation activity and selectivity requires a prior optimization of reduction conditions for each catalyst system. The study of the reducibility of the catalysts systems by TPR and CO dissociation proved to be especially valuable techniques. The temperature-programmed-reduction (TPR) curves in Figure 30 illustrate the variations in reducibility, which are related to the ability to dissociate CO. Ru, which chemisorbs hydrogen more strongly than Co, assists in the reduction of Co.

3.4 Slurry-phase FT

A slurry-phase FT reactor operates with a finely divided catalyst suspended in an oil medium. Using a precipitated Fe catalyst, the slurry-reactor FT was demonstrated in high single-pass conversion with a low H_2/CO ratio (0.6) syngas. Koelbel and Ralek (1980, 1984) provide excellent reviews of their pioneering work for the period from conception to 1970.

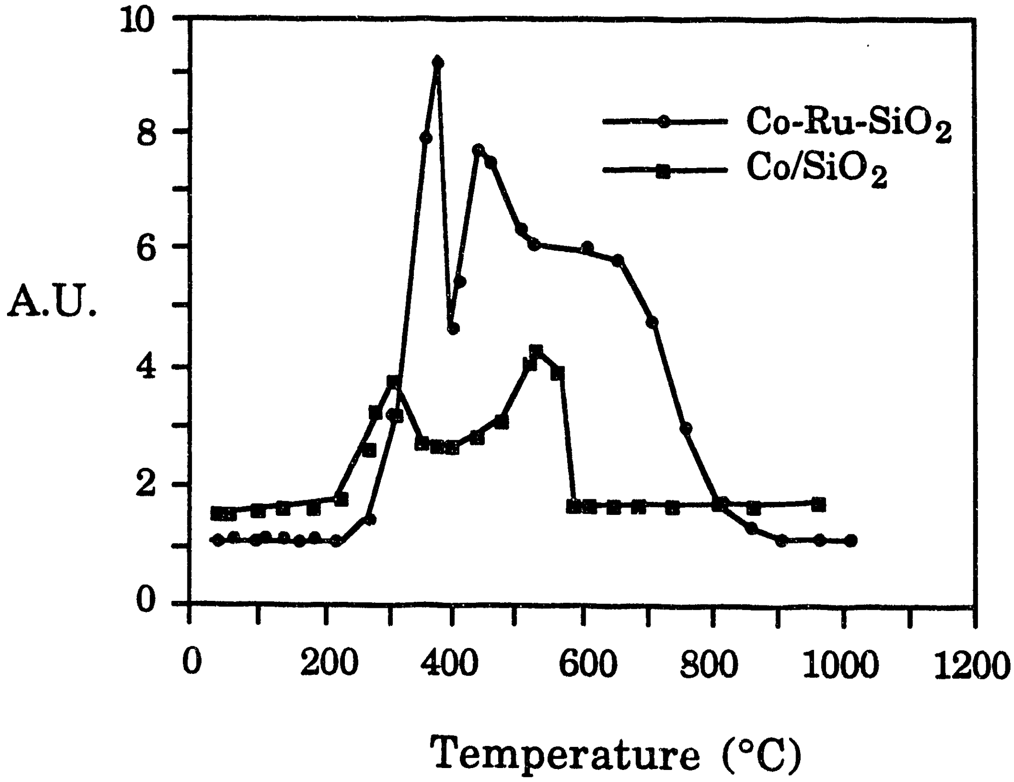


Figure 30. TPR of $Co/SiO_2$and $Co-Ru-SiO_2$ catalyst (Reprinted with permission from Chaumette et al., Copyright 1992, American Chemical Society)

The hydrodynamics of three-phase slurry systems have been studied extensively in order to provide engineering design for appropriate catalytic reactors for optimum performance (O'Dowd et al. 1985; Bukur et al. 1991; Stern et al. 1985; Kuo et al. 1987). A comprehensive review "Assessment of State-of-the-art Hydrodynamic Models" is being published (Zhou and Srivastava 1992). Heat transfer properties have also been studied (Saxena and Srivastava 1986). Laboratory evaluations for bubble column reactors have been performed in bench-scale, mechanically stirred, slurry reactors.

Much interest has been aroused by the potential economic improvements based on the high conversion per pass, resulting in lowered recycle requirements, discussed later (Gray et al. 1991; Fox et al. 1990).

The suitability of various iron-based catalysts for slurry-phase operation has been reviewed (Rao et al. 1990, 1992a, 1992b, 1992c) including those prepared by precipitation, fusion, ultrafine particles, and catalysts produced by laser pyrolysis. They concluded that there is a need for additional research for synthesis of reproducible active and stable catalysts.

There has been considerable research by industry, much unpublished.

A DOE-sponsored research program has resulted in the development of an Fe-based catalyst having FT and water gas shift activities that are higher than those of the commercial Ruhrchemie Fe catalyst. The catalyst developed has favorable suspension behavior in slurry medium. Plans are to manufacture sufficient quantities of this catalyst for study in the Alternative Fuels Development Unit in Laporte, TX. This important scale-up test is being sponsored by DOE, Air Products, Exxon, Shell Oil, and Statoil (Norway). The test was carried out during August 1992, and preliminary reports have been favorable.

3.4.1 Fuelco Slurry FT Plant Operation

Fuel Resources Development Co. (Fuelco), a wholly owned subsidiary of Public Service Company of Colorado based in Denver, has described a technology named Synhytech (Synthetic Hydrocarbon Technology). A small 50-bpd unit was constructed in 1989 for converting syngas to liquid fuels using a slurry catalyst technique employing a Fe-based catalyst (Rowley 1990). An update by C. B. Benham is scheduled for the 1992 International Pittsburgh Coal Conference. The Synhytech process is shown in Figure 31 and the synthesis reactor in Figure 32. Products include naphtha, diesel fuel, and wax. Special attention was given to the environmental aspects of producing a diesel of good cetane value.

In 1992 a 230-bpd plant was placed in operation (Fennig 1991). Diesel fuel from the process provided to Detroit Diesel had the properties shown in Table 17 (Bennethum and Windsor 1991). From their engine tests they concluded "We were surprised at the reduction in particulates that we measured compared to a DF-1 fuel used with the same engine. The particulate reduction was much greater than would be expected from the aromatics and sulfur reductions. Our conclusion was that the presence of oxygenates contributed significantly to the PM reduction measured."

It is interesting to note that the feed to the Fuelco plant is municipal landfill gas, whose typical composition is about 47% CH_4, 47% CO_2, 3.7% N_2, and 0.8% O_2. O'Leary and Tansel (1990) have described technology for recovery collection systems. Fuelco indicated that it regards liquid fuels manufacture more practical than building a pipeline, at least for some locations. Furthermore, the plant can be moved.

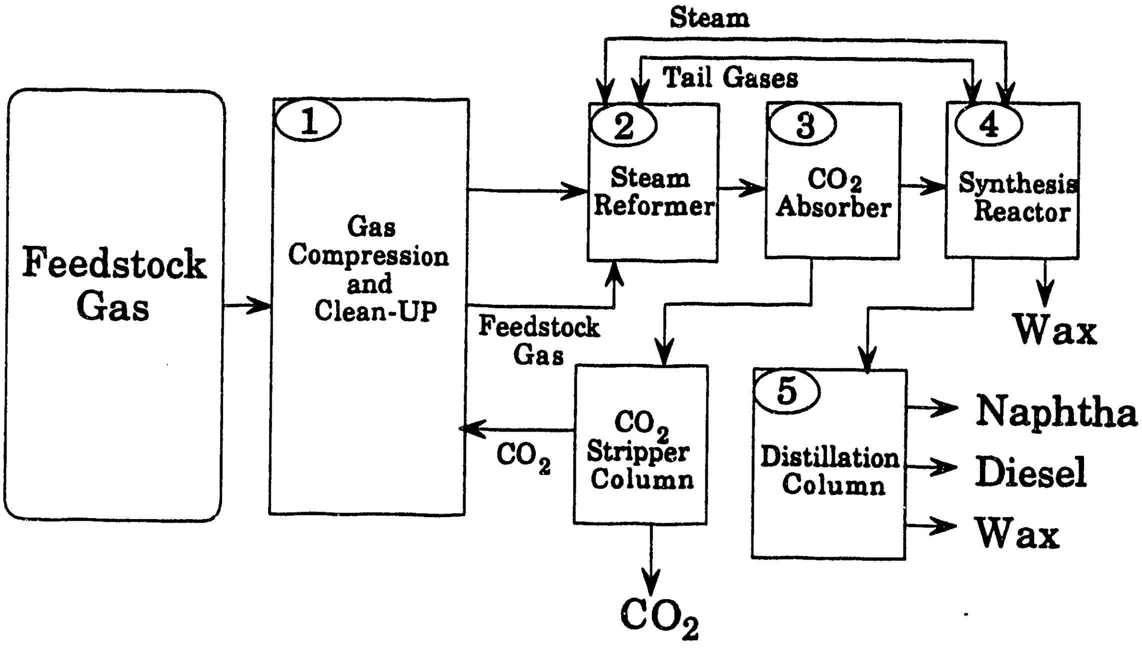


Figure 31. How a Synhytech plant works (Fennig 1990)

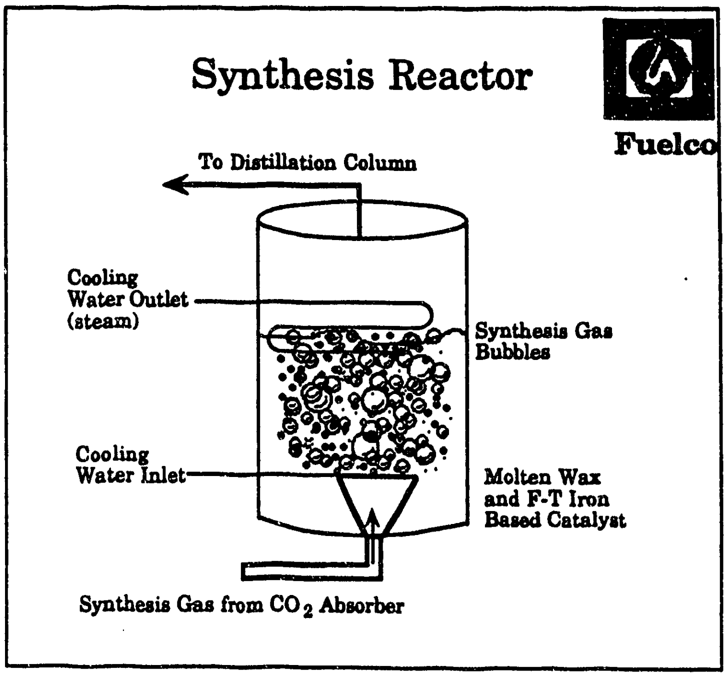


Figure 32. Synhytech synthesis reactor (Rowley 1990)

Table 17. Synthetic Diesel Fuel Specifications (Bennethum and Winson 1991)

ASTM[a] Distillation, °F	
IBP[b]	332
90%	514
EP	555
Cetane Index	62
Sulfur Content, wt %	< .001
Cloud Point, °F	-2
Pour Point, °F	-6
Conradson Carbon on 10% Residuum, wt %	.05
Flash Point, °F	146
Bottom Sediment & Water, vol. %	< .025
Kinematic Viscosity @ 100°F, cSt[c]	189
API[d] Gravity @ 60°F	48.5
Aromatics, wt %	0
Paraffins, wt %	47
Olefins, wt %	41
Alcohols, wt %	6
Other Oxygenates, wt %	6
Heat of Combustion, Btu/lb	18,585
Heat of Combustion, Btu/gal	128,230

[a] ASTM = American Society of Testing and Materials
[b] IBP = initial boiling point
[c] cSt = centi stokes
[d] API = American Petroleum Institute

3.4.2 Cobalt Catalyst for Slurry-phase FT

Both cobalt and iron-based catalysts have been used commercially for FT synthesis. The catalyst used by Germany during World War II was $Co/MgO/ThO_2/SiO_2$. The Germans carried on research to substitute Fe for Co but such catalysts were not installed during World War II. However, the SASOL units use Fe-based catalysts. There has been considerable interest in Co catalysts, particularly for use in slurry-phase FT operation to produce higher molecular weight hydrocarbons, including waxes. As has long been noted, cobalt catalysts are generally more reactive for hydrogenation compared to Fe, leading to less olefin and alcohol production. Co is not active as a water gas shift catalyst (as is Fe). Thus, oxygen, introduced by

CO, is rejected as H_2O with Co and as CO_2 by Fe catalysts, although the H_2/CO ratio in the syngas is also influential in how oxygen is rejected. As may be expected, a high H_2/CO ratio favors rejection as H_2O.

Shell has reported the good agreement of the observed carbon number distribution to the ASF model. Figure 25 shows a few typical examples for Fe, Ru, and Co type catalysts with alphas varying between 0.75 and 0.95.

Goodwin (1991) has reviewed current directions in FT catalysts and pointed out that a number of patents have been issued involving Co (see Table 18). He suggested that the inclusion of a metal in addition to Co is to permit reduction of the Co at a lower temperature, thereby providing a larger Co metal area and consequent higher activity (Eri et al. 1989). It has long been known that Ni and Co are not readily reduced when supported on Al_2O_3.

It has been suggested that, for Ru/Co-containing catalysts, the advantage may be that ruthenium promotes hydrogenolysis and the intimate association of ruthenium with cobalt might allow carbon deposits to be gasified by hydrogenolysis in cobalt-containing catalysts.

3.5 MTG and Related Processes

The MTG process represents a different approach to conversion of syngas to gasoline. Syngas is first converted to methanol, which is then converted nearly quantitatively to a high-octane gasoline over a catalyst containing ZSM-5 (see Figure 33). This process is based on the discovery by scientists at Mobil of the capability of an unusual molecular sieve catalyst, ZSM-5.

Invented by scientists at Mobil (Meisel et al. 1976; Meisel 1988), the process technology was developed by Mobil under the joint technical direction of Mobil and DOE (Mills 1977) with a funding formula of 30% Mobil: 70% DOE. The MTG process has been installed (1985) in New Zealand using a fixed-bed catalyst mode. Production of 14,500 bpd continues successfully, supplying one-third of New Zealand's gasoline needs. Part of the gasoline production is exported to Japan. The syngas is manufactured from off-shore natural gas.

To improve process technology, a second generation MTG technology has been developed based on the use of a fluid-bed reactor. As shown in Table 19, fluid-bed MTG gives higher yield of higher quality gasoline than fixed-bed MTG. This yield and quality advantage combined with improved energy utilization results in a cost advantage over fixed-bed MTG of at least 10% for the total complex. Fluid-bed operation has been demonstrated in a 100-bpd semiworks unit in Wesseling, Germany, and is deemed ready for commercialization (Tabak and Yurchak 1990).

Mobil has developed further modifications to the MTG process. Examination of the reaction pathway for methanol conversion to hydrocarbons (Figure 34) indicates that the reaction proceeds through olefinic intermediates. In the MTO process, methanol is converted to olefins. In the MTO/MOGD process (Figure 35), light olefins first formed are reacted further to produce gasoline and diesel. Product yields and quality are illustrated in Table 20 (Yurchak and Wong 1991).

3.5.1 TIGAS

Seeking to improve the economics of the MTG process, H. Topsøe Co. has developed technology for an integrated gasoline synthesis by modifying the three process steps: syngas production, methanol synthesis, and conversion, in order to be able to operate all steps at the same pressure and the last two steps in a

Table 18. Patented Cobalt-Containing FT Catalysts (Goodwin 1991)

Company	Typical Catalyst Constituents			
	Primary	Secondary 1	Secondary 2	Support
Gulf	Co	Ru	oxides	alumina
Exxon	Co	Re/Ru	oxides	titania
Shell	Co	w/w/o noble metal	ZrO_2	silica
Statoil	Co	Re	oxides	alumina

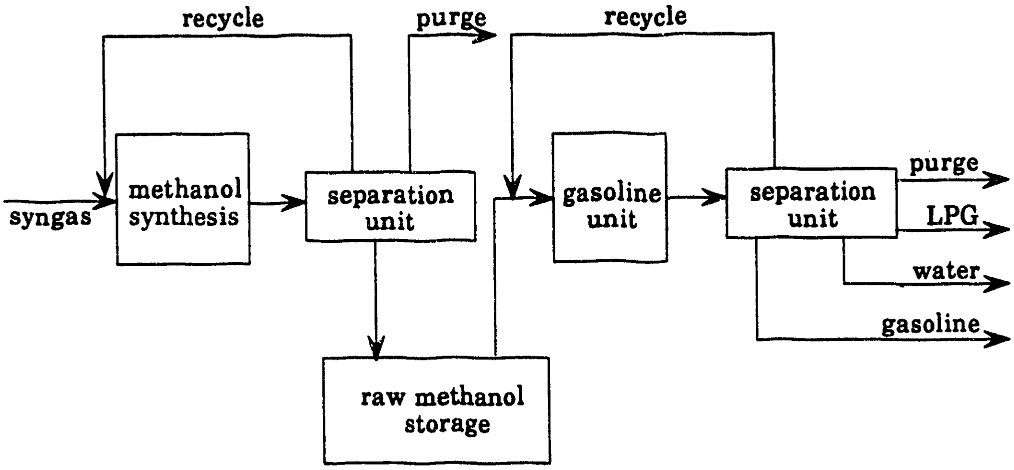


Figure 33. Two-stage MTG process

single synthesis loop, without isolating the synthesized methanol. The Topsøe Integrated Gasoline Synthesis (TIGAS) process, shown in Figure 36, utilizes combined steam reforming and autothermal reforming for syngas production (Topp-Jorgensen 1986, 1988). A multifunctional catalyst is used to produce methanol and DME instead of only methanol. The production of MeOH and DME allows higher syngas conversion. The process has been demonstrated on a process unit, operated for 10,000 hours during the period of 1984–1987.

The basic problem of process integration is that the process steps are preferably carried out at very different pressures: synthesis gas production at 15–20 bar, MeOH synthesis at 50–100 bar, and the MTG process at 15–25 bar.

In the integrated loop, the recycle stream from the high pressure separator will have to pass the oxygenate catalyst. Because a Cu-based catalyst is used, any unsaturated compounds in the recycle gas are hydrogenated. The olefin content in the product from integrated process is low, resulting in a stable gasoline product.

The highest gasoline octane, RON, in the TIGAS process, is a few numbers lower than in the normal MTG process. Process flexibility and lower investment are main advantageous features of the TIGAS process.

Table 19. MTG Hydrocarbon Yields (Tabak and Yurchak 1990)

	Fixed Bed	Fluidized Bed
Hydrocarbon Product, wt %		
Light Gas	1.3	4.3
Propane	4.6	4.4
Propylene	0.2	4.3
iso-Butane	8.8	11.0
n-Butane	2.7	2.0
Butenes	1.1	5.8
C_{5+} Gasoline	81.3	68.2
	100.00	100.0
C_{5+} Gasoline (including Alkyate)	83.9	91.2
Gasoline Octane Numbers		
RON	93	95
MON	83	85

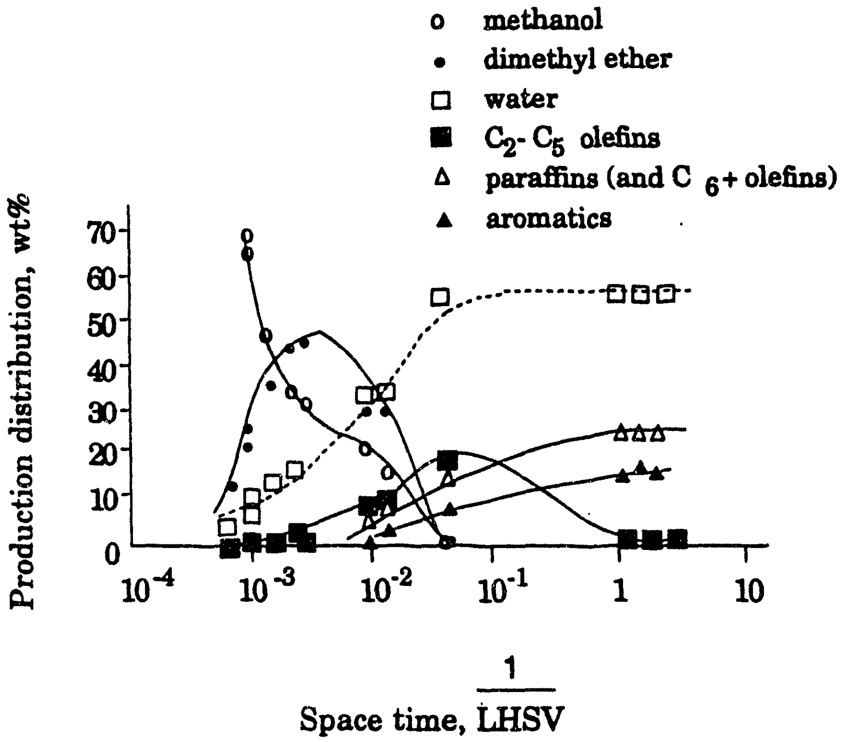


Figure 34. Reaction pathways for conversion of methanol to hydrocarbons over ZSM-5 catalyst (MTG). (Reprinted with permission from Chang and Silvestri, Copyright 1977, Academic Press)

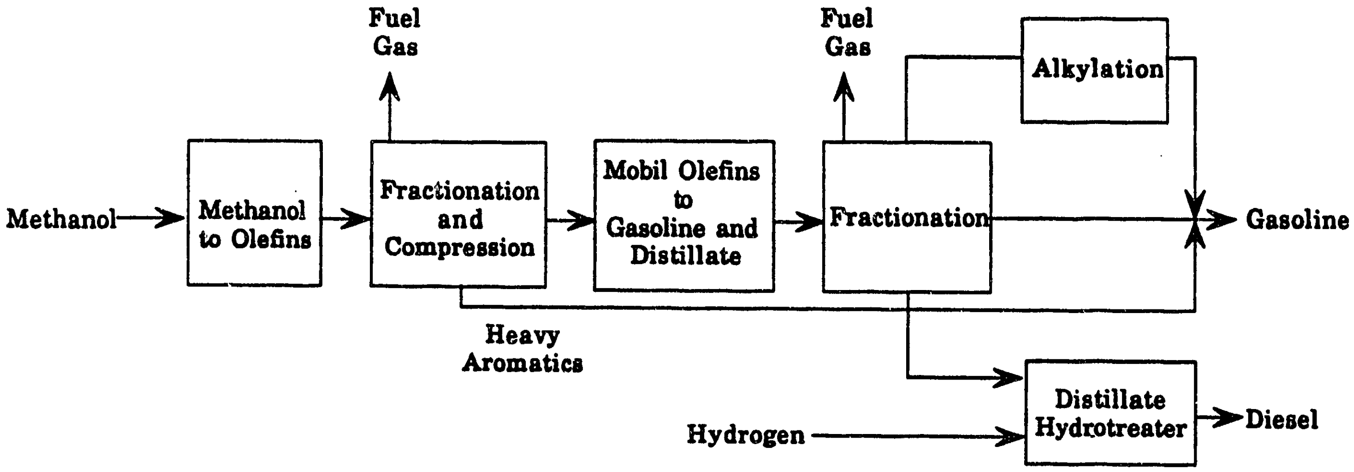


Figure 35. Integrated MTO/MOGD process

Table 20. MTO/MTOG Product Yields (Tabak and Yurchak 1990)

Distillation/Gasoline Ratio		0.65	0.95
Product Yield, wt %			
LPG		5.1	5.1
Gasoline		57.0	48.0
Diesel		37.9	46.9
		100.0	100.0
Product Quality			
Gasoline	R+O	92.5	91.8
	M+O	85.6	85.3
	(R+M)/2	89.1	88.6
Diesel Cetane Number		50	50

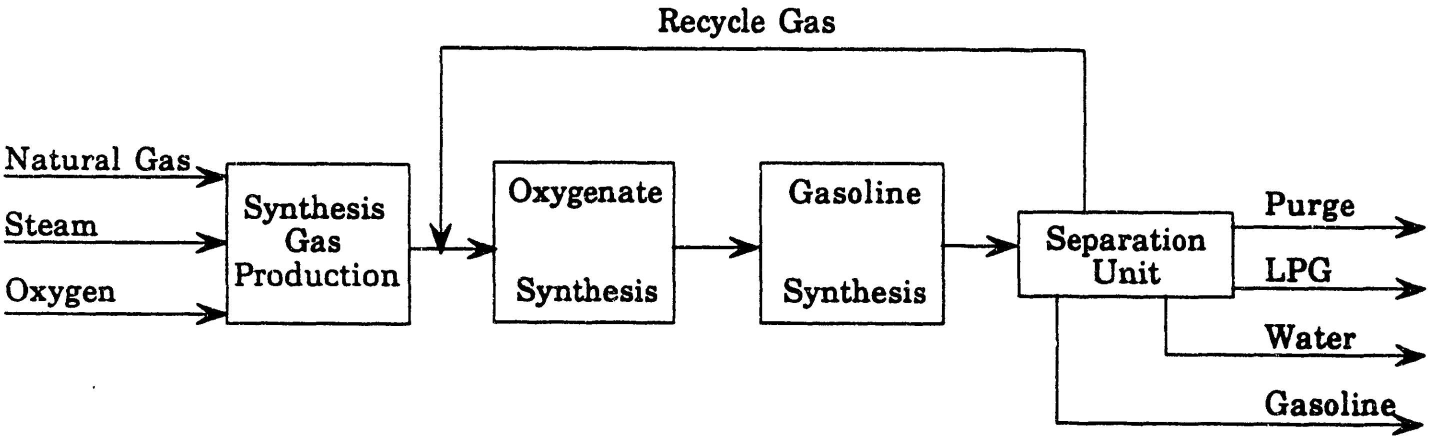


Figure 36. Gasoline from natural gas with the TIGAS process (Topp-Jorgensen 1988)

4.0 Chemistry of Syngas Catalysis

There is an immense scientific literature on the catalytic chemistry of hydrogenation of CO and CO_2. There are 1,700 references cited in "New Trends in CO Activation," (Guczi 1991). There are comprehensive reviews of alcohol synthesis (Herman 1991) and FT catalysis (Bartholomew 1991). Other chapters describe fundamental research on characterization of catalyst surface structure and interactions with CO and H_2 utilizing modern instrumental techniques.

The potential for design of alcohol synthesis catalysts assisted by knowledge-based expert systems ("artificial intelligence") has been described by Hu et al. (1991).

4.1 Methanol

The main features desired in a methanol synthesis catalyst are (1) good hydrogenation ability, which is generally considered to be a limiting factor in the reaction; (2) activation of CO without dissociation as otherwise methane formation occurs; (3) activation energy < 15 kcal/mole; and (4) absence in the support of undesirable components such as active alumina (excessive dehydration ability). Another requirement is a stable Cu metal dispersion.

Characteristics of a commercial $Cu\text{-}ZnO/Al_2O_3$ catalyst are total area of 60–100 square meters per gram, Cu area (by N_2O) of 20 meters per gram, and ZnO area of 55 square meters per gram.

Very comprehensive reviews of catalytic synthesis of methanol over $Cu\text{-}ZnO/Al_2O_3$ are provided by Bart and Sneeden (1987) and Waugh (1992).

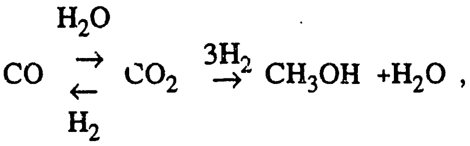
The nature of the catalytically "active" site has been very controversial, particularly the existence and importance of Cu° and Cu^{1+}. It has been established that the methanol productivity for a given type of $Cu\text{-}ZnO/Al_2O_3$ catalyst and a given $H_2/CO/CO_2$ feedstock is proportional to the copper metal surface area. However, there is evidence that a $Cu^\circ\text{-}Cu^{1+}$ redox couple is important. It is known that the presence of Cu^{1+} is strongly dependent on the gas phase composition, particularly the presence of H_2O and CO_2. Under industrial conditions, catalysts contain both metallic and oxidized copper. It may be that copper/ZnO contiguity is important. The effect of supports has been investigated by Robinson et al. (1991).

A wide range of mechanisms has been proposed for methanol synthesis based on experimental evidence from kinetics, use of isotopic labeling, trapping of intermediates, variation of feed components, and spectroscopic studies of catalyst surfaces (Stiles et al. 1991; Smith et al. 1990, 1991). It is now recognized that more than one mechanism may lead to methanol synthesis, produced by hydrogenation of both CO and CO_2 at different rates as a function of the catalyst composition and feed and reaction conditions. The catalytic behavior is sensitive to the gas phase environment: the activities and selectivities in CO/H_2 and CO_2/H_2 reactions are different.

Until 1975, the more generally accepted mechanism corresponded to the reaction:

$$CO_2 \underset{H_2O}{\overset{H_2}{\rightleftarrows}} CO \xrightarrow{2H_2} CH_3OH \; .$$

An alternative scheme is

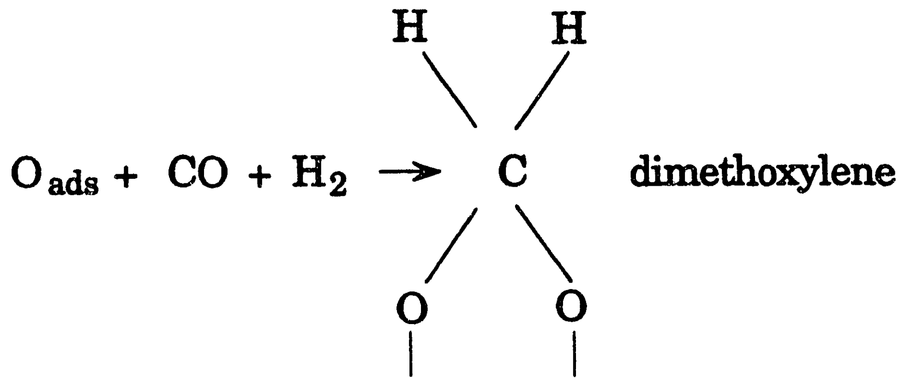


$$CO \underset{H_2}{\overset{H_2O}{\rightleftarrows}} CO_2 \xrightarrow{3H_2} CH_3OH + H_2O \ ,$$

where CO hydrogenation proceeds by initial formation of CO_2 and its subsequent hydrogenation to methanol. It has been established, particularly by isotopic labeling experiments, that the second mechanism is the predominant route for Cu-ZnO/Al_2O_3 catalysts under usual industrial conditions for methanol synthesis (Rosovskii et al. 1977; Chinchen et al. 1986, 1988).

In summary, kinetic and isotopic studies (Bart and Sneeden 1987) over an industrial synthesis catalyst in CO/CO_2/H_2 syngas allow the conclusions that (1) hydrogenation of CO_2 to methanol predominates over CO hydrogenation and copper metal is the active component, (2) CO is converted to CO_2 probably via the regenerative shift reaction, and (3) the reaction steps in the water gas shift reaction are independent of those in methanol synthesis; that is, the two reactions have no common adsorbed intermediate species. In addition to their direct participation in the reaction mechanism, CO_2 and H_2O contribute to maintain an optimum oxidation state of the catalyst and therefore its activity and stability.

It has been suggested that methanol formation proceeds through the formation of formate and methoxy intermediates. Identification of such species by trapping and spectroscopic examination has led to the postulate that formate, dimethoxylene, and methoxy groups are intermediates linked through oxygen to the metal copper site. From infrared studies using Cu-ZnO/Al_2O_3, Bailey (1992) proposes the reaction sequence shown in Figure 37.



CO → dimethoxylene → formate → formaldehyde → methoxy → methanol

Figure 37. Reaction scheme for methanol synthesis over Cu-ZnO/Al_2O_3 (Bailey 1992)

4.1.1 Schottky Junctions

In a different approach, it has been proposed (Frost 1988) that the Schottky junctions at the interface between metals and oxide in the catalyst affect the surface chemistry of the oxides in a way that correlates with catalytic behavior. It is suggested that this theory can predict the existence and properties of new catalysts.

4.1.2 Supported Platinum Group VIII Metals

Research has provided much insight into the very high increase in CO hydrogenation activity and selectivity of rhodium/alumina catalysts brought on by molybdena addition. Gilhooey et al. (1986), found wide variations in apparent activation energies and pre-exponential factors. Foley et al. (1990) found a bimodal distribution of particles with larger particles enriched in rhodium. They proposed two separate sites leading to oxygenates and hydrocarbons. Oxygenate production is attributed to chemistry at the smaller, molybdenum-rich sites and the role of molybdenum is to act as a textural promoter. Bhore et al. (1988) propose a dual-site mechanism in which CO is activated by Rh and H_2 by MoO_{3-x} with migration of the activated hydrogen to the activated CO. A major point is that while Rh is capable of activating H_2, such activation is inhibited by CO. As a consequence of increasing the hydrogenation capability by the molybdena, which is rate limiting, the overall catalytic activity for CO conversion is greatly accelerated.

4.2 Higher Alcohols

Efficient carbon-carbon bond formation is one of the major triumphs of catalysis. Recently, an understanding has been developing of the assembly of C-C bonds in terms of surface science. Idriss, Libby, and Barteau (1992) and Idriss, Kim, and Barteau (1993) have recently reported three different classes of C-C bond formation reactions on single crystal surfaces of TiO_2 under ultrahigh vacuum (UHV) conditions. A study of carbon-carbon bond formation via aldolization of acetaldehyde on single crystal and polycrystalline TiO_2 surfaces reflected the influence of surface heterogeneity. These studies represent an extension of stoichiometric reactions observed on single crystals in UHV toward the creation of novel catalysts.

The reaction mechanisms for formation of higher alcohols under industrial conditions has been intensively investigated. Superimposed on a thermodynamic background is a kinetically controlled chain growth mechanism that is dominated by the two routes shown in Figure 38 (Forzatti et al. 1991). The first route entails aldol-type condensations occurring according to the "normal" mode (β_N) leading to higher aldehydes and to the "oxygen retention reversal" (ORR) mode (β_{ORR}) (Smith et al. 1990) leading to ketones. In the ORR mode, the aldol intermediate of the condensation undergoes hydrogenation + dehydration of the carbonyl group and retention of the anionic oxygen rather than dehydration with loss of hydroxyl oxygen. The second route entails the stepwise C_1 additions on the carbonyl carbon atom, which are assumed to occur both in normal (α_N) and in the reverse mode (α_{ORR}); in particular this route with R_1CCHO replaced by HCCHO in Figure 38 is responsible for the first C-C bond formation of the chain growth process ($C_1 \rightarrow C_2$ step).

Klier et al. (1992a, 1992b) have described their combination of experimental data and theoretical calculations in support of the mechanism for $C_n + C_1$ and $C_n + C_2$ chain growth in oxygenate synthesis in which the efficient and dominant aldol addition with oxygen retention reversal is caused by bonding of alkoxide oxygen of the intermediate 1,3-keto-alkoxide to the alkali ion while the carbonyl group is released for hydrogenation by a cis-trans isomerization thereof. The role of the alkali promoter is to activate the beta carbon of the reacting aldehyde or ketone and to add a second aldehyde (Figure 39).

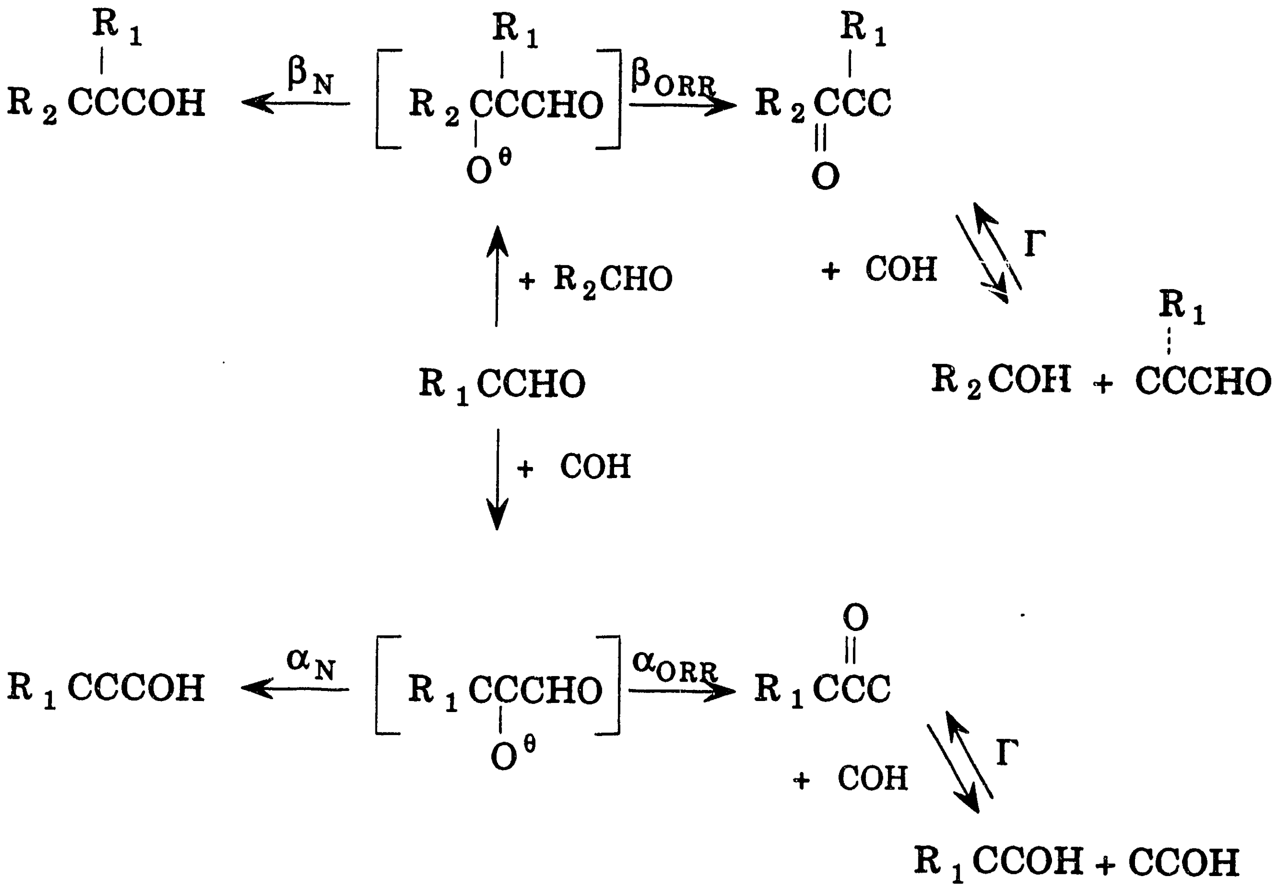


Figure 38. **Reaction mechanism involved in chain growth scheme** (Reprinted from Forzatti et al. 1991 by courtesy of Marcel Dekker, Inc.)

Lietti et al. (1991) emphasize the importance of formaldehyde and rapid aldol-like condensation reactions and fast hydrogenation to alcohols to explain the observed distribution of oxygenated products.

An overall mechanism for higher alcohol synthesis has been proposed by Kienemann et al. (1991), which they believe best accounts for observations obtained with probe molecules and temperature programmed desorption studies (see Figure 40 Special attention was given to first C-C bond and branched-product formation.

The identification of species of molybdenum active for alcohol synthesis was investigated by Muramatsu et al. (1992).

It should be noted that the presence of CO_2 in syngas is important; this has been studied by Calverley and Smith (1991).

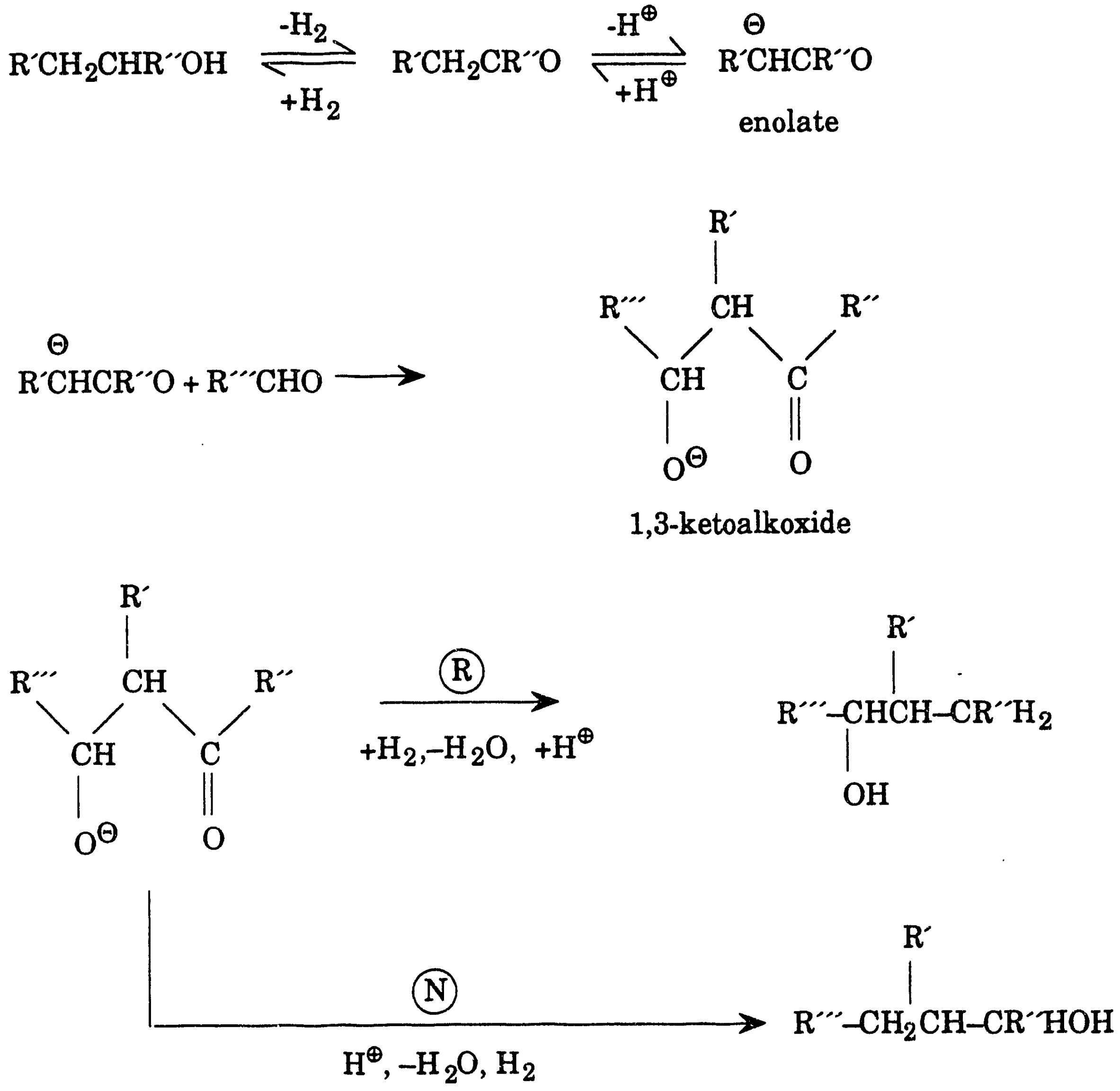


Figure 39. "Aldol coupling with oxygen retention reversal" (Klier et al. 1992a, 1992b)

4.3 Hydrocarbons

The chemistry of FT catalytic reactions has been reviewed recently by Dry (1990) and by Bartholomew (1991).

Research in Japan has been described in "Progress in C_1 Chemistry in Japan" (Japan 1989) and in Energy Conversion and Utilization with High Efficiency, Section BO1A-OO, "Catalyst Development of Coal Conversion to Synthetic Fuels," which contains descriptions of syngas conversion research (Japan 1990). Iglesia and associates have published several significant articles (1992a, 1992b, 1992c).

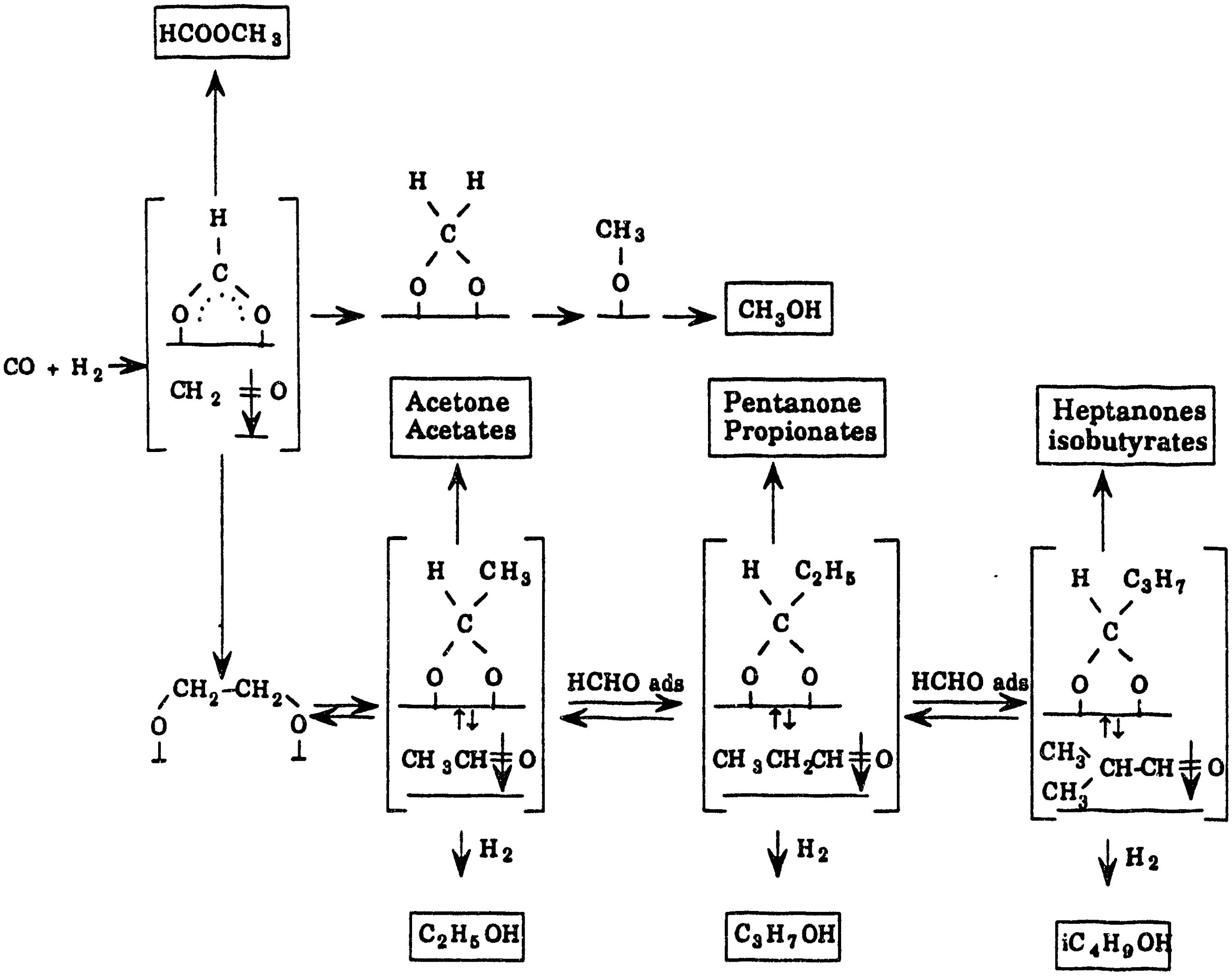


Figure 40. Overall mechanism for higher alcohol synthesis on Co-ZnO-Al_2O_3 (Reprinted with permission from Kienemann et al., Copyright 1991, American Chemical Society)

Research progress on FT has been reported by Satterfield and associates with emphasis on product distribution of the FT synthesis on iron catalysts (Matsumoto and Satterfield 1989; Donnelly and Satterfield 1989). Carbon distribution numbers are described by a modified ASF distribution with two chain growth probabilities (Donnelly and Satterfield 1989).

Cobalt catalysts have also been examined by Yates and Satterfield (1991a, 1991b). The inhibiting effect of CO was determined quantitatively and a Langmuir-Hinshelwood-type rate equation was developed. The apparent E_{act} was 94 kilojoules per mole.

The feasibility of using a mechanical mixture of a $Co/MgO/SiO_2$ FT catalyst and a $Cu\text{-}ZnO/Al_2O_3$ water-gas-shift catalyst for hydrocarbon synthesis in a slurry reactor was established. (Chanenchuk, Yates, and Satterfield 1991).

Ruthenium FT catalysts have been examined by various investigators including Krishna and Bell (1992), who determined the dynamics of chain initiation, propagation, and termination.

There have been many attempts to utilize molecular sieves in FT synthesis catalysts. For example, Zhou et al. (1991) tested a catalyst prepared using zeolite-entrapped osmium carbonyl clusters and determined that at low conversions a non-ASF distribution of C_1–C_5 hydrocarbons was produced.

Studies by Goodwin and co-workers, (Oukaci et al. 1988), provide strong evidence for the bifunctional nature of zeolite-supported FT Ru catalysts and new insight into the role of exchanged cations and acidity in determining hydrocarbon selectivity. Their reaction scheme is depicted in Figure 41.

It is pertinent for production of fuels to comment on the hydrocracking reaction of waxy FT hydrocarbons. The symmetrical product distribution shown in Figure 27 is indicative of primary cracking and suggests a reaction mechanism by which the occurrence of C-C bond scission on an α, β, and γ position from the terminal carbon atoms is disfavored. A new reaction mechanism has been proposed by Sie (1992); see Ansorge and Hoek 1992, and Figures 42 and 43.

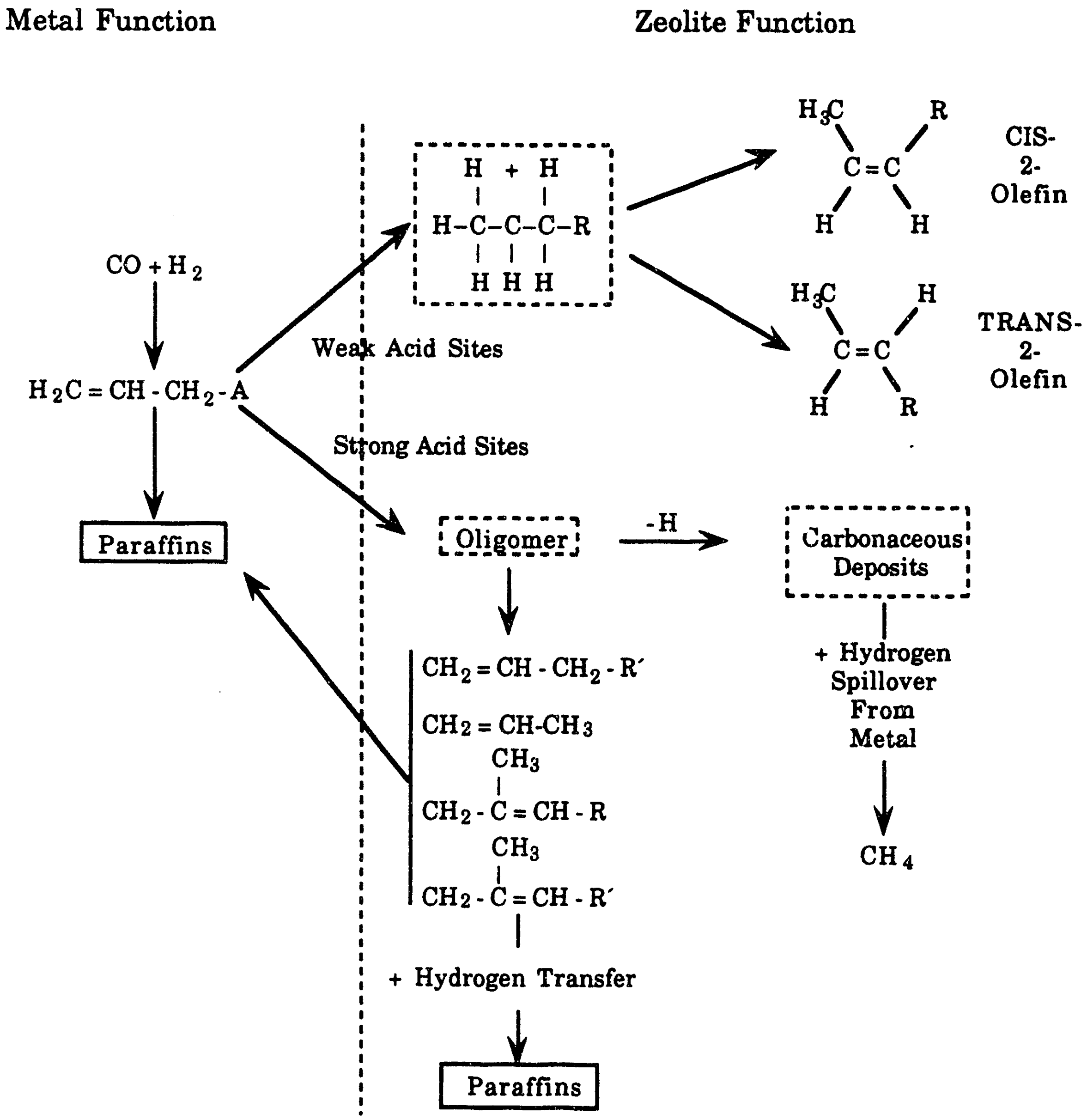


Figure 41. Reaction scheme for CO hydrogenation on zeolite-supported metal catalysts (Reprinted with permission from Oukaci et al., Copyright 1988, by Academic Press)

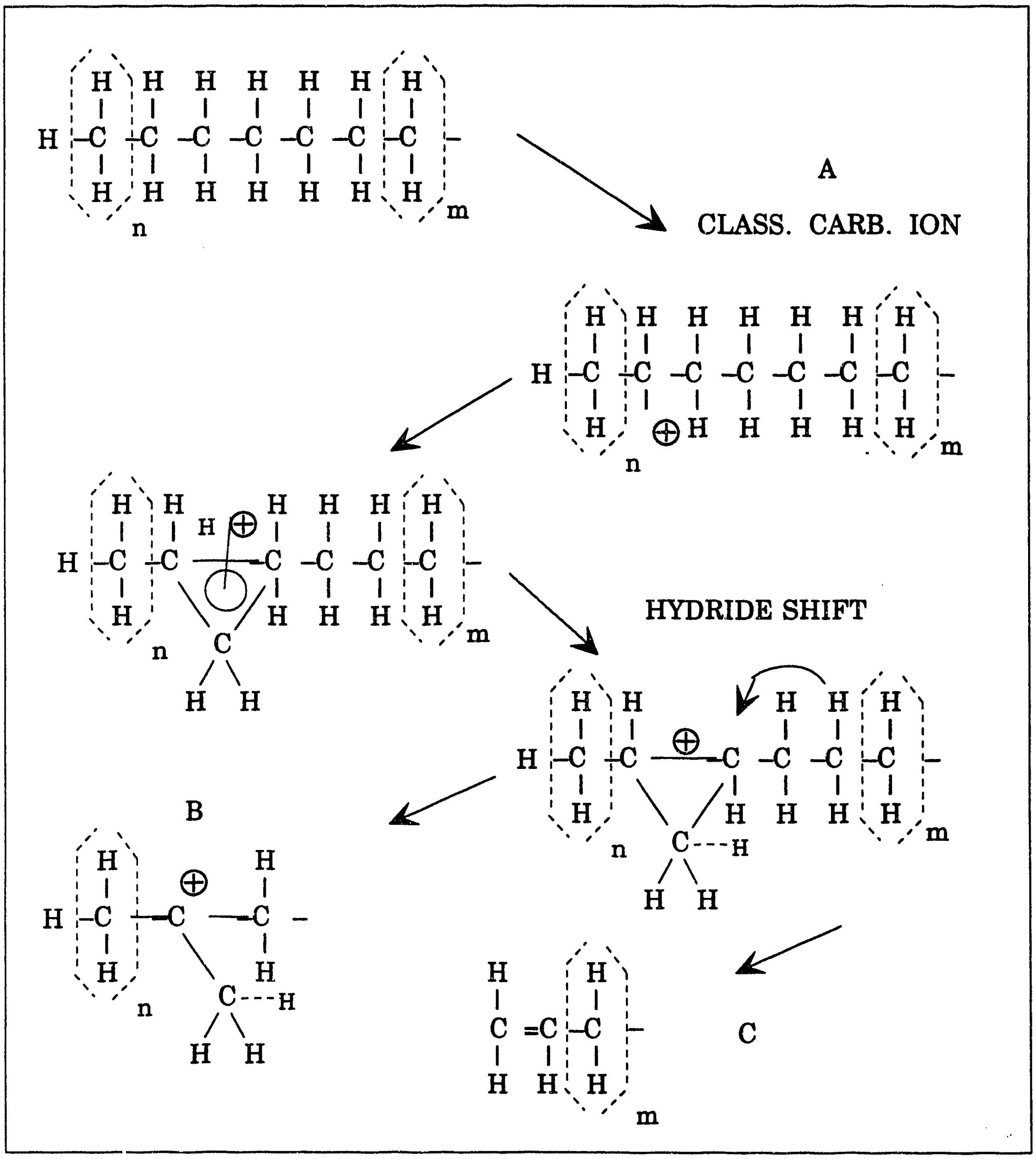


Figure 42. New mechanism for acid cracking of paraffins (Ansorge and Hoek 1992)

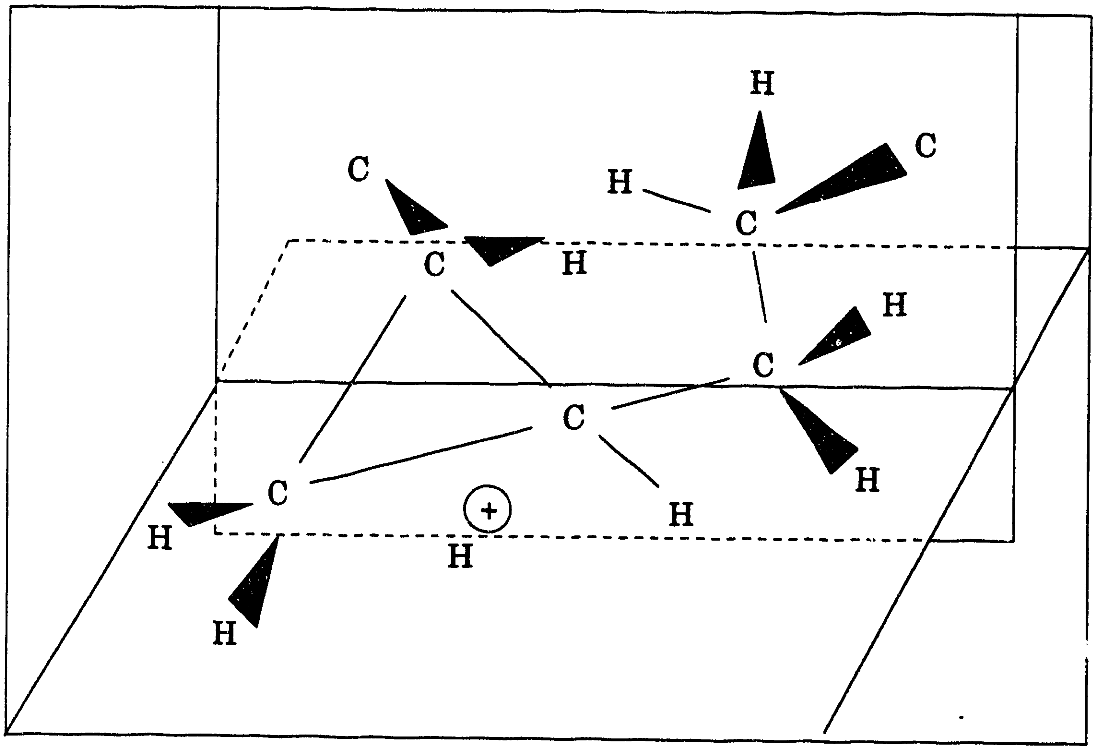


Figure 43. Cyclopropyl cation intermediate in three dimensional interpretation (Ansorge and Hoek 1992)

5.0 Economics

It is fair to say that the economics of synfuels manufacture is such that under usual commercial circumstances, on an energy equivalent basis, synfuels would cost nearly twice that of fuels made from petroleum, now available at about $20 per barrel.

A comparison published by the National Research Council (1990) illustrates the panel consensus of *equivalent* costs of alternate automotive fuels (see Table 21). For this comparison gas was priced at $4.20/thousand cubic feet (mcf). A 15% energy efficiency advantage was assumed for methanol.

This report concludes that the use of wood for methanol production is one of the more attractive methods for using biomass. In the study, wood and coal feed costs were approximately the same and, for the same size plant, gasification and process costs would be about the same.

The production of the greenhouse gas, CO_2, could well have a major effect on the choice of raw materials for transportation fuels. Biomass-based fuels are considered to be greenhouse-gas neutral. In Europe, an environmental tax on oil of about $10 per barrel is being considered.

Many social issues are discussed in reports by the International Energy Agency, Paris, (1990b, 1991), as well as by Gushee and Bamberger (1989), in the United States.

Beyond conventional economic considerations are social values that alter values assigned to fuels. It is pertinent to point out the cost of subsidizing the Gasohol program in the United States. The federal tax benefit is 54 cents per gallon of alcohol used in Gasohol. In 1987, there were 55,000 barrels per day ethanol fuel sales (about present volume), corresponding to a subsidy of nearly $500 million annually. There is an additional subsidy for the corn used to produce the ethanol (Sperling and DeLuchi 1989).

Table 21. Equivalent Crude Cost of Alternative Fuels (in 1988 dollars per barrel, at 10% discounted cash flow) (National Research Council 1990).

Process	Cost Estimate for Current Published Technology
Heavy oil conversion	25
Tar sand extraction	28
Coal liquefaction	38
Western shale oil	43
Methanol via coal gasification	35–40
Methanol via natural gas at	
$4.89/mcf	45
$3.00/mcf	37
$1.00/mcf	24

Environmental considerations are shaping selection of fuels and, consequently, R&D relative to their manufacture and use (DeLuchi et al. 1988; International Energy Agency 1991). In the United States, the EPA has determined that more than 100 city areas have not attained the sufficiently low levels of CO or O_3 deemed essential for health. The CAAA of 1990 requires gasoline in 44 city areas in 1992 winter months to contain 2.7% oxygen, equivalent to 15% MTBE or 8% ethanol. In 1995, gasoline in nine city areas must contain 2% oxygen year-round.

Fuels are now evaluated on their performance qualities (Mills 1990, 1992). These alter fuel economics. Better environmental performance justifies higher prices. Thus, while the current price of gasoline at the refinery is 65 cents per gallon, MTBE with 87% as large a heat of combustion, sells at 100 cents per gallon. It can be considered that fuel prices are determined by heat of combustion, octane or diesel rating, and environmental properties. Thus the price of MTBE may be considered to be determined as 57, 20, and 23, respectively, for a total of 100. Thus 23 cents per gallon is justified by environmental benefits.

Attention is drawn to the fact that synfuels manufacture is capital intensive. Capital costs dominate (Fox 1990, 1992). The cost of synfuels is dominated by capital costs rather than by raw materials. The money needed for plant construction, plant maintenance, taxes, and profit generally accounts for about 70% of the selling price of synfuels.

Cost estimates for alternative fuels are dependent on a number of factors other than technology (Notari 1991). Location is especially important because it greatly affects raw materials and construction costs.

Criteria for estimating the value of new and improved synfuels technology are based on (1) the potential to improve economics of manufacture, particularly by lowering plant costs; (2) technology that produces fuels having environmental benefits in manufacture and use; and (3) higher selectivity to more valuable products. Item (3) includes fuels having high engine performance qualities. Also included are coproduct chemicals or electricity. Chemicals such as waxes, olefins, and oxygenates can fulfill a critical role for a few plants. A larger potential is for coproduction of fuels and electricity.

5.1 Oxygenate Fuels

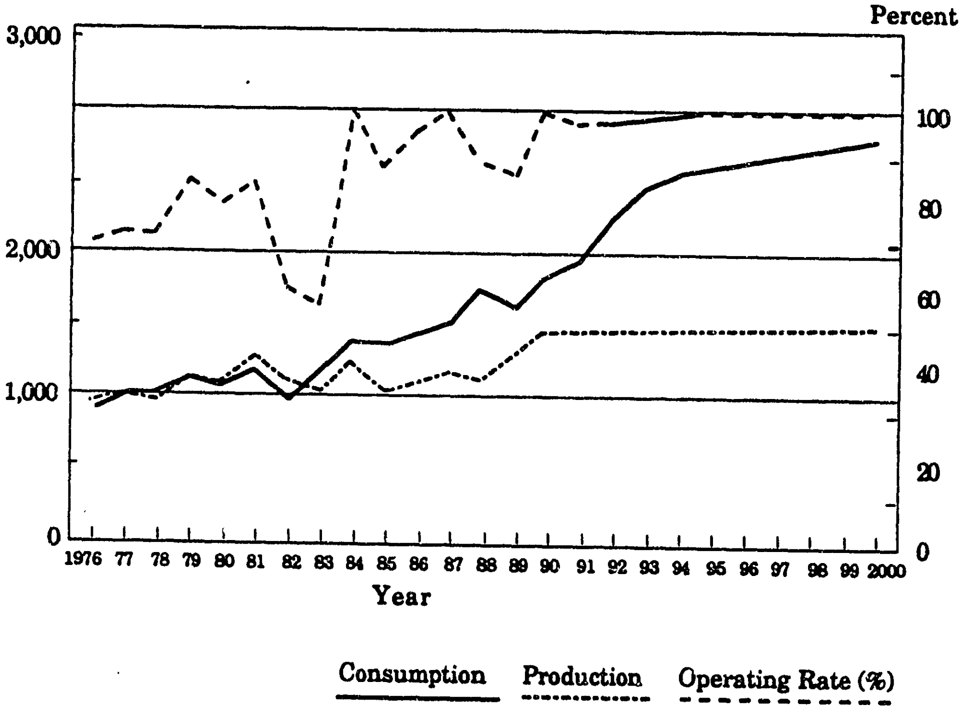
As background the price and supply of methanol are given in Figures 44 and 45.

Cost estimates for production of methanol vary widely from 19 to 71 cents per gallon according to Kermode et al. (1989). Cohen and Muller estimate manufacturing cost of methanol to be 64 cents per gallon selling price for U.S. production using gas at $4 per million Btu. Comprehensive studies have been made by Bechtel (Fox et al. 1990).

Courty et al. (1990) have published their calculations for the cost of methanol and mixed alcohols using advanced technology. Their results are presented in Figure 46 starting with natural gas at either $2.00 or $0.50 per million Btu and illustrate the distribution of production costs.

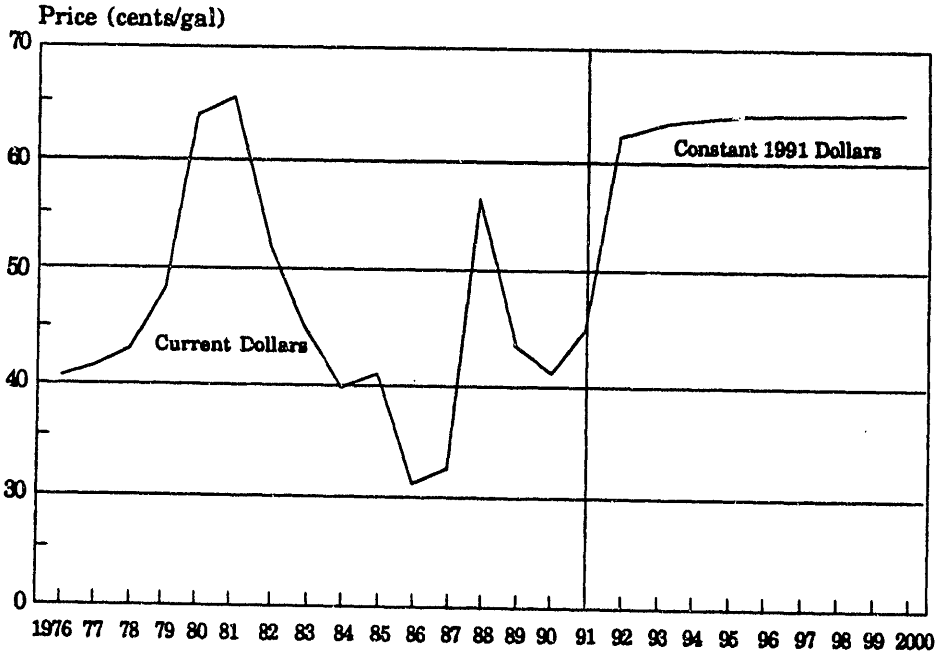
About 40%–60% of capital costs is required for the manufacture of purified syngas from natural gas (see Figure 47).

Although the costs of the methanol loop represent only about 22% of the capital costs, and selectivity to methanol is about 99%, there are improvements of economic consequence possible in the synthesis loop. The introduction of a much more active $Cu\text{-}ZnO/Al_2O_3$ catalyst by ICI in 1966 made possible the lowering of synthesis temperature to 250° from 350°C and pressure to 5–10 MPa from 30 MPa. Centrifugal compressors can be used at the lower pressure instead of the more expensive reciprocal compressors.



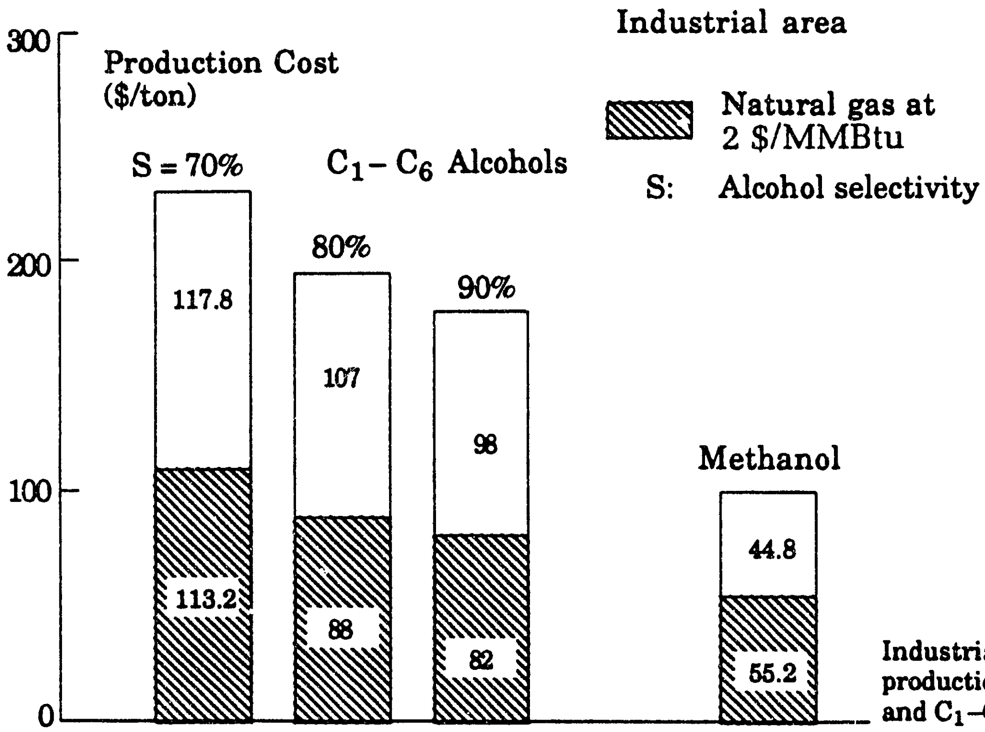
Source: *The Pace Consultants, Inc.*, Pace Petrochemical Service, Sept. 1991

Figure 44. Methanol, supply and demand (Kern et al. 1991)

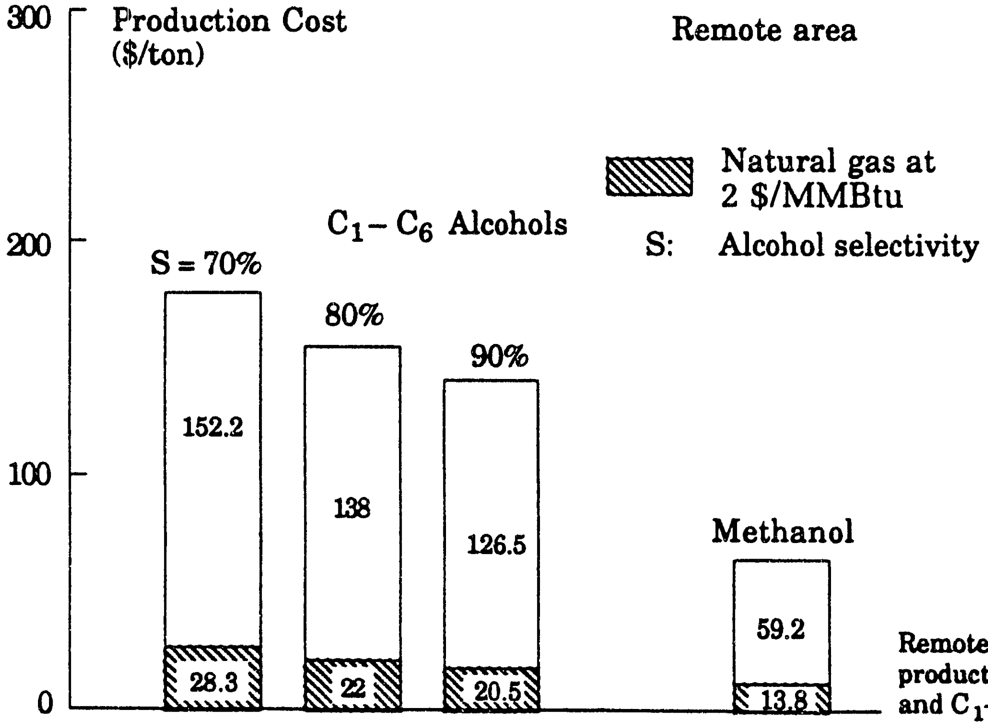


Source: *The Pace Consultants Inc.*, Sept. 1991

Figure 45. Methanol historical pricing (Kern et al. 1991)



Industrial area, breakdown of production costs of methanol and C_1–C_6 alcohols



Remote area, breakdown of production costs of methanol and C_1–C_6 alcohols

Figure 46. Breakdown of production costs of methanol and C_1-C_6 alcohols, industrial and remote area (Chaumette et al. 1992)

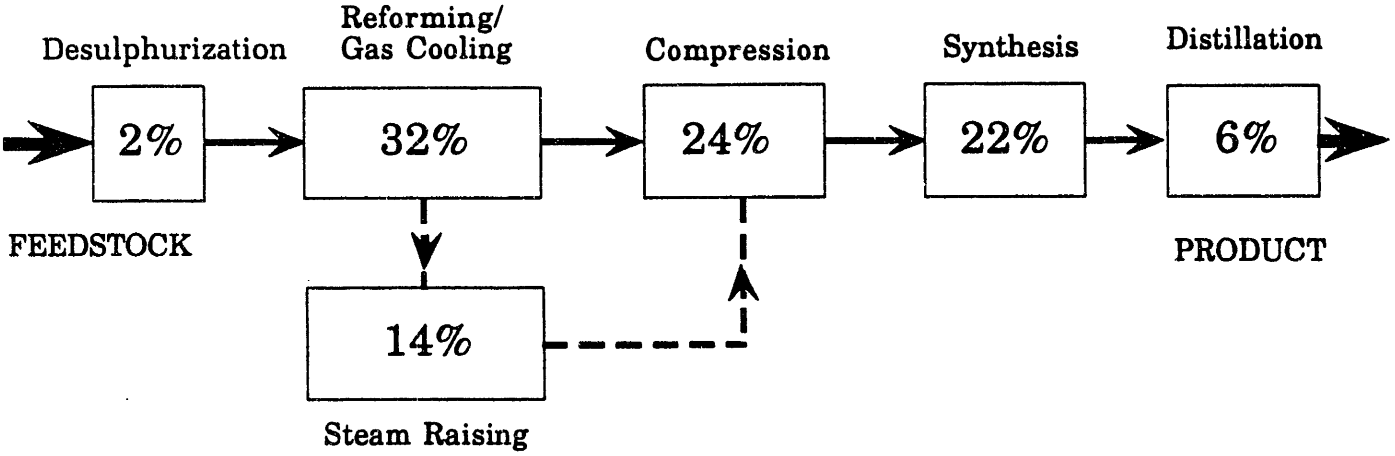


Figure 47. Methanol plant capital cost breakdown (ICI Company brochure)

It has been estimated (Bew 1981) that the new catalyst made possible the savings of 5% in *overall* plant costs, a relatively large amount in a large plant.

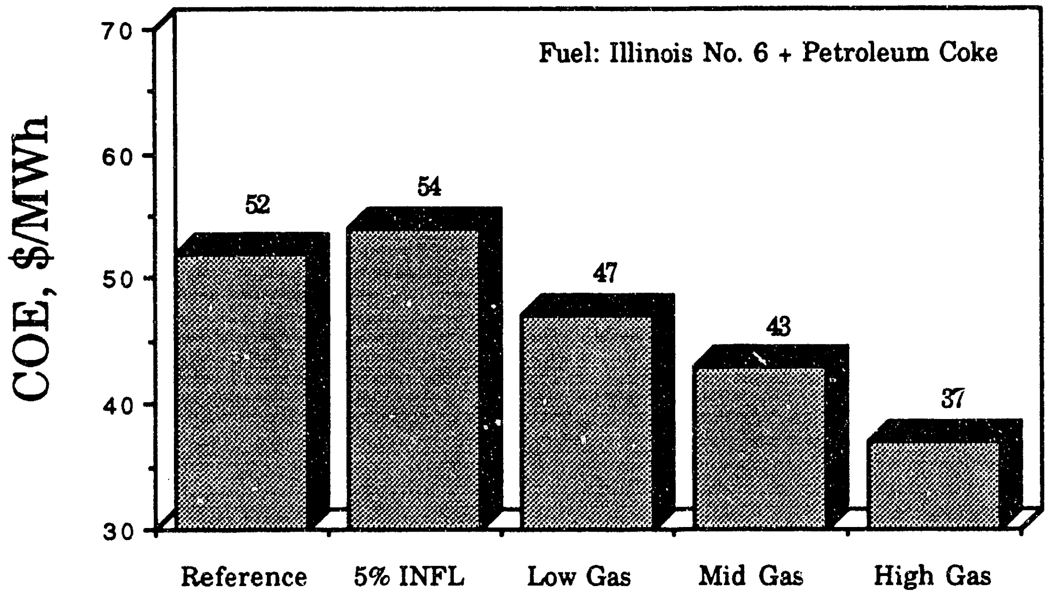
A marked advantage (about 10%) has been estimated for slurry-phase methanol synthesis and for once-through design using LPMEOH technology over conventional vapor phase technology (Nizamoff 1989). The potential economic advantage of coproduction of electricity and methanol have been made by Kern et al. (1991). The advantage is expressed in terms of lower electricity costs (Figure 48). The economic conclusions are critically dependent on the future price of natural gas. Other studies are being made by the Tennessee Valley Authority (TVA) with emphasis on environmental benefits.

EPRI has published a conceptual design and cost evaluation of the Brookhaven process performed by the Stone and Webster Company, which shows a reduction in capital cost of 73% and a reduction of methanol delivery cost to 80% of that for a conventional plant at a Middle East location. It is clear that the question is whether or not technical problems can be overcome, particularly inactivation of the catalyst by H_2O or CO_2.

Potential economic advantages being evaluated are: higher conversion per pass; coproduction of methanol and DME; catalysts of high activity that can operate at lower temperature and use air-blown syngas; catalyst systems having high selectivity to ethanol or isobutanol; or isomerization of DME to ethanol.

5.2 Hydrocarbon Fuels

The decrease in plant costs achieved by SASOL by using a fixed-fluid instead of an entrained-fluid bed synthesis is shown in Table 22 for production of synfuels from natural gas. The cost of a SASOL



Comparison of Cases 1 & 3, Reference Plant Operating at 85% Capacity Factor
Co-Production Plant Operating at 90% Electrical Capacity Factor with Spare
Gasifier and Methanol Plant Operating at 80%

Figure 48. Levelized cost of electricity, vapor phase methanol coproduction (Kern et al. 1991)

Table 22. Capital Cost Comparison, SASOL Circulating- and Fixed-fluidized Bed Synthesis Units (Jager et al. 1990)

		Relative Capital Cost			
Type	Number of Reactors	Pressure	Reactors	Gasloop	Total Plant
S-CFB (base)	3	normal	1.00	1.00	1.00
S-FFB	2	normal	0.46	0.78	0.87
S-FFB	2	high	0.49	0.71	0.82

fixed-fluid bed is estimated to be 50% of a SASOL CFB reactor and the total plant is 15% cheaper. Additionally, a gain in energy efficiency is reported.

The production of chemicals has taken on new importance at SASOL in providing economic justification for FT. SASOL has reported that because of the decreased profitability of synfuels manufacture, it has expanded production of higher value products, particularly olefins and waxes.

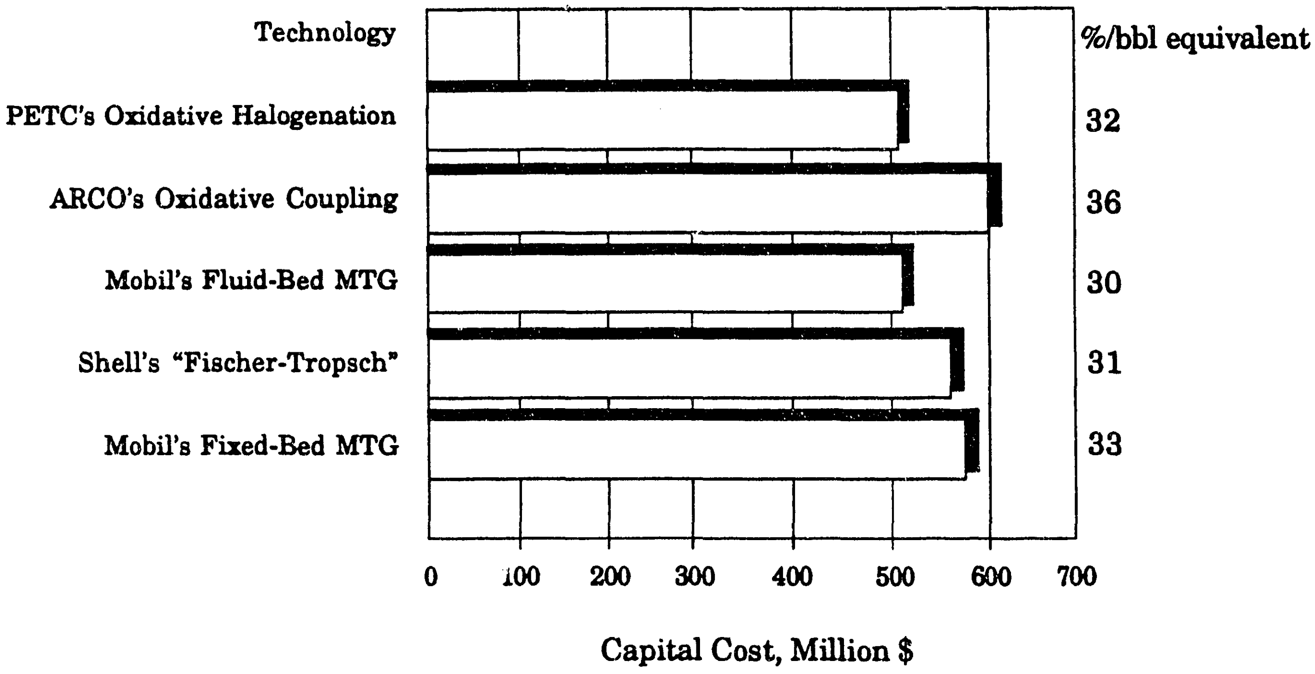
The cost of the MTG New Zealand plant of about 14,000-bpd plant has been reported at $1,200 MM. Experience has led to substantially decreased estimates for the fixed-bed configuration. Also, the use of fluid-bed design has been reported to provide for cost savings (Figure 49, Srivastava et al. 1992). Further, the TIGAS process offers savings over the original New Zealand plant.

The economics of the new "wax and crack" concept being installed in Malaysia depends on sale of gasoline, diesel, and wax. The relatively high value of the wax can be an important factor in this 13,000-bpd plant that costs $660 million to install.

Greatest interest is being expressed in new estimates for the use of slurry reactors. Gray et al. (1991) have examined five plant configurations: a SASOL type plant using a Lurgi gasifier and Synthol FT synthesis; a plant using a Shell gasifier and Synthol FT; a plant using Shell gasifier and slurry FT; a plant using Lurgi gasification and Arge synthesis; and a plant using Shell gasification and Arge synthesis (Table 22). Wyoming coal was used in all cases. Total plant output was about 83,500 barrels per day in each case.

Plant construction costs in 1989 dollars vary from $3,995 to $2,883 MM, a decrease of 28%. The required selling price of the final gasoline and diesel products are calculated from standard economic parameters. Calculations were based on 75/25 debt to equity ratio, 25-year project life, 34% income tax, no price escalation above general inflation, 3% general inflation, 15% return on equity, 8% interest on debt, and 5-year construction period.

The results are shown in Table 23. It is striking that, by using modern gasifier and slurry FT, the overall energy efficiency can be increased from 44% to 59% and the required selling price decreased from $59 to $42 per barrel. This price is for finished products, which is as low or lower than has been calculated for direct coal liquefaction.



Comparison of approaches at 14,500-BPD capacity, U.S. Gulf Coast basis.

Figure 49. Natural gas conversion to liquids (Srivastava et al. 1992)

Table 23. Improvements in Indirect Coal Liquefaction (Gray et al. 1991)

Case	LURGSYNW Lurgi +	LURGARGE Lurgi +	SHELSYNW Shell +	SHELARGE Shell +	SHELSLUW Shell +
Configuration:	Synthol F-T	ARGE F-T	Synthol F-T	ARGE F-T	Slurry F-T
Coal Feed (TPSD AR)[a]					
Gasifer	46,489	42,337	43,197	47,742	42,707
Steam Plant	7,969	10,111	0	0	0
TOTAL Plant Coal	54,458	52,448	43,197	47,742	42,707
Energy Input (MMBtu/h)					
Coal	38,618	37,197	30,632	33,855	30,285
Electricity	17	96	356	25	280
TOTAL	38,635	37,107	30,988	33,880	30,565
Plant Outputs (BPSD)[b]					
Alcohols	4,444	1,762	4,586	1,836	1,954
Propane LPG	7,146	4,467	7,426	4,037	4,207
Butane LPG	4,701	5,403	4,957	5,522	5,560
Gasoline	59,607	36,450	58,701	32,494	33,953
Diesel	7,663	35,419	7,924	39,617	37,828
TOTAL	83,561	83,501	83,594	83,505	83,503
Output Energy (MMBtu/h)	16,980	17,902	16,967	18,022	17,362
Overall Efficiency (HHV%)	**44**	**48**	**55**	**53**	**59**
Plant Construction Costs ($MM 1989)					
Gasification	496.64	465.15	720.53	772.80	714.80
Shift	0	0	101.15	87.17	19.90
Gas Cleaning	485.30	454.71	202.79	224.14	177.52
Syngas Reforming Loop	434.05	394.69	273.96	63.23	212.78
FT Synthesis	415.42	441.18	409.29	403.53	333.47
Raw Product Refining	332.53	293.20	309.91	264.96	239.75
FT Catalyst Preparation	136.17	119.83	139.21	123.26	62.99
Oxygen Plant	469.13	367.74	507.45	497.83	469.50
Coal Handling/Drying	192.83	181.96	244.53	262.27	242.58
Power Gen. and Dist.	148.29	169.13	119.20	140.16	86.05
Steam Generation	416.89	449.96	0	41.34	0
Balance of Plant	467.35	420.05	366.50	377.01	323.82
TOTAL Construction Cost	3,994.60	3,757.60	3,394.52	3,257.70	2,883.17
TOTAL Capital Required	6,087.99	5,723.67	5,189.11	4,988.77	4,406.45
NET Annual Operating Cost	465.91	432.33	412.86	393.71	350.68
Required Selling Price of Products ($/bbl)					
Gasoline/Diesel	**58.89**	**54.65**	**54.32**	**47.88**	**42.48**
Delta Percent Change	-7.76	=6.08	-6.15	-11.28	

---

[a] TPSD AR = tons per standard day as received

[b] BPSD = barrels per standard day

A frequently stated research goal is to reduce the cost of syncrude produced from coal, gas, or biomass from estimated $40 to $30 per barrel. Advanced technology described in this report, brought to fruition, promises to accomplish this goal. One pathway is the slurry FT and another is improved methanol synthesis.

But new concepts concerning environmental protection have entered the economic picture. A potential advantage to synfuels from biomass—considered to be carbon dioxide neutral—may provide an advantage that may be equivalent to $10 per barrel compared to petroleum.

A further direction to make synfuels economically attractive is the potential for producing higher price products. Syngas conversion can produce fuels with premium engine performance (high octane or cetane values), which sell at a premium.

A higher price can be achieved through fuels that provide environmental benefits. This has been demonstrated by MTBE. About $10 per barrel of its selling price can be attributed to its qualifications, which make its incorporation in gasoline blends desirable for environmental benefits and its overall compatibility.

Future Research Opportunities

6.0 Potential

Liquid oxygenate and hydrocarbon fuels manufactured from syngas have high performance characteristics. Their use provides efficient engine performance and environmental benefits.

There is the potential for substantially increased use of MTBE and other oxygenates in gasoline blends. There are opportunities for manufacture of ethanol or isobutanol from syngas and their use in blends, depending on whether future technology can decrease costs of their manufacture from syngas.

Fuels consisting entirely or mostly of oxygenates also have much potential. In the long term, of the oxygenates, methanol appears to be the fuel of choice in vehicles designed for its use. However, if methanol, now being marketed as M85, proves unacceptable because of its poisonous character, ethanol may become the preferred alcohol fuel.

Important new technology for manufacture of hydrocarbon diesel fuel from syngas provides opportunities for this type of fuel. Diesel fuel performs with high efficiency in well-established engines. The diesel from syngas has an excellent cetane rating and is reported to be environmentally superior to conventional diesel fuel.

The main barrier to synfuels from syngas is their cost relative to gasoline made from petroleum at today's prices. As described in this report, there is the potential to lower the cost of liquid synfuels from syngas by new and improved catalytic synthesis technology, which can

- Lower the cost of manufacture by 10%–30%, particularly by lowering plant investment costs
- Justify higher-than-gasoline price by 10%–15% by providing improved engine performance
- Justify higher-than-gasoline price by 35% by providing environmental benefits (MTBE is an example)
- Improve the economics of synfuel manufacture by providing for high-price coproducts: chemicals or electricity
- Provide for liquid synfuels from biomass that are not subject to future taxes on CO_2 emissions. This could be a $10 per barrel advantage over fuels from petroleum.

To accomplish these objectives, a combination of research approaches is needed: fundamental science and innovative and exploratory chemistry, as well as engineering/developmental research. New ideas could open up unexpected opportunities. A modest improvement in a near-commercial process could serve an important function of crossing the threshold in making it commercially viable.

Specific research opportunities are summarized in Tables 24 and 25 in terms of technical objectives, potential benefits, and research concepts/approaches to achieve objectives. The nature and status of accomplishments and problems to be overcome are reviewed in the detailed report.

Table 24. Research Opportunities for Oxygenates

Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Methanol	
• Achieve nearly complete conversion of syngas in a single pass	• Avoid cost of separation and recycle	• More efficient heat removal from reactor; removal of methanol from reactor; high-activity catalysts operating at low temperature
• Provide efficient coproduction of methanol and dimethyl ether	• Cheaper plant; provide valuable new fuel	• Combination catalysts; slurry-phase catalysts
• Provide efficient methanol synthesis in combination with coproduction of electricity	• Utilize plant full time; choose optimum electricity/methanol mix; environmental benefits	• Once-through operation; engineer processes adapted to load-following and variable production demands
	Ethanol	
• Develop catalysts that will provide selective conversion of syngas to ethanol	• Lower cost ethanol; use for ETBE	• Isomerization of dimethyl ether; homologation of methanol; biocatalysis
	Isobutanol[1]	
• Discover technology that will provide selective conversion of syngas to isobutanol	• Possible preferred competitor to MTBE	• Recycle lower alcohols; alkali (Cs) modified catalysts
	Ethers[2]	
• Make isobutylene from syngas	• Avoids need for petroleum for manufacture of MTBE	• Convert syngas in a single step by combination catalysts

Table 24. Research Opportunities for Oxygenates (Concluded)

Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Methanol	
• Achieve nearly complete conversion of syngas in a single pass	• Avoid cost of separation and recycle	• More efficient heat removal from reactor; removal of methanol from reactor; high-activity catalysts operating at low temperature
	Syngas Fuel	
• Convert methanol to syngas	• Increases useable Btu by utilizing waste heat for converting methanol to syngas with a higher Btu content	• Catalysts that operate over a wide temperature range

[1] Improved synthesis of isobutanol could be important for its conversion to isobutylene for manufacture of MTBE and ETBE.

[2] Efficient processes, including catalytic distillation, have been developed for conversion of alcohols and iso-olefins to ethers. Thus, research opportunities for improved alcohol synthesis are most pertinent in improving ether technology.

Table 25. Research Opportunities for Hydrocarbons

Technical Objectives	Potential Benefits	Research Concepts/Approaches
	Synthesis of Wax and Hydrocracking[1]	
• Improve selectivity to desired gasoline and diesel fractions	• More economical production of higher quality fuels	• Catalysts based on molecular sieves; improved multimetal cobalt catalysts; reactor engineering and process integration
	Slurry Phase Fischer-Tropsch[2]	
• Improved and optimized catalysts for this new type of catalytic processing	• Make this process economically competitive	• Catalysts designed for controlled suspension/settling; catalysts that facilitate separation from heavy hydrocarbon products; reaction engineering and process integration

---

[1] Recent research and development results have opened up new opportunities for converting syngas to an intermediate hydrocarbon product that is then hydroprocessed to high-quality fuels.

[2] Recent engineering and economic estimates have provided great encouragement for FT synthesis that is carried out using a slurry catalyst system. Operability tests on a larger scale have been recommended as crucial; an important test was recently carried out.

6.1 Integral Syngas Production/Fuel Synthesis

There is an opportunity to combine catalytic syngas production with fuel synthesis with large potential savings. The desired overall reaction is

$$CH_x + H_2O \rightarrow CH_3OH + CO_2 \, .$$

The concept is combination catalysts that promote steam reforming and methanol synthesis.

6.2 Fundamental Catalytic Science and Engineering

Modern processes for selective synthesis of high-performance fuels from syngas have benefited greatly from advances in fundamental catalytic science and engineering. The knowledge of kinetics and thermodynamics and determination of reaction mechanisms has contributed greatly to improved technology of modern processes. There are critical opportunities to more clearly delineate critical catalyst structure/performance relationships. There is much promise that the new instrumentation and research techniques for fundamental catalytic surface science characterizations will lead to the design of even more selective catalysts that are not otherwise achievable.

References

Anderson, R.B. (1984). *The Fischer-Tropsch Synthesis.* New York: Academic Press.

Ansorge, J.; Hoek, D. (1992). "Conversion of Natural Gas to Clean Transportation Fuels: the Shell Middle Distillate Synthesis Process (SMDS)." American Chemical Society, Preprints, Division of Petroleum Chemistry; Vol. 37 (3), p. 833.

Arakawa, H.; Hansoka, T.; Takeuchi, K.; Matsuzaki, T.; Sugi, Y. (1988). *Proceedings of the 9th International Congress on Catalysis*; Edited by M.J. Phillips and M. Terman. Ottawa, Canada: Chemical Institute of Canada; Vol. 2, pp. 602-609.

Baglin, E.G.; Atkinson, B.G.; Nicks, L.J. (1981). "Methanol Synthesis Catalysts Form Thoria-Copper Intermetallics, Preparation and Evaluation." *Industrial and Engineering Chemistry – Product Research and Development*; Vol. 20, pp. 87-90.

Bailey, S. (1992). Private communication. ICI.

Bart, J.C.J.; Sneeden, R.P.A. (1987). "Copper-Zinc Oxide-Alumina Methanol Catalysts Revisited." *Catalysis Today*; Vol. 2 (1), pp. 1-124.

Bartholomew, C.H. (1991). "Recent Developments in Fischer-Tropsch Catalysis." *New Trends in CO Activation.* Edited by L. Guczi. Amsterdam-Oxford-New York-Tokyo: Elsevier; pp. 158-224.

Bauman, R.D.; Epstein, M.; Kern, E.E. (1991). "Coal Gasification-Based Integrated Co-Production Energy Facilities." *Proceedings of the American Power Conference; October 1991.*

Bennethum, J.E.; Winsor, R.E. (1991). "Towards Improved Diesel Fuel." SAE Technical Paper. 912325.

Berty, J.M.; Krishnan, C.; Elliott, J.R. (1990). "Beat the Equilibrium." *Chemical Technology,* Vol. 20, pp. 624-629.

Bew, D.G. (1981). "Economic of Aspects of Catalytic Processes." *Catalysis and Chemical Processes.* Edited by R. Pearce and W.R. Patterson. New York-Toronto: Wiley; pp. 64-87.

Bhore, N.A.; Bischoff, K.B.; Manogue, W.H.; Mills, G.A. (1988). "Syngas Conversion by $RhMoAl_2O_3$ Catalysts: Structure/Function Identification." *Proceedings of the 9th International Congress on Catalysis*; Edited by M.J. Phillips and M. Ternan. Ottawa, Canada: Chemical Institute of Canada, Vol. 2, pp. 594-601.

Bhore, N.A.; Bischoff, K.B.; Manogue, W.H.; Mills, G.A. (1990). "CO Hydrogenation over Rh-Molybdena-Alumina Catalysts: Selectivity Control Using Activation Energy Differences." *Novel Materials in Heterogeneous Catalysts.* Edited by R.T. Baker and L.L. Murrell. American Chemical Society Symposium Series, No. 437. Washington, DC: American Chemical Society, pp. 256-264.

Brockwell, H.L.; Sarathy, P.R.; Trotta, R. (1991). "Synthesize Ethers." *Hydrocarbon Processing.* Vol. 70 (9), pp. 133-144.

Brown, D.M.; Bhatt, B.L.; Hsiung, T.H.; Leonard, J.J.; Waller, F.J. (1991). "Novel Technology for the Synthesis of Dimethyl Ether from Syngas." *Catalysis Today*; Vol. 8, pp. 279-304.

Brown, D.M.; Henderson, J.L.; Hsiung, T.H.; Studer, D.W. (1990). "LPMEOH: Beyond LaPorte-Next Steps to Commercialization." EPRI 15th Annual Conference on Fuel Science and Conversion, Palo Alto, California; June.

Bukur, D.B.; Daly, J.G.; Patel, S.A. (1990). *Hydrodynamics of Three-Phase Fischer-Tropsch Bubble Column Reactors.* DOE/PC/90012-10 (DE9101420).

Bukur, D.B.; Mukesh, D.; Patel, S.A.; Rosynek, M.P.; Zimmerman, W.H. (1991). *Development and Process Evaluation of Improved Fischer-Tropsch Slurry Catalysts.* DOE Contract DE-AC22-85PC80011. Washington, DC: U.S. Department of Energy, April 1990.

Calverley, E.M.; Smith, K.J. (1991). "The Effects of Carbon Dioxide Methanol, and Alkali Promoter Concentration on the Higher Alcohol Synthesis over a $Cu/ZnO/Cr_2O_3$ Catalyst." *Journal of Catalysis*; Vol. 130, pp. 616-626.

Catalytica. (1991). "Oxygenate Fuels: Challenge and Opportunities." Mountain View, CA: Catalytica.

Chanenchuk, C.A.; Yates, I.C.; Satterfield, C.N. (1991). "The Fischer-Tropsch Synthesis with a Mechanical Mixture of a Cobalt Catalyst and a Copper-Based Water Gas Shift Catalyst." *Energy and Fuels*; Vol. 5 (6), pp. 847-855.

Chang, C.D.; Silvestri, A.J. (1977). "The Conversion of Methanol and Other O-Compounds to Hydrocarbons Over Zeolite Catalysts." *Journal of Catalysis*; Vol. 47, pp. 249-259.

Chang, C.D. (1983). "Hydrocarbons from Methanol." *Catalysis Review-Science and Engineering*, Vol. 25 (1), pp. 1-118.

Chang, C.D. (1984). "Methanol Conversion to Light Olefins," *Catalysis Review–Science and Engineering*; Vol. 26 (1), p. 323.

Chaumette, P.; Verdon, C.; Kiennemann, A.; Bougana, S. (1992). "Middle Distillates from Syngas on Modified Cobalt Catalysts." American Chemical Society, Preprints, Petroleum Chemistry Division; Vol. 37 (3), pp. 833-843.

Chem Systems. (1992). Private communication.

Chinchen, G.C.; Waugh, K.C.; Wan, D.A. (1986). "The Activity and State of the Copper Surface in Methanol Synthesis Catalysts." *Applied Catalysis*; Vol. 25, p. 101.

Chinchen, G.; Mansfield, K.; Spencer, M. (November 1990). "The Methanol Synthesis—How Does It Work?" *Chemical Technology*; pp. 692-699.

Chinchen, G.; Denny, P.J.; Jennings, J.R.; Spencer, M.S.; Waugh, K.C. (1988). "Synthesis of Methanol." *Applied Catalysis*; Vol. 36, pp. 1-65.

Christiansen, J.A. (1919). U.S. Patent No. 1,302,011.

Cohen, L.H.; Muller, H.L. (1989). "Methanol as Fuel Economics." *Encyclopedia of Chemical Processing and Design*; Edited by J.J. McKetta, New York: Marcel Dekker; pp. 10-24.

Comotti, P.; Marengo, S.; Martinengo S.; Zanderighi, L. (1991). "Synthesis of Mixed Alcohols over Rh/ZrO_2 : Investigation on Promoter Effects and Influence of Operating Parameters." See *ISAF*, pp. 73-77.

Courty, P.E.; Chaumette, P.; Rainbault, C.; Travers, P.H. (1990). "Production of Methanol-Higher Alcohol Mixtures from Natural Gas via Syngas Chemistry." Revue de L'Institut Française du Petrol; Vol. 45 (4), Julillet-Aut. pp. 561-578.

Courty, P.E.; Chaumette, P. (1987). "Syngas is a Promising Feedstock in the Near Future." *Energy Progress*; Vol. 7 (1), pp. 23-29.

Curry-Hyde, H.E.; Wainwright, M.S.; Young, D.J. (1991). "Improvements to Raney Copper Methanol Synthesis Catalyst Through Zinc Impregnantion-IV Practical Considerations." See *ISAF*, pp. 49-54.

Daly, F.P. (1984). "Methanol Synthesis Over a Cu/ThO_2 Catalyst." *Journal of Catalysis*; Vol. 89, p. 131.

DeCanio, E.C.; Storm, D.A. (1991). "Carbon Monoxide Adsorption by K(CoRhMoAl_2O_3) Higher Alcohol Catalysts." *Journal of Catalysis*; Vol. 132 (2), pp. 375-387.

DeLuchi, M.A.; Johnston, R.A.; Sperling, D. (1988). "Methanol vs. Natural Gas Vehicles: A Comparison of Resource Supply, Performance, Emissions, Fuel Storage, Safety, Costs, and Transitions." SAE 881656.

Department of Energy, (1990) *Costs of Methanol Production from Biomass*. DOE/PE-0097P. Washington, DC: DOE Office of Policy Planning.

Dippo, J.; Karpuk, M.; Cowley, S. (1991). "Design of a Methanol Dehydration Reactor for Cold-Starting Methanol-Fueled Engines." See *ISAF*, pp. 580-585.

Donnelly, T.J.; Satterfield, C.N. (1989). "Performance Testing with a Gas-Liquid-Solid System in a Mechanically Stirred Reactor: the Fischer-Tropsch Synthesis." *Applied Catalysis*; Vol. 56, pp. 231-251.

Donnelly, T.J.; Satterfield, C.N. (1989). "Product Distributions of the Fischer-Tropsch Synthesis on Precipitated Iron Catalysts." *Applied Catalysis*; Vol. 52, pp. 93-114.

Dry, M.E. (1981). "The Fischer-Tropsch Synthesis." *Catalysis Science and Technology*. Edited by J.R. Anderson and M. Boudart. Springer Verlag; Vol. 1, pp. 159-256.

Dry, M.E. (1990a). "Fischer-Tropsch Synthesis over Iron Catalysts." *Catalysis Letters*; Vol. 7, pp. 241-252.

Dry, M.E. (1990b). "The Fischer-Tropsch Process-Commercial Aspects." *Catalysis Today*; Vol. 6 (3), pp. 183-206.

Dry, M.E.; Hoogendoorn, J.C. (1981). "Technology of the Fischer-Tropsch Process." *Catalysis Review-Science and Engineering,* Vol. 23 (1&2), p. 265.

Ecklund, E.E. (1991). "Dissecting the Alternative Motor Fuels Implementation Dilemma." See *ISAF*.

Ecklund, E.E.; Mills, G.A. (1989). "Alternate Fuels; Progress and Prospects." *Chemical Technology*; Vol. 19 (9), p. 549; Vol. 19 (10), p. 626.

Ehwald, H.; Ewald, H.; Gutshick, D.; Hermann, M.; Miessner, H. (1991). "A Bicomponent Catalyst for the Selective Formation of Ethanol from Synthesis Gas." *Applied Catalysis*; Vol. 76, pp. 153-169.

Ellgen, P.C.; Bartley, W.J.; Bhasin, M.M.; Wilson, T.P. (1979). "Rhodium-Based Catalysts for Conversion of Synthesis Gas to Two-Carbon Chemicals." *Hydrocarbon Synthesis from Curbon Monoxide and Hydrogen. Advances in Chemistry Series.* American Chemical Society Symposium Series, No. 178. Edited by E.L. Kugler and F.W. Steffgen, Washington, DC: American Chemical Society; pp. 147-157.

Eri, S.; Goodwin, J.G.; Marcelin, G.; Riis, T. (1989). U.S. Patent No. 4,801,573.

Falbe, J., ed. (1982). *Chemical Feedstocks from Coal.* New York-Brisbane-Toronto: Wiley & Sons; p. 647.

Fennig, T.L. (1991). "Developing Environmentally Responsible Energy Resources." Presented at the Waste-to-Energy Conference, Fargo, ND, June.

Foley, H.C.; Hong, A.J.; Brinen, J.S.; Allard, L.F.; Garratt-Reed, A.J. (1990). "Bimetallic Catalysts Comprised of Dissimilar Metals for the Reduction of CO with H." *Applied Catalysis*; Vol. 61, pp. 351-375.

Forzatti, P.; Tronconi, E.; Dasquon, I. (1991). "Higher Alcohol Synthesis." *Catalysis Review–Science and Engineering*; Vol. 33 (1 & 2), pp. 109-168.

Fox, J.M. (1990). "Fischer-Tropsch Reactor Selection." *Catalysis Letters*; Vol. 7, pp. 281-292.

Fox, J.M.; Degen, B.D.; Cady, G.; Deslate F.D.; Summers, R.L. (1990). *Slurry Reaction Design Studies.* DOE/PC/89867-T2 (DE91005752). Washington, DC: U.S. Department of Energy.

Fox, J.M. (1992). "The Different Catalytic Routes to Methane Valorization," submitted to *Catalysis Review–Science and Engineering.*

Frohning, C.D.; Koelbel, H.; Ralek, M.; Rottig, W.; Shnur, F.; Shulz, H. (1982). *Fischer-Tropsch Process in Chemical Feedstocks from Coal.* New York-Brisbane-Toronto: Wiley & Sons; pp. 300-342.

Frost, J.C. (1988). "Junction Effect Interactions in Methanol Synthesis Catalysis," *Nature* 334, August 18.

Gilhooey, K.; Jackson, S.D.; Rigby, S. (1986). "Steady-State Effects in the Medium Pressure Hydrogenation of Carbon Monoxide over Rhodium Catalysts." *Journal of Applied Catalysis*; Vol. 21, pp. 349-357.

Goehna, H.; Koenig, P. (1989). "The OCTAMIX Process." *Proceedings of the DOE Indirect Liquefaction Contractors' Review Meeting; Nov. 13-15, 1989, Pittsburgh, PA;* Washington, DC: U.S. Department of Energy; pp. 59-83.

Goodwin, J.G., Jr. (1991). "Current Directions in Fischer-Tropsch Catalysis." American Chemical Society, Preprints, Division of Fuel Chemistry; Vol. 36 (1), pp. 156-159.

Gray, D.; ElSawy, A.; Tomlinson, G. (1991). "Quantification of Progress on Indirect Coal Liquefaction." *Proceedings of the DOE Liquefaction Contractors' Review Meeting*; Pittsburgh, PA: U.S. Department of Energy; pp. 344-356.

Gushee, D.E.; Bamberger, R.L. (1989). "Methanol Fuel: Economics and Implementation: a Review of Current Studies." Congressional Research Service; 89-562 RCO.

Guczi, L., ed. (1991). *New Trends in CO Activation.* Amsterdam-Oxford-New York-Tokyo: Elsevier; p. 494.

Haag, W.O.; Kuo, J.C.; Wender, I. (1987). "Gasification for Synthesis of Fuels and Chemicals." Chapter 5 in *Coal Gasification: Direct Application and Syntheses of Chemicals and Fuels.* DOE/ER-0326. pp. 117-205.

Haigwood, M.B. (1991). "Worldwide MTBE Capacity Growing at an Accelerated Pace." *Fuel Reformation.* Washington, DC: Information Resources, Inc., pp. 52-60.

Hansen, J.B.; Joensen, F. (1991). "High Conversion of Synthesis Gas to Oxygenates in Natural Gas Conversion." *Natural Gas Conversion Symposium Proceedings.* Edited by A. Holman et al., Amsterdam: Elsevier; pp. 457-467.

Herman, R.G. (1991). "Classical and Non-Classical Routes for Alcohol Synthesis." *New Trends in CO Activation, Studies in Surface Science and Catalysis*; Vol. 64. Edited by L. Guczi. Amsterdam-Oxford-New York-Tokyo, Elsevier; p. 265.

Hohlein, B.; Mausbeck, D.; Supp, E.; Konig, P. (1991). "Selective Catalysis for Synthesis of Energy Alcohols: Status and Outlook." See *ISAF*, pp. 43-48.

Hu, X-D.; Foley, H.C.; Stiles, A.B. (1991). "Design of Alcohol Synthesis Catalysts Assisted by Knowledge-Based Expert System." *I&EC Research*; Vol. 30, pp. 1419-1427.

Idriss, H.; Kim, K.S.; Barteau, M.A. (1993). "Carbon-carbon Bond Formation via Aldolization of Acetaldehyde on Single Crystal and Polycrystalline TiO_2 Surfaces." *Journal of Catalysis*; Vol. 139, p. 113.

Idriss, H.; Libby, M.; Barteau, M.A. (1992). "Carbon-carbon Bond Formation on Metal Oxides; from Single Crystals toward Catalysis." *Catalysis Letters*; Vol. 15, p. 13.

Iglesia, E.; Reyes, S.C.; Madon, R.J.; Soled, S.L. (1992). "Selectivity Control and Catalyst Design in the Fischer-Tropsch Synthesis Sites, Pellets and Reactors." *Advances in Catalysis and Related Subjects.* Edited by H. Pines, et al. New York: Academic Press; in press.

Iglesia, E.; Reyes, S.C.; Soled, S.L. (1992). "Reaction-transport Selectivity Modes and Design of Fischer-Trposch Catalysts." *Computer-Aided Design of Catalysts and Reactors.* Edited by E.R. Becker and C.J. Pereira; New York: Marcel Dekker; in press.

Iglesia, E.; Soled, S.L.; Fiato, R.A. (1992). "Fischer-Tropsch Synthesis on Cobalt and Ruthenium; Metal Dispersion and Support Effects on Reaction Rate and Selectivity." *Journal of Catalysis*; Vol. 137(1), pp. 212-224.

Iglesia, E.; Vroman, H.; Soled, S.; Baumgartner, J.; Fiaro, R.A. (1991). "Selective Catalysts and Their Preparation for Catalytic Hydrocarbon Synthesis." U.S. Patent 5,036,032.

International Energy Agency (1990). "Production of Alcohols and Other Oxygenates from Fossil Fuels and Renewables." Rue André-Pascal, Paris, France.

International Energy Agency (1990). "Substitute Fuels for Road Transport." Rue André-Pascal, Paris, France.

International Energy Agency (1991). *Program of Research, Development, and Demonstration on Alternative Motor Fuels.* 1991 Annual Report, Paris, France.

ISAF. (1991). IX International Symposium on Alcohol Fuels, ISAF-Firenza, Florence, Italy; Nov.

Jackson, S.D.; Brandeth, B.J.; Winstan, L. (1986). "Carbon Monoxide Hydro-genation over Group VIII Metals Supported on Tungsten and Molybdenum Trioxides." *Applied Catalysis*; Vol. 27, pp. 325-333.

Jager, B.; Dry, M.E.; Shingles, T.; Steynberg, A.P. (1990). "Experience with a New Type of Reactor for Fischer-Tropsch Synthesis." *Catalysis Letters*; Vol. 7, pp. 293-302.

Japan. (1990). "Energy Conversion and Utilization with High Efficiency." Ministry of Education, Science and Culture; Nishikawa, Y. General Chairman; Hashimoto, K., Chairman Subarea B, Conversion of Various Resources to Energy.

Japan. (1989). *Progress in C_1 Chemistry in Japan*, edited by the Research Association for C_1 Chemistry, Amsterdam-Oxford-New York-Tokyo: Elsevier.

Jones, C.J.; Jager, B.; Dry, M.D. (1992). "Fixed-bed Reactor Successful in Fuels from Coal Synthesis." *Journal of Oil and Gas*; 1992. pp. 53-56.

Keim, W.; Falter, W. (1989). "Isobutanol from Synthesis Gas." *Catalysis Letters*; Vol. 3, pp. 59-64.

Kermode, R.I.; Nicholson, A.F.; Jones, J.E. Jr. (1989). "Methanol from Coal-cost Projections." *Encyclopedia of Chemical Processing and Design*; Vol. 30; Edited by J.J. McKetta. New York: Marcel Dekker; pp. 1-10.

Kern, E.E.; Chmielewski, R.G.; Havemann, S.D.; Baumann, S.D. (1991). "Coal Gasification-Based Integrated Coproduction Energy Facilities." 10th Annual EPRI Conference, October.

Kienemann, A.; Idriss, H.; Kieffen, R.; Chaumette, P.; Durand, D. (1991). "Studies of the Mechanism of Higher Alcohol Synthesis over Cu-ZnO-Al_2O_3 Catalysts by Catalytic Tests, Probe Molecules, and Programmed Desorption Studies." *I&EC Research*; Vol. 29, pp. 1130-1138.

King, L.J.; Green, C. (1991). "Dimethyl Ether as an Ignition Source for Heavy-Duty Methanol Engines." See *ISAF*, pp. 367-371.

Kip, B.J.; Hermans, E.G.F.; Wolput, J.H.M.C.; Hermans, N.M.A.; Van Grondelle, J.; Prins, R. (1987). "Hydrogenation of CO over Rhodium/Silica Catalysts Promoted with Molybdenum Oxide and Thorium Oxide." *Applied Catalysis*; Vol. 35, pp. 109-139.

Klasson, K.T.; Ackerson, M.D.; Clausen, E.C.; Gaddy, J.L. (1992). "Bioliquefaction of Coal Synthesis Gas." American Chemical Society, Preprints, Division of Fuel Chemistry; Vol. 37 (1), pp. 464-471.

Klier, K.; Herman, R.G.; Himelfarb, P.B.; Young, C.W.; Hou, S.; Marcos, J.A. (1992a). "C-C Bond Formation via B-Addition with Oxygen Retention Reversal in Oxygenate Synthesis." 10th International Congress in Catalysis, Hungary. 10 pp.

Klier, K.; Herman, R.G.; Johansson, M.A.; Feeley, O.C. (1992b). "Synthesis of C_5 Ethers from Methanol and 2-Methyl-1-Propanol." American Chemical Society, Preprints, Division of Fuel Chemistry; Vol. 37 (1), pp. 236-246.

Koelbel, H.; Ralek, M. (1980). "The Fischer-Tropsch Synthesis in Liquid Phase." *Catalysis Review-Science and Engineering*; Vol. 21 (2), pp. 225-274.

Krishna, K.R.; Bell, A.T. (1992). "Estimates of the Rate Coefficients for Chain Initiation, Propagation, and Termination during Fischer-Tropsch Synthesis over Ra/TiO_2." Submitted to *Journal of Catalysis.*

Kuczynski, M.; Dyevaar, M.H.; Pieters, R.T.; Westerterp; K.R. (1987). "Methanol Synthesis in a Countercurrent Gas-Solid-Solid Trickle Flow Reactor." *Chemical Engineering Science*; Vol. 42 (8), p. 1887.

Lander, E.P.; Hubbard, J.N.; Smith, L.A. Jr. (1983). "The MTBE Solution: Octanes; Technology, and Refinery Profitability." National Petroleum Refiners Association, Am-83-50.

Lee, S. (1990). *Methanol Synthesis Technology.* Boca Raton, FL: CRC Press.

Lietti, L.; Tronconi, E.; Forzatti, P.; Nassur, E.B. (1991). "Formation of C_{2+} Oxygenates from C_1 Oxygenates at Atmosphere Pressure." See *ISAF*, pp. 67-72.

Liu, Z.; Tierney, J.W.; Shah, Y.T.; Wender, I. (1988). "Kinetics of Two-Step Methanol Synthesis in the Slurry Phase." *Fuel Processing Technology*; Vol. 18, pp. 185-199.

Liu, Z.; Tierney, J.W.; Shah, Y.T.; Wender, I. (1989). "Methanol Synthesis via Methyl Formate in a Slurry Reaction." *Fuel Processing Technology*; Vol. 23, pp. 149-167.

Marengo, S.; Martinengo, S.; Zanderighi, L. (1992). "Alcohols from Syngas: Characterization and Bench-Scale Performance of Rh Catalysts Promoted by Mo and Fe." American Chemical Society, Preprints, Division of Petroleum Chemistry; Vol. 37 (3), pp. 821-830.

Matsumoto, D.K.; Satterfield, C.N. (1989). "Effects of Temperature and H_2/CO Ratio on Carbon Number Product Distribution from Ion Fischer-Tropsch Catalysts." *Energy & Fuels*; Vol. 3, pp. 249-254.

Maulclin, C.H.; Riley, K.L. (1990). "Process for the Preparation of Surface Impregnated Dispersed Cobalt Metal Catalysts." U.S. Patent No. 4,977,126.

Meisel, S.L.; McCullough, J.P.; Lechthaler, C.H.; Weinz, P.B. (1976). "Gasoline From Methanol in One Step." *Chemical Technology*; Vol. 6, p. 86.

Meisel, S.L. (1988). "Catalysis Research Bears Fruit." *Chemical Technology;* Vol. 18(1), pp. 32-37.

Mills, G.A. (1977). "Alternative Fuels from Coal." *Chemical Technology*; Vol. 7 (7), pp. 418-423.

Mills, G.A. (1988). *Catalysts for Fuels from Syngas-New Directions for Research.* London: IEACOM Research; p. 109.

Mills, G.A. (1990). "High Performance Oxyfuels." American Chemical Society, Preprints, Division of Fuels Chemistry; Vol. 35 (1), p. 241.

Mills, G.A. (1992). "Liquid Fuels from Syngas - Progress Report." American Chemical Society, Preprints, Division of Fuels Chemistry; Vol. 37 (1), pp. 116-123.

Morandi, F.; Trotta, R.; Pecci, G.; Sposini, M. (1988). "European Oxygenate Experience." *Energy Progress*; Vol. 8 (1), pp. 1-5.

Muramatsu, A.; Tatsumi, T.; Tominaga, H. (1992). "Active Species for Molybdenum for Alcohol Synthesis from CO-H_2." *Journal of Physical Chemistry*; Vol. 96, pp. 1334-1340.

Murchison, C.B.; Conway, M.M.; Stevens, R.R.; Quarderer, G.J. (1988). "Mixed Alcohols from Syngas over Molybdenum Catalysts." *Proceedings of the 9th International Congress on Catalysis*; Edited by M.J. Phillips and M. Ternan. Ottawa, Canada: Chemical Institute of Canada; pp. 626-633.

National Research Council of the United States. (1990). *Fuels to Drive Our Future*: Washington, DC: National Academy Press.

Natta, G.; Columbo, U.; Pasquon, I. (1957). "Direct Synthesis of Higher Alcohols from CO and H_2." *Catalysis.* Edited by V.P. Emmett. New York: Reinhold; pp. 131-174.

Nizamoff, A.J. (1989). "Economics of Liquid-Phase Methanol Process." *Proceedings of the DOE Indirect Liquefaction Contractors Meeting; Nov. 13-15, 1989*, Pittsburgh, PA: U.S. Department of Energy, pp. 39-58.

Notari, B. (1991). "C-1 Chemistry: A Critical Review." *Catalytic Science and Technology*; Vol. 1, pp. 55-76.

Nunan, J.G.; Brogdan, C.E.; Klier, K.; Smith, K.J.; Young, C.W.; Herman, R.G. (1989). "Higher Alcohol and Oxygenate Synthesis over Cerum-Doped Cu/ZnO Catalysts." *Journal of Catalysis*; Vol. 116, p. 195.

O'Hare, T.E.; Sapienza, R.S.; Mahajan, D.; Skaperdas, (1986). "Low Temperature Methanol Process." *21st State-of-the-Art Symposium; Marco Islands.* American Chemical Society, Industrial and Engineering Chemical Division.

O'Leary, P.; Tansel, B. (1990). "Landfill Gas Movement, Control and Uses from Solid Waste Landfills," University of Wisconsin at Madison, Engineering Professional Development in *Solid Waste and Landfills.*

Oukaci, J.C.; Wu, S.G.; Goodwin, J.G. (1988). "Effect of Si/Al Ratio on Secondary Zeolite-Supported Metal Catalysts." *Journal of Catalysis*; Vol. 110, pp. 47-57.

Owen, G.; Hawkes, C.J.; Lloyd, D.; Jennings, J.R.; Lambert, R.M.; Nix, R.M. (1987). "Methanol Synthesis Catalysts from Intermetallic Precursors: Binary Lauthanide-Copper Catalysts." *Applied Catalysis*; Vol. 33, p. 405-430.

Paggini, A.; Sanfilippo, D.; Dybkjaer, I.B. (1986). "Implementation of the Methanol Plus Higher Alcohol Process by Snamprofetti, Enichem, Haldor Topsoe MAS Technology." *VII International Symposium on Alcohol Fuels*, Oct. 20-23, Paris.

Palekar, V.M.; Tierney, J.W.; Wender, I. (1990). "A Novel Synthesis of Methanol." *Proceedings of the 7th International Pittsburg Coal Conference*, pp. 622-631.

Piel, W.J. (1991). "Oxygenate Flexibility for Future Fuels." Presented at the National Conference on Reformulated Gasolines and the Clean Air Act Implementation; Washington, DC, October.

Poutsma, M.L.; Clek, L.F.; Ibarabia, D.A.; Risceh, A.P.; Rabo, A.J. (1978). "Selective Formation of Methanol from Synthesis Gas over Palladium Catalysts." *Journal of Catalysis*; Vol. 52, pp. 157-168.

Rao, V.U.S.; Gormley, R.J. (1990). "Bifunctional Catalysts in Syngas Conversions." *Catalysis Today*; Vol. 6 (3), p. 207.

Rao, V.U.S.; Stiegel, G.J.; Bose, A.C.; Cinquegrane, G.J.; Srivastava, R.D. (1992a). "Iron-based Catalysts for Slurry-Phase Fischer-Tropsch Synthesis." American Chemical Society, Division of Fuel Chemistry; Vol. 37 (1), pp. 184-191.

Rao, V.U.S.; Stiegel, G.J.; Cinquegrane, G.J.; Srivastava, R.D. (1992b). "Iron-based Catalysts for Slurry-Phase Fischer-Tropsch Process-Technology Review." *Fuel Processing Technology*; Vol. 30, pp. 83-107.

Reagan, W.J. (1992). AMOCO. Private Communication.

Roberts, G.W.; Lim, P.K.; McCutchen, M.S.; Mawson, S. (1992). "The Thermodynamics of Higher Alcohol Synthesis." American Chemical Society, Division of Petroleum Chemistry; Vol. 37 (1), p. 225.

Robinson, W.R.A.M.; Mol, J.C. (1991). "Support Effects in Methanol Synthesis Over Copper-Containing Catalysts." *Applied Catalysis*; Vol. 76, pp. 117-129.

Rock, K.; Greenough, P.; Halsig, C-P; Semerak, H.; Tschorn, H. (1992). "Feed Pretreatment and Oxygenate Production from Refinery Stream." AIChE Meeting

Rowley, A. (1990). "Developing Enviromentally Responsible Energy Measures. *Proceedings of the DOE Indirect Liquefaction Contractors Meeting*, Nov. 1990. Pittsburgh, PA: U.S. Department of Energy, pp. 291-298.

Rozovskii, A.Y.; Liu, G.I.; Iberov, L.G.; Slivinskii, E.V.; Loktev, S.M.; Kagan, Y.B.; Bashkirov, A.N. (1977). "Mechanism of Methanol Synthesis from CO_2 and H_2." Translated from *Kinetic I Kataliz*; Vol. 18 (3), pp. 691-699.

Santacesaria, E.; DiSerio, M. (1991). "A Synthetic Route to Ethanol by Methanol Homologation." See *ISAF*, pp. 94-98.

Sapienza, R.A.; Slegeir, W.A.; O'Hare, T.W.; Mahasan, D., U.S. Patent No. 4,614,749.

Satterfield, C.N.; Huff, G.A., Jr. (1980). "Effects of Mass Transfer on Fischer-Tropseh Synthesis in Slurry Reactors." *Chemical Engineering Science*; Vol. 35, pp. 195-202.

Sie, S.T. (1992). "Acid-Catalyzed Cracking of Paraffinic Hydrocarbons. 1. Discussion of Existing Mechanisms and Proposal of a New Mechanism." *Industrial and Engineering Chemistry I&EC Research*. Vol. 31, pp. 1881-1889.

Sie, S.T.; Eilers, J.; Menderhoud, J.K. (1988). "Consequences of Fischer-Tropsch Chain Growth Kinetics for Process Mode Selection and Product Selectivity." *Proceedings of the 9th International Congress on Catalysis*; Edited by M.J. Phillips and M. Ternan. Ottawa, Canada: Chemical Institute of Canada; Vol. 2, pp. 743-750.

Sie, S.T.; Senden, M.M.G.; Wechem, H.M.H. (1991). "Conversions of Natural Gas to Transportation Fuels via a Shell Middle Distillate Synthesis Process (SMDS)." *Catalysis Today*; Vol. 8, pp. 371-394.

Slaa, J.C.; Simons, R.G.J.; Busser, G.W.; van Ommen, J.G.; Ross, J.R.H. (1991). "Cu/ZnO/Al_2O_3 based Catalysts for the Synthesis of Methanol and Higher Alcohols from CO + H_2." See *ISAF*, pp. 55-60.

Slegier, W.; Sapienzo, R.; O'Hare, T.; Mahajan, D.; Foran, M.; Skaperdas, G. (1984). "Methanol Synthesis at Low Temperature." 9th EPRI Contractors Meeting, Palo Alto, CA; May [1984].

Smith, K.J.; Herman, R.G.; Klier, K. (1990). "Kinetic Modelling of Higher Alcohol Synthesis Over Alkali-Promoted Cu/ZnO and MoS_2 Catalysts," *Chemical Engineering Science*; Vol. 45, p. 2639-2651.

Smith, K.J.; Klier, K. (1992). "An Overview of Higher Alcohol Synthesis." Preprints, American Chemical Society, Division of Petroleum Chemistry; Vol. 37 (1), p. 214.

Smith, K.J.; Young, C-W.; Herman, R.G.; Klier, K. (1991) "Development of a Kinetic Model for Alcohol Synthesis over a Cerion-Promoted CuZnO Catalyst." *Industrial and Engineering Chemistry I&EC Research*; Vol. 30, pp. 61-71.

Sperling, D.; DeLuchi, M.A. (1989). "Transportation Energy Futures." *Annual Review Energy*: Vol. 14, pp. 375-424.

Spindelbalker, C.; Schmidt, A. (1986). "Sauerstoffhaltige kraftstoff extender." *Erdoel Erdgas Kohle*; Vol. 102, p. 469.

Srivastava, R.D.; Zhou, P.; Stiegel, G.J.; Rao, V.U.S.; Cinquegrane, G. (1992) "Direct Conversion of Methane to Liquid Fuels and Chemicals." *Royal Society of London*; Specialist Periodic Report, *Catalysis*; Vol. 9, pp. 187-228.

Stiles, A. (1977). "Methanol, Past, Present, and Speculation on the Future." *AIChE Journal*; Vol. 23 (3), pp. 362-375.

Stiles, A.B.; Chen, F.; Harrison, J.B.; Hu, X-D.; Storm, D.A.; Yang, H.X. (1991). "Catalytic Conversion of Synthesis Gas to Methanol and Other Oxygenated Products." *I&EC Research*; Vol. 29, pp. 811-821.

Sudhakar, C.; Bhore, N.A.; Bischoff, K.B.; Manogue, W.H.; Mills, G.A. (1988) "Molybdena-enhanced $RhAl_2C_3$ Catalyst." *Catalysis 1987.* Edited by J. Ward. Amsterdam-Oxford-New York-Tokyo: Elsevier; pp. 115-124.

Supp, E.; Quinkler, R.F. (1984). "The Lurgi Low-Pressure Methanol Process." *Handbook of Synfuels Technology.* Edited by R.A. Meyers. New York: McGraw Hill; pp. 2-113.

Supp, E. (1990) *How to Produce Methanol from Coal.* Berlin-New York-London-Paris-Tokyo: Springer Verlag; pp. 301.

Tabak, S.A.; Yurchak, S. (1990). "Conversion of Methanol over ZSM-5 to Fuels and Chemicals." *Catalysis Today*; Vol. 6 (3), pp. 307-327.

Tonner, S.P.; Trimm, D.L.; Wainright, M.S.; Cant., N.W. (1983). "The Base-Catalyzed Carbonylation of Higher Alcohols," *Journal of Molecular Catalysis*; Vol. 18, p. 215.

Topp-Jorgensen, J.; Rostrup-Nielsen, J.R. (19 May 1986). "Integrated Process Offers Lower Gas-to-Gasoline Investment." *Journal of Oil and Gas,* pp. 68-69.

Topp-Jorgensen, J. (1988). "Topsoe Integrated Gasoline Synthesis-The TIGAS Process." *Methane Conversion.* Edited by D.M. Bibby; C.D. Chang; R.F. Howe; and S. Yurchak. Elsevier: Amsterdam-Oxford-New York-Tokyo: Elsevier; pp. 293-305.

Trimm, D.L.; Wainwright, M.S. (1990). "Steam Reforming and Methanol Synthesis." *Catalysis Today*; Vol. 6 (3), p. 261.

Tronconi, E.; Lietti, L.; Forzatti, P.; Pasquon, I. (1989). "Higher Alcohol Synthesis Over Alkali Metal-Promoted High Temperature Methanol Catalysts." *Applied Catalysis*; Vol. 47, pp. 317-333.

Underwood, R.P.; Waller, F.S.; Weist; E.L. (1991). "Development of Alternative Fuels from Coal-Derived Syngas." *Proceedings of the DOE Liquefaction Contractors' Meeting,* Pittsburgh, PA: U.S. Department of Energy; Sept. 3-5, 1991.

Unzelman, G.H. (1989a). "Ethers in Gasolines-1." *Journal of Oil and Gas*; April 10, 1989. pp. 33-49.

Unzelman, G.H. (1989b). "Ethers will Play Larger Role in Octane, Environmental Specs for Gasoline Blends." *Journal of Oil and Gas*; April 17, 1989. pp. 45-49.

van der Burgt, M.; van Klinken, J.; Sie, T. (April 1990). "The Shell Middle Distillate Synthesis Process." *The Institute of Petroleum Review*; pp. 204-209.

van der Burgt, M.J.; van Klinken, J.; Sie, S.T. (1985). "The Shell Middle Distillate Synthesis Process." 5th Worldwide Synfuels Symposium; Washington, DC. November 11-13, 1985, pp. 11-13.

Van Rensburg, S.T.J. (1990). "The Mossgas, Gas to Fuel Process." *a SAIChE Paper Chem. SA*; February, pp. 41-42.

Velocci, A.L. Jr. (1991) "Creating Liquid Fuels from Natural Gas." *The Lamp*; Vol. 73 (3), pp. 14-17.

Wender, I.; Klier, K. (1989). "Review of Indirect Liquefaction," Chapter 5 in *Coal Liquefaction—a Research Needs Assessment,* DOE/ER-0400. Vol. II, Contract DE-AC01-87ER30110, Washington, DC: U.S. Department of Energy.

Westerterp, K.R.; Kuczynski, M. (1986). "Retrofit Methanol Plants with this Converter System." *Hydrocarbon Processing*; pp. 80-83.

Westerterp, K.R.; Kucznski, M.; Kamphius, C.H. (1989), "Synthesis of Methanol in Reactor System with Interstage Product Removal." *Industrial Engineering Chemical Research*; Vol. 28 (6), p. 763-771.

Westerterp, K.R.; Bodewes, T.N.; Vrijand, M.S.A.; Kuczunski, M. (1988). "Two New Methanol Converters." *Hydrocarbon Processing*; pp. 69-73.

Wilson, T.; Kasai, P.M.; Ellgen, P.C. (1981). "The State of Manganese Promoter in Rhodium-Silica Gel Catalysts." *Journal of Catalysis*; Vol. 69, pp. 193-201.

Xiaogding, X.; Doegburg, E.B.M.; Scholten, J.J.F. (1987). "Synthesis of Higher Alcohols from Syngas—Recently Patented Catalysts and Tentative Ideas on the Mechanisms." *Catalysis Today*; Vol. 2, pp. 125-170.

Yates, I.C.; Satterfield, C.N. (1991a). "The Hydrocarbon Selectivity of Cobalt Fischer-Tropsch Catalysts." DOE/PC/79816-T1. (Available from D.S.T.I and from N.T.I.S.)

Yates, I.C.; Scatterfield, C.N. (1991b). "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalysis." *Energy and Fuels*; Vol. 5, pp. 168-173.

Yoon, H.; Stouffer, M.R.; Dudt, P.J.; Burke, F.P.; Curran, G.P. (1985). "Methanol Dissociation for Fuel Use." *Energy Progress*; Vol. 5 (2), pp. 78-83.

Yurchak, S.; Wong, S.S. (1991). "Mobil Methanol Conversion Technologies." *Hydrocarbon Asia*; July/August. pp. 38-48.

Zhou, P.L.; Maloney, S.D.; Gates, B.C. (1991). "Design of a Stable, Selective Catalyst for CO Hydrogenation: Osium on Basic Y Zeolite." *Journal of Catalysis*; Vol. 129, pp. 315-329.

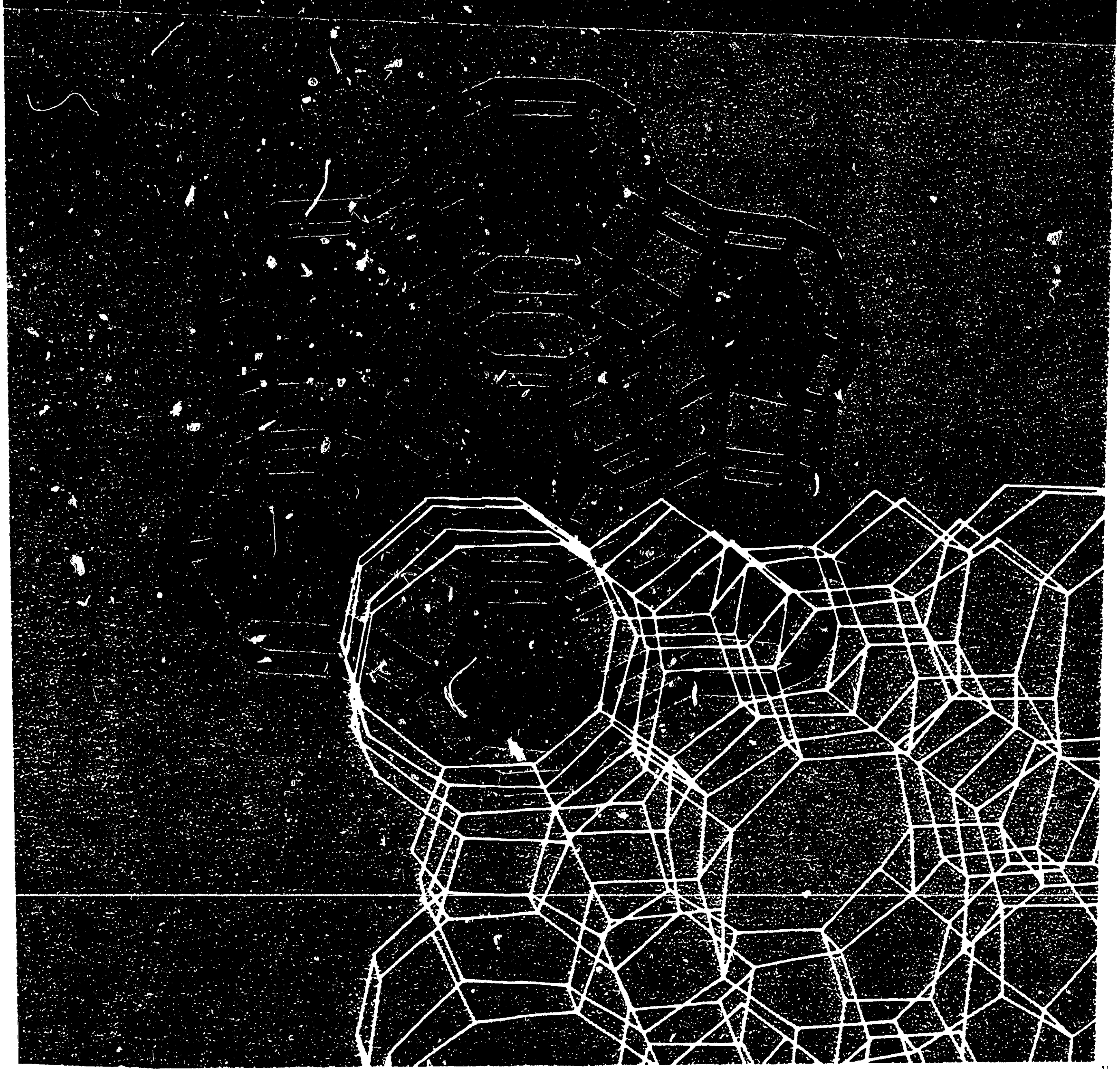
Zhou, P.; Srivastava, R. (1992). "Assessment of State-of-the-Art Hydrodynamic Models and Correlations for Slurry Bubble Column Reactors." DOE Draft.

Appendix

Catalysts for Fuels from Syngas

IEA
COAL RESEARCH

Catalysts for fuels from syngas



Catalysts for fuels from syngas: new directions for research

G Alex Mills

IEACR/09
IEA Coal Research, London
August 1988

ISBN 92-9029-159-1

This report, produced by IEA Coal Research, has been reviewed in draft form by nominated experts in member countries and their comments have been taken into consideration. It has been approved for distribution by the Executive Committee of IEA Coal Research.

IEA Coal Research

IEA Coal Research was established in 1975 under the auspices of the International Energy Agency (IEA) and is currently supported by fourteen countries.

IEA Coal Research provides information and analysis of all aspects of coal production and use, including:

- supply, mining and geosciences;
- transport and markets;
- coal science;
- coal utilisation technology;
- environmental effects;
- by-products and waste utilisation.

IEA Coal Research produces:

- periodicals including *Coal abstracts*, a monthly current awareness journal giving details of the most recent and relevant items from the world's literature on coal, and *Coal calendar*, a comprehensive descriptive calendar of recently-held and forthcoming meetings of interest to the coal industry;
- technical assessments and economic reports on specific topics throughout the coal chain;
- bibliographic databases on coal technology, coal research projects and forthcoming events, and numerical databanks on reserves and resources, coal ports and coal-fired power stations.

Specific enquiries about this report should be addressed to: G Alex Mills, Center for Catalytic Science and Technology, Chemical Engineering Department, University of Delaware, DE 19716, USA

General enquiries about IEA Coal Research should be addressed to:

Dr David Merrick
Head of Service
IEA Coal Research
14–15 Lower Grosvenor Place
London, SW1W 0EX
United Kingdom

Telephone: 01-828 4661
Telex: 917624 NICEBA G
Fax: 01-828 9508

Abstract

The science and technology of catalytic conversion of synthesis gas to liquid hydrocarbon and oxygenate fuels has been reviewed. The objective has been to identify exploratory research results and new catalytic concepts whose development could lead to significant improvements in indirect coal liquefaction. From an assessment of present technology, it is concluded that there are three major opportunities to improve syngas conversion processes by means of new and improved catalysts which provide a) higher selectivity to high performance fuels, b) decreased plant investment costs, c) improved thermal efficiency.

During the past decade there has been an intensive world-wide research effort on catalytic reactions of synthesis gas, mixtures of hydrogen and carbon oxides. A vast range of ideas has been tried including the use of zeolites, metal complexes, multifunctional catalyst and, recently, biocatalysis. Moreover, the scientific design of catalysts is being approached with some success. Also, an important route for improved synthesis of liquid fuels is through use of catalysts specially designed to function in systems which improve process engineering.

An evaluation has been made of the results of more than 300 recent research papers in the context of their potential to fulfil needs for improved synthesis gas conversion catalysts. This evaluation has led to a description of opportunities for new research directions in catalysis for indirect coal liquefaction. These can find application in 1) further improvements for catalytic systems under development, 2) innovative catalytic processes, or 3) new scientific catalytic approaches. It is concluded that there are excellent research opportunities for improvements in indirect coal liquefaction for production of both hydrocarbon and oxygenate liquid fuels. It has been estimated that catalysts having improved capabilities for syngas conversion have the potential to improve the economics of synthetic fuels manufacture by 10% to 30%.

Contents

Figures

Tables

1 Introduction

This report is concerned with catalytic technology for indirect coal liquefaction, the two-step process in which coal is first converted to synthesis gas (syngas: a mixture of hydrogen and carbon oxides) which is then reacted catalytically to produce liquid fuels. The focus is on catalysis, both the science and application, for the conversion of syngas to hydrocarbon and/or oxygenate liquid fuels, particularly those suitable for transportation use. Coal gasification is not included in this study.

This report seeks to identify

1) the essential role of the catalyst as well as needed research to overcome generic problems,
2) promising exploratory research results and new catalytic concepts applicable to indirect coal liquefaction, and
3) an assessment of the potential of new research directions to significantly improve coal indirect liquefaction processes.

Proceeding from a brief review of the background of catalysis in CO hydrogenation reactions, emphasis has been placed on new scientific concepts and techniques and on experimental results of novel exploratory research to delineate possible new directions for research. As may be expected, these new directions are based on preliminary, exploratory results and indeed are often controversial. Also, references often appear in progress reports which may be difficult to locate.

Input to the study was provided from the literature (not including patents) and a review and discussions of ongoing research projects with scientists at various research establishments. The ultimate objective of research is to provide the technical basis for the economical manufacture of synthetic fuels. Therefore, research has been reviewed with this objective in mind. This was assisted by an estimation of the potential of successful research to overcome chemical and engineering barriers and so to contribute to more economical manufacture. These considerations have led to an assessment of opportunities for new directions for research.

1.1 Historical synopsis

Two processes for converting coal to liquid transport fuels were used in Germany during World War II. Direct liquefaction (Bergius) involves the direct catalytic hydrogenation of coal to liquids which are further refined. In contrast, indirect liquefaction involves two steps, first the conversion of coal by partial oxidation in the presence of steam to synthesis gas ($H_2 + CO + CO_2$) which, after purification, is reacted catalytically in a second step to form liquid hydrocarbon fuels (Fischer-Tropsch, FT). The hydrocarbons produced by the Bergius and by the FT process differ greatly, the Bergius product being characterised by its aromatic nature while the FT product consists mainly of paraffins of various chain lengths. The FT process was used to produce about 15% of fuels in Germany during World War II but it and the Bergius process were discontinued after World War II, since they were not economically competitive with widely available petroleum. However, the FT process is now being used at SASOL in South Africa on a large scale, particularly with the two large plant expansions made in the 1980s.

It should be noted that in the past decade or so, there have been significant improvements in coal gasification technology for syngas manufacture, particularly high-temperature pressurised-processes (entrained, fluid and moving bed) which provide more economical syngas, free from tar and methane. These processes have been demonstrated on a commercial plant scale. They are of interest for production of electricity from coal with environmental protection, as well as synthetic fuels manufacture. Since coal gasification costs are a major economic cost in indirect coal liquefaction economics, these advances in coal gasification technology are seen as important in improving commercial opportunities for indirect liquefaction. The high temperature Winkler process has been successfully demonstrated in a plant operating at 950°C and 1.0 MPa converting 30 t/h German brown coal to syngas which is used to synthesise about 14 t/h methanol

(Rheinbraun, 1986). Significant also is the large scale use of a Texaco gasifier for conversion of coal to syngas: at Cool Water, USA, for generation of electricity; at Syntheses-Anlage Ruhr in Germany for acetic acid production, and at Eastman (Larkin, 1986) for the manufacture of acetic anhydride. Improved gasification technology has also been demonstrated by Westinghouse and British Gas-Lurgi.

It is also significant that methanol, which is manufactured from syngas, and long utilised for chemicals purposes and also employed as a premium fuel in racing cars, has recently entered into public commercial use for automobile transportation, albeit in a small way. Methanol manufacture has grown to be one of the largest synthetic chemicals worldwide. Syngas is being manufactured from coal in some parts of the world, but at present most is made from natural gas.

Further, in what may be regarded as a hybrid process in New Zealand, syngas made from off-shore natural gas is converted into methanol which is then transformed into high octane gasoline over a molecular sieve catalyst. Beginning in 1986, this MTG (methanol-to-gasoline) process now supplies 14,500 barrels per day of gasoline, one-third the gasoline needs in that country.

Additionally, in some 13 countries, synthetic methanol is reacted with isobutylene to form MTBE (methyl tertiary butyl ether) which is blended into gasoline as an octane-enhancer, now more important with phase-down of tetraethyl lead. MTBE is remarkable in that its high-performance characteristics make it economically attractive despite depressed world oil prices.

At the present time, with the special exception of MTBE, synthetic fuels do not compete economically with petroleum, priced at about 18 $/bbl. In fact under conventional commercial economic conditions, synthetic fuels would be two to three times as expensive as oil at 18 $/bbl.

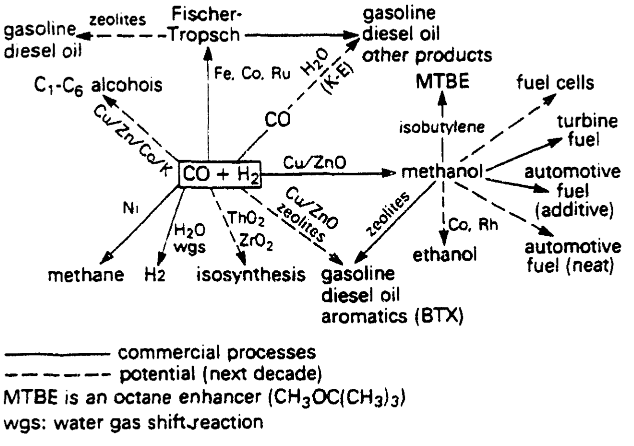


Figure 1 **Commercial or near commercial processes for the production of liquid fuels from synthetic gas** (Wender and Seshadri, 1984)

1.2 Chemicals from syngas for fuel use

There is a remarkable diversity of chemicals which can be synthesised by catalytic hydrogenation of carbon oxides, Figures 1 and 2 (Wender and Seshadri, 1984). As noted, specific catalysts have been developed which provide for the selective manufacture of different hydrocarbon and oxygenate products, many of which are suitable for fuel use. This diversity is further expanded by products (for example, MTBE) obtained by reactions of H_2 and CO with a third molecule. While synthetic fuels are the main theme of this review, there is some discussion of chemicals from syngas (in addition to methanol). This is to be found in: Section 2.1.5 on higher oxygenates which includes C_1-C_6 alcohols, isobutanol, MTBE, TAME; Section 2.2.3 on C_2 oxygenates; and Section 3.6 which discusses hydrocarbons, namely olefins and isoparaffins.

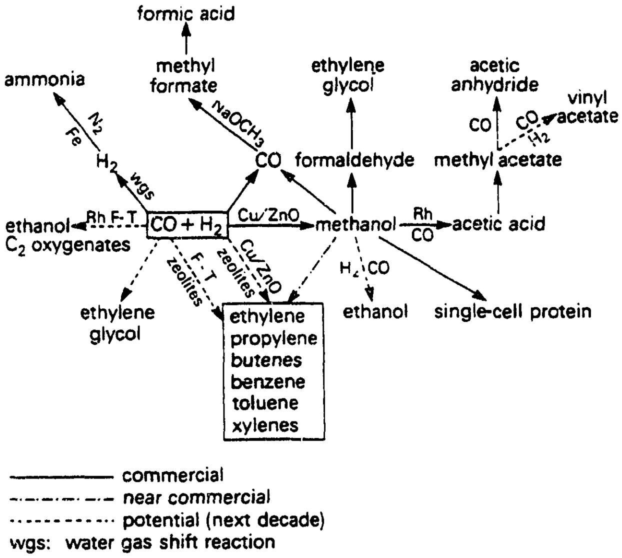


Figure 2 **Commercial, near commercial and potential chemicals from synthetic gas** (Wender and Seshadri, 1984)

1.3 Chemical reactions, thermodynamics

The catalytic chemistry of syngas reactions to hydrocarbon and oxygenates has been discussed extensively, both in earlier reviews (Emmett, 1956; Natta, 1955, 1957; Storch and others, 1951) and recently (Anderson, 1984; Dry, 1981, 1982, 1986, 1987; Falbe, 1967, 1970, 1977, 1980, 1982; Keim, 1983, 1986; Klier, 1982; Poels and Ponec, 1983; Ponec, 1982; Sachtler, 1984; Stiles, 1977; and Vannice, 1976, 1987). Process steps and principal reactions for synthetic fuels process are summarised in Figure 3.

Both thermodynamic and kinetic considerations are of critical importance. Fortunately, thermodynamic information on syngas reactions has been well established. Heats of reaction are shown in Figure 4 and free energy values in Figure 5 as a function of temperature (Anderson, 1984). Thermodynamic considerations impose limitations for maximum conversions. Figure 6 shows the maximum methanol which can be produced with a $H_2/CO = 2$, at 300°C at various pressures.

Heat release in CO hydrogenation is a serious problem since exothermic reactions can raise the temperature and limit the conversion potential. Higher temperatures also can affect adversely catalyst activity and stability.

Reaction mechanisms and related kinetics of syngas reactions have been studied extensively. A crucial concept in determining product selectivity is the nature of the chemisorption of CO. It is believed that when chemisorption occurs in a non-dissociative manner, the addition of activated hydrogen proceeds to formation of methanol. Alternatively, CO chemisorbed dissociatively forms a type of active carbon species (not a true carbide) which adds hydrogen to form an active CH_x surface species which can add hydrogen to form methane.

For metals there exists a relationship between their position in the periodic table and their ability to chemisorb CO dissociatively. A dividing line has been established for ambient temperature (Broden and others, 1976) between metals that chemisorb CO nondissociatively and those which have at least some crystal faces that split the CO molecule into surface carbon and oxygen. Figure 7 shows a section of the periodic table wherein elements on the right-hand side of the borderline adsorb CO nondissociatively and vice versa.

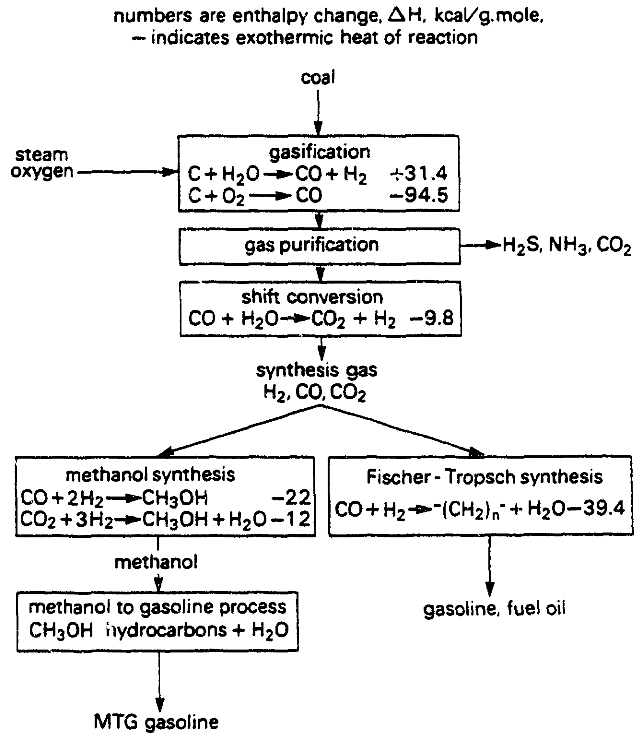


Figure 3 Process steps in indirect coal liquefaction (Mills and Ecklund, 1987)

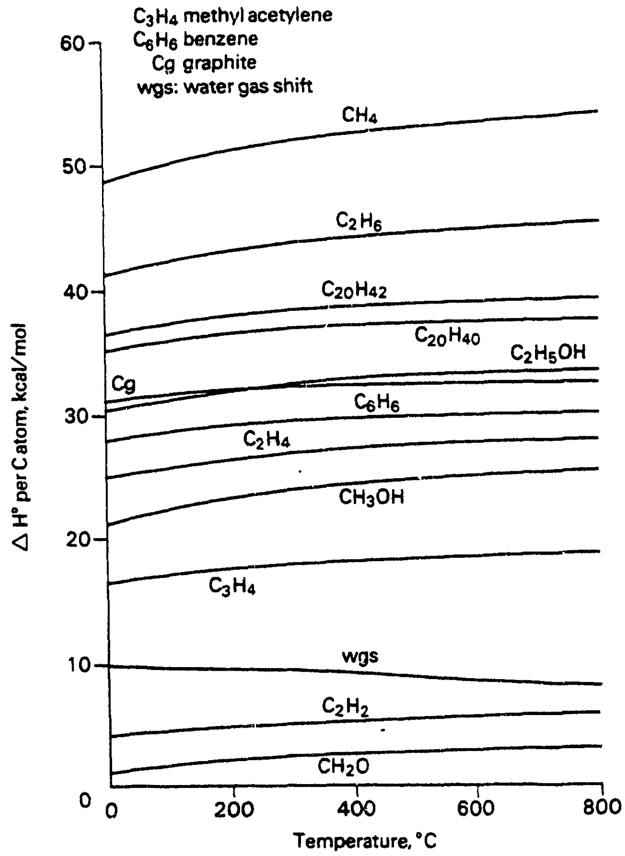


Figure 4 Standard heats of reaction per carbon atom in the organic product (Anderson, 1984)

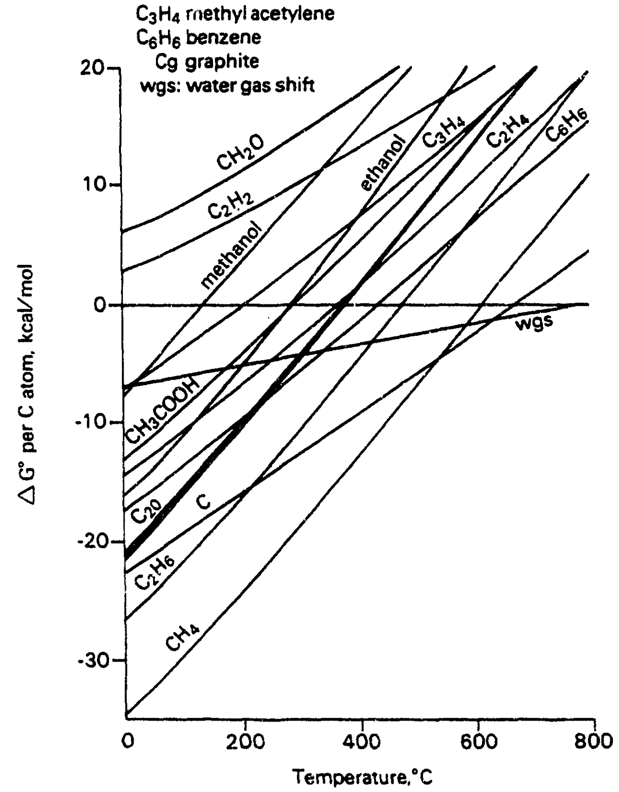


Figure 5 Standard free energies of reaction per carbon atom of the organic product (Anderson, 1984)

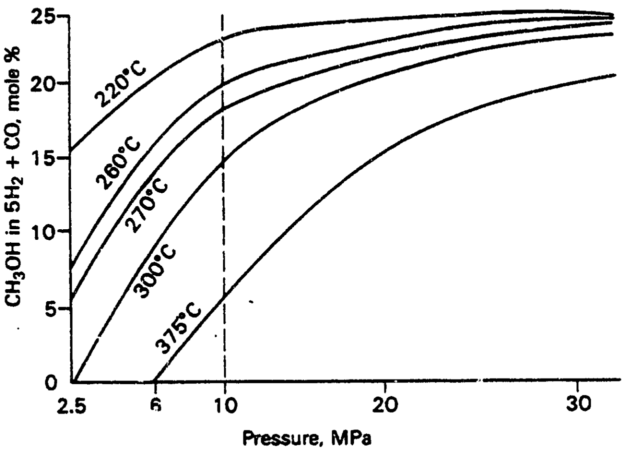


Figure 6 Methanol equilibrium as a function of temperature and pressure

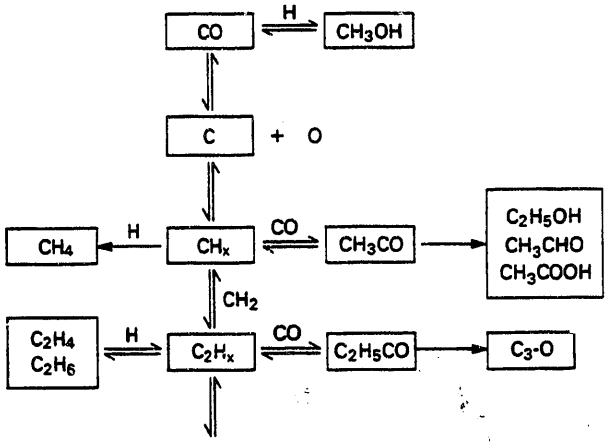
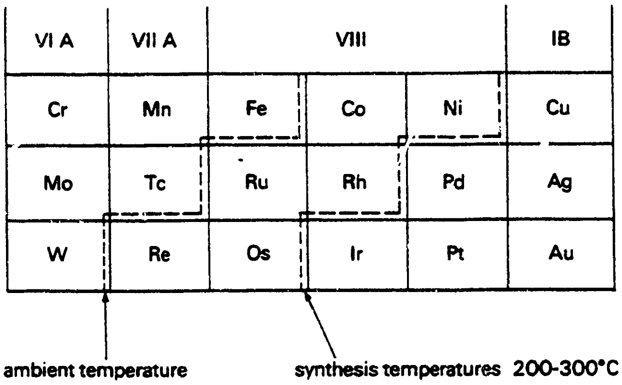


Figure 8 Kinetic model for CO/H_2 reactions over rhodium catalysts (Sachtler, 1984)



VI A	VII A	VIII			IB
Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

ambient temperature

synthesis temperatures 200-300°C

dotted lines separate metals on the left which split CO from those on the right which adsorb CO nondissociatively.

Figure 7 CO chemisorption on transition metals (Broden and others, 1976)

It must be emphasised (Klier, 1982) that nondissociative chemisorption of CO, which appears to be a necessary condition for its hydrogenation to methanol, is not a sufficient prerequisite. For example, gold chemisorbs CO nondissociatively at ambient temperature but it is not a methanol synthesis catalyst. Certain forms of rhodium have been found to be catalysts of intermediate activity and selectivity for methanol. All of these metals have the common property that they lie close to the high-temperature borderline in Figure 7. Moreover, metals guiding the synthesis selectivity to methanol are to the right, but not far to the right of this boundary. This indicates that good methanol catalysts chemisorb CO with moderate strength, which is sufficient to perturb this molecule to allow it to react with hydrogen but insufficient to break it or any intermediates into fragments.

Furthermore, by a chain growth mechanism CH_x can undergo CO insertion and then add hydrogen to form higher alcohols or hydrocarbons as shown in Figure 8 (Sachtler, 1984).

Chain growth has been recognised as having certain similarities to polymerisation reactions where the distribution of product chain length is a consequence of relative rates of propagation, R_p, and termination, R_t. The weight fraction, W_i of a product with carbon number C_i is given by the equation:

$$\log (W_i/C_i) = (\log \alpha)C_i + K$$

where α is the probability of chain growth = $R_p/(R_p + R_t)$ and K is a constant. This equation, sometimes known as the Anderson-Shulz-Flory, or ASF, equation, has as a consequence that only C_1 products such as methane or methanol can be made in near quantitative selectivity. All other products will have well-defined maximum allowable selectivities illustrated in Figure 9 for hydrocarbon synthesis.

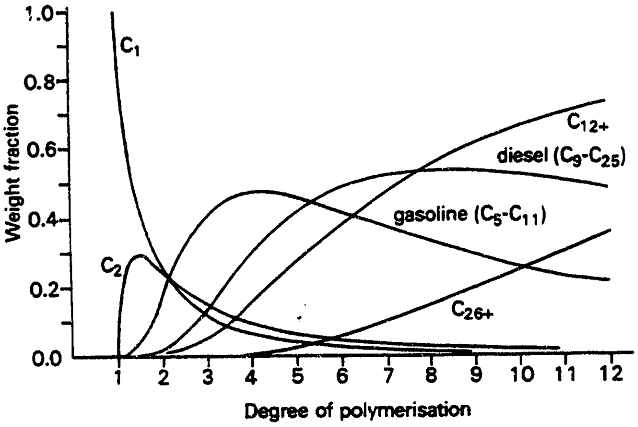


Figure 9 Yield of selected product fraction with increasing degree of polymerisation

From a practical viewpoint, in the Fischer-Tropsch process, there is a wide distribution of hydrocarbon chain lengths. For instance maximum gasoline (C_5-C_{11}) is 47%, and maximum diesel (C_{12}-C_{17}) is 40%. A generic problem in conducting catalytic syngas reactions is the formation of too much low-value methane. Much research is directed towards improving product distribution, by circumventing the ASF distribution limitation. This has been accomplished in a number of instances, particularly when secondary reactions are involved or by the use of shape selective zeolite catalysts.

1.4 Approaches to catalytic research

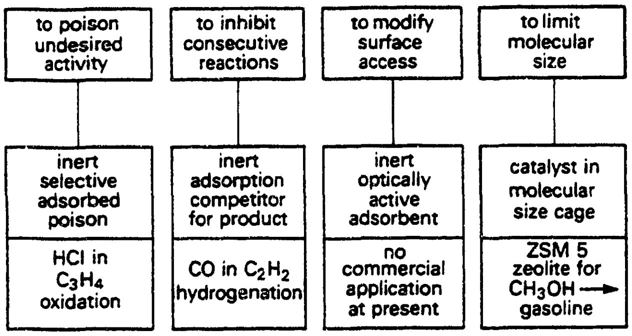
The role of the catalyst is to hasten those CO hydrogenation reactions which form desired products, to avoid the wide variety of competing reactions which are possible, to do so at high enough velocity (catalyst activity) to be commercially useful, to do so at relatively low temperatures and pressures, and to continue to be active and selective in stable operation for long periods of time.

In general, catalyst improvements are sought which can

- provide for high selectivity for fuels having high performance value in fuel applications;
- decrease capital costs;
- improve thermal efficiency.

Catalytic research has followed several approaches:

- The classical approach to catalyst research has been to vary composition and method of catalyst preparation, to correlate these variables with catalyst performance, and then to try modifications in catalyst preparation. Modifications are made on the basis of an assessment of the data and a perceptive knowledge, by those skilled in the art, of the effect of catalyst constituents on the chemistry of desired reactions, and also avoidance of those which cause loss of activity or selectivity. The scientific literature on catalyst preparation is not large. One reference (Andrew, 1981) does describe options to increase selectivity, Figure 10.



to poison undesired activity	to inhibit consecutive reactions	to modify surface access	to limit molecular size
inert selective adsorbed poison	inert adsorption competitor for product	inert optically active adsorbent	catalyst in molecular size cage
HCl in C_3H_4 oxidation	CO in C_2H_2 hydrogenation	no commercial application at present	ZSM 5 zeolite for $CH_3OH \rightarrow$ gasoline

Figure 10 **Typical devices to enhance catalyst selectivity** (Andrew, 1981)

- The catalytic reaction chemistry is determined with a view to identifying and improving critical steps. For this approach, reaction mechanisms are determined using kinetic studies, isotopic tracers, chemisorption measurements, and so on.
- Fundamental catalyst structure/performance relationships are determined using modern instrumental techniques, seeking on the basis of a surface science approach, a scientific understanding to be able to predict and design improved catalysts.
- Catalysts are developed which are suited to new process requirements dictated by improved process engineering.
- Catalysts for synthesis of specific chemicals for fuel use.
- Catalysts to test novel concepts.

It will be convenient to examine catalyst research according to each of these approaches, at least to a certain extent.

2 Oxygenate fuels from syngas

This chapter first discusses catalysts which contain ZnO, a key component of classical catalysts for manufacture of alcohols. Then catalysts which do not contain ZnO are reviewed. Finally, there are brief remarks on the catalytic dissociation of methanol to syngas for fuel use.

2.1 ZnO-based catalysts

Following a background summary, this section discusses:

- research on preparational variations for catalyst improvement;
- studies to determine reaction chemistry;
- studies to identify catalyst structure/performance relationships;
- catalysts designed for improved process engineering;
- synthesis of higher oxygenate, namely C_1-C_6 alcohols, isobutanol, MTBE, TAME.

Research to create catalysts capable of hydrogenating CO to methanol began about 1913. A wide and confusing variety of catalysts appeared in the early patent literature (Stiles, 1983). This research culminated in 1923 in the first commercial manufacture of methanol from syngas in Germany by BASF. A ZnO/Cr_2O_3 catalyst was used and remained the catalyst of choice until the 1960s when it was supplanted by the much more active $Cu/ZnO/Al_2O_3$ catalyst, introduced by ICI (Rogerson, 1984). Higher activity is important in that it permits reaction rates of commercial interest at lower temperatures. Lower temperatures, because of thermodynamic limitations mentioned earlier, permit the use of lower pressures resulting in economic savings in plant investment and operation. Earlier catalysts were operated at 300–400°C and 30–35 MPa pressure, whilst modern copper-containing catalysts are operated at 250–300°C and 5–10 MPa. However, the copper catalysts are more readily poisoned by sulphur and halides and hence more stringent syngas purification is required. Nevertheless, there is an overall saving, estimated at about 5% of methanol manufacturing costs (Bew, 1981), a relatively large amount in large plants. This is a significant improvement considering the many years of development for methanol synthesis which provide for reaction selectivity of 99%. The improved process economics were made possible by advances in purification technology, and the use of less expensive centrifugal compressors, suitable for large-scale use, all of which advantages depended on the improved properties of this new catalyst. This emphasises the need to coordinate the search for improved catalyst performance with engineering/manufacturing needs and capabilities (Dybkyjaer and Hansen, 1985; Supp, 1985).

2.1.1 Variation in catalyst preparation

While early (1913–23) patent literature on catalysts for methanol manufacture was chaotic, gradually there emerged the concept of a mixed oxide consisting of ZnO and a difficultly reducible oxide, particularly Cr_2O_3. Of great value to the achievement of stable catalyst performance was the recognition and prevention of antiselectivity by iron contamination, derived from $Fe(CO)_5$ transported from reactor walls and deposited on the catalyst.

Marschner and others (1982) have reviewed catalyst composition and manufacture for both high pressure and low pressure methanol synthesis. For the latter, they show the following compositions, taken from patents.

	Atomic %	
	ICI	Lurgi
Cu	90–25	80–30
Zn	8–60	10–50
Cr	2–30	–
V	–	1–25
Mn	–	10–50

As far as can be determined from the literature, the first test involving copper-containing catalysts in an industrial synthesis took place in a Polish chemical combine in Oswiecim. The catalyst was prepared by precipitation with sodium aluminate from copper and zinc solutions. Care was taken to ensure maximum removal of alkali from the filter cake. The catalyst had the following composition in weight%: 62.5 CuO, 25.0 ZnO, 7.5 Al_2O_3, 5.0 H_2O.

Beginning in 1976, three international symposia have addressed catalyst preparation science, including papers on ZnO catalysts. The optimum composition of Cu/Zn/Al was studied and the atom ratio 1/0.6/0.08 was reported best (Kotera and others, 1976). It was suggested that Cu metal plays a dominant role. Catalyst structure was examined by CO chemisorption and X-ray powder diffraction.

Utilising the methanol dissociation to syngas reaction as a measure of catalytic properties of Cu/ZnO catalysts (Okamoto and others, 1984), it was concluded that ZnO plays a major role, being considered to act synergistically to provide increased concentration of CH_3OH molecules as a reservoir. Cu-ZnO is seen as a bifunctional catalyst. Copper metal activates CH_3OH to form HCHO, this being the rate controlling step. It is considered that Cu is a major active species, since ZnO alone shows negligible activity <200°C.

The structure of this type of catalyst was delineated (Okamoto and others, 1983; Herman and others, 1981) by electron microscopy and X-ray emission microanalysis with the conclusion that alumina is amorphous, the ZnO is crystalline, that Cu occurs as crystallites and as a solute in ZnO. The active phase was said to be the Cu-ZnO solid solution. It was concluded that alumina stabilises the highly active and morphologically favourable form. The physical nature of the catalyst depends critically on the precursor – it 'remembers' the original precursor morphology. While most Cu segregated to larger metallic particles, the ideal catalyst was considered to be a micromonolith having the composition 8 Cu, 50 Zn, 42 Al_2O_3, atomic percentages. The alumina acts as a 'glue.'

From further morphological studies (Himelfarb and others, 1984) it was concluded that ternary polycrystalline platelets (Cu/Zn/Al) and a binary lace-like Cu/ZnO morphology are active in methanol synthesis, which activity is believed to be a result of the intimate dispersion of Cu an ZnO crystallites in both morphologies. The alumina is regarded as a support.

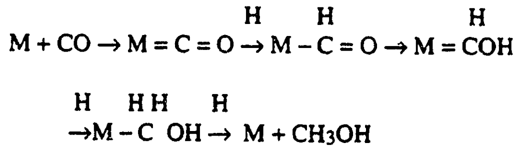
The concept of preparing a special preferred ternary precursor (Petrini and others, 1983) was attempted by the synthesis of hydrotalcite-like $(Cu,Zn)_6Al_2(CO)_3(OH)_{16}{\cdot}4H_2O$ (Gherardi and others, 1983). This structure decomposes to oxides at a lower temperature than hydroxycarbonate phases. This leads to the smallest crystal size oxides which on reduction give rise to copper crystallites of extremely small size. These small crystallites are due to the 'perfect' distribution of elements inside the ternary structure (no catalyst performance data are presented in this paper).

In summary, the approach described in this section is to prepare special precursor structures which result in a superior catalysts.

2.1.2 Reaction chemistry determination

Many studies have been devoted to determining the mechanism of methanol synthesis. Two options have generally been considered.

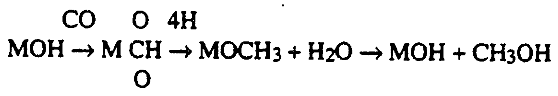
a) carbon-down



$$M + CO \rightarrow M = C = O \xrightarrow{H} M - \overset{H}{C} = O \rightarrow M = \overset{H}{C}OH$$

$$\overset{H}{\rightarrow} M - \overset{HH}{C}\ OH \overset{H}{\rightarrow} M + CH_3OH$$

b) oxygen-down



$$MOH \xrightarrow{CO} M\,\overset{O}{\underset{O}{C}}H \xrightarrow{4H} MOCH_3 + H_2O \rightarrow MOH + CH_3OH$$

Surface intermediates, namely formyl, formate and methoxide, have been identified by infrared measurements and trapping techniques. In addition, kinetic studies and isotopic tracer methods have gone far in delineating catalytic reaction mechanisms. These are discussed in detail in review references. However, it must be pointed out that in contrast to the above mechanisms, there is considerable evidence that for the Cu and ZnO systems, the reaction to methanol proceeds through CO_2, not CO (Bowker and others, 1981, 1983, 1984). This is discussed later.

2.1.3 Catalyst structure/performance identification

A major research effort has been made to identify the structural nature of catalyst surface on an atomic scale, since it is believed that it is the chemical nature of active surface sites which determines their catalytic properties (Ghiotti and Buccuzzi, 1987). The recent development of instrumental techniques (Kelley, 1987) now make it possible to 'see' atoms and complexes on the surface. This has led to an enormous research effort to identify critical surface structures in scientific terms with the expectation of advancing catalyst synthesis from an art to a science and making possible preparations of catalysts of superior properties by design.

One research team (Chinchen and others, 1984) extending research by Rozovskii and others (1977) sought the basis for catalytic reactivity of $Cu/ZnO/Al_2O_3$, by providing answers to a series of questions.

Q. Is methanol synthesised from CO or CO_2?
A. From CO_2 (isotopic labelling experiments).

Q. What is the role of supports, ZnO and Al_2O_3?
A. Surprisingly, they are not unique (determined by omitting them).

Q. What is the critical oxidation state of copper in the catalyst?
A. Copper metal (from the observation that there is a

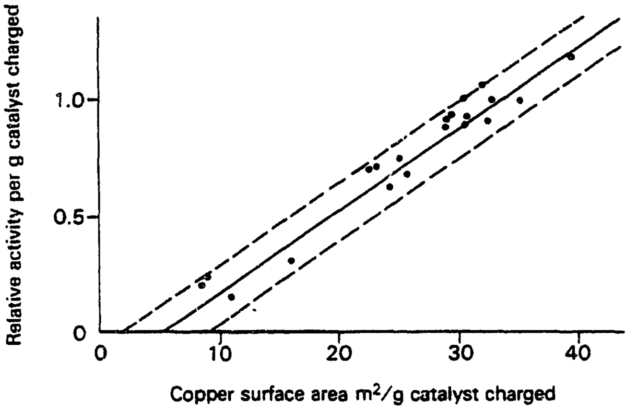


Figure 11 Linear correlation between activity and copper surface (95% confidence limits) for $Cu\text{-}ZnO\text{-}Al_2O_3$

linear dependence of synthesis activity on total Cu area) (*see* Figure 11).

Further, these investigators believe that it is a copper metal or copper metal/copper oxide combination which is implicated in the rate determining step.

Additional mechanism studies (temperature programmed reaction spectroscopy) showed formate ion surface species believed involved in the following mechanism:

$$CO_2^-{}_{(a)} + H_{(a)} \rightarrow HCO_2^-{}_{(a)}$$

$$HCO_2^-{}_{(a)} + 3H_{(a)} \rightarrow CH_3OH_{(g)} + O^-{}_{(a)}$$

where the subscripts $_a$ and $_g$ relate to adsorbed and gas phase species respectively. The negative charge on the adsorbed CO_2 and formate species may be less than unity.

It was noted that each copper site at which methanol is synthesised will become oxidised as a consequence of the synthesis reaction. Thus, the active site consists of a Cu surface atom in close proximity to an oxide surface site, a view similar to that proposed by others (Akomoto and others, 1983) and to that proposed for ZnO catalysts not containing Cu (Bowker and others, 1981, 1983, 1984).

The point was also made that oxidation of CO on partially oxidised copper constitutes part of the shift reaction. The shift reaction under methanol synthesis reaction conditions does not involve a formate ion intermediate.

$$\begin{array}{c} CO_2 + H_2 \Leftrightarrow \text{complex} \Leftrightarrow CH_3OH \\ \Uparrow \\ \text{does not} \\ \Downarrow \\ CO + H_2O \end{array}$$

Liu and others (1988) found the active state in a working catalyst to be Cu^0. They conclude that methanol synthesis proceeds through multiple routes and that the main role of CO_2 is to maintain a high concentration of surface hydroxyl which provides a new pathway for CO hydrogenation and so the overall rate of methanol synthesis is speeded up.

Other investigators have held the strong view that Cu^{1+} rather than Cu is critical to methanol synthesis (Klier, 1982; Herman and others, 1981; Karwacki and others, 1984; Parris and Klier, 1984). They see three basic catalyst morphologies, large Cu particles (>0.1 micron), Cu/Zn/Al polycrystal platelets, and a binary Cu/ZnO morphology. Ternary platelets and binary lace-like morphologies are believed active in methanol synthesis which is believed to be a result of the intimate dispersion of the Cu and ZnO crystallites in both morphologies. The alumina component, which appears to be amorphous, is a structural support in the platelets and widens the Cu/Zn ratio range for which high dispersion of Cu and ZnO can be obtained. These conclusions, particularly the importance attributed to Cu^{1+}, were the result of electron microscope studies and supported by XPS data that claim that Cu^{1+} must be maintained on the catalyst surface for continued activity for methanol synthesis (Karwacki and others, 1984). Strong shifts in Cu binding energy for reduced catalysts indicate that Cu^{1+} is incorporated into the ZnO lattice.

Chaumette and others (1988) have shown that carbonates and formates are key intermediates in methanol synthesis for Cu-Zn-Al catalysts. Copper, zinc oxide, and interacting carbonate entities and gas phase CO_2 are all indispensible. Carbonate species appear to be essential since they increase copper dispersion and constitute a part of the active centres along with the Cu^0/Cu^{1+} couple and ZnO. It is believed that the CO_3^{2-}/CO_2 solid-gas equilibrium is associated with the Cu^0/Cu^{1+} redox couple.

Ponec (1988) has the opinion that the role of Cu^{m+} in methanol synthesis is as follows: when the catalyst is very well reduced, the only centres of H (coming from Cu^0 surface) + CO reactions are the Cu^+ ions in ZnO, SiO_2 or Al_2O_3. The catalyst is then better the more of these centres that have survived the reduction. Intermediate on the way to methanol is a formyl which is stabilised by a plus charge and a formate formed from it or directly from CO_2. When the catalyst is partially oxidised by CO_2 or H_2O, a high number of new centres is being formed. Cu ions are stabilised most likely by the oxide (ZnO, Cr_2O_3, Al_2O_3) which is situated on Cu^0; this oxide is transferred there during the preparation steps. In this way migration of H_{ads} to these centres is easy.

While the precise surface chemistry of syngas reactions over ZnO catalysts remains somewhat controversial, much has been established (Chinchen and others, 1988). It is believed that this scientific knowledge can provide the basis for the design of improved catalysts and also can act as an inspiration for novel ideas.

2.1.4 Catalysts designed for improved process engineering

The relatively high heat release in CO hydrogenation has required limitation in the conversion per pass in order to avoid temperature increases which are detrimental to catalyst stability and selectivity and also occasion adverse thermodynamic limitations. This results in expensive recycle of unreacted syngas. Subsequent to reaction, non-converted reactants must be separated from the products, the product methanol removed by condensation and the reactants recirculated to the reactor by a compressor. As a consequence there has been an effort to apply process engineering ideas which could diminish plant investment and operating costs. Such engineering approaches to heat control have required the development of appropriate catalyst technology.

It has been noted that while energy requirements for methanol manufacture have been cut by one third since 1923, methanol manufacture remains a large energy consumer.

A major effort is under way to develop a liquid-phase methanol synthesis process in which catalyst particles are suspended in an inert liquid medium. This system prevents excessive temperature increase and so permits greater syngas conversion to methanol in one pass. This decreases expensive recycle. Some believe that this process has the potential to be the most efficient and economical means of producing methanol from coal.

This approach has required the development of appropriate catalyst technology for this system. Catalyst activity maintenance is a key factor and experimental data have been obtained to select catalyst withdrawal/addition scheduling and temperature programming for optimum operation as shown in Figure 12 (Lewnard and others, 1986).

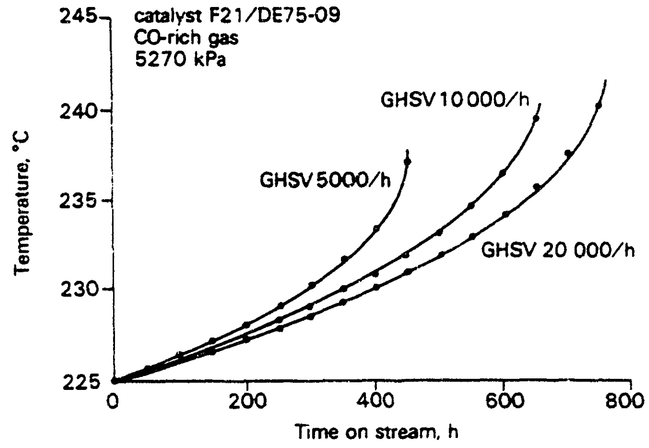


Figure 12 Temperature programming for a LPMEOH (Lewnard and others, 1986)

The liquid slurry catalyst process has been operated successfully in a Process Development Unit (PDU) on a 5–8 t/d methanol scale (Tsao and Heydorn, 1985; Tsao and Rao, 1986; Studer and others, 1987). The so-called LPMEOH™ (liquid phase methanol) continues to be developed vigorously. Further scale-up to commercial size has been proposed.

Liquid systems with suspended catalysts have also been investigated for hydrocarbon synthesis from syngas, discussed later, following original work by Koelbel. To assist in the development of efficient slurry reactors, much basic engineering flow data has been developed for three phase flow dynamics.

One recent novel approach to circumventing thermodynamic limitations is to remove methanol in the reactor itself (Westerterp and Kuczynski, 1986). Selected for this approach was a trickle flow principle in which catalyst pellets form a stationary packed bed and solid adsorbent trickles downward over (through) the packed bed. This Gas-Solid-Solid-Trickle-Flow-Reactor (GSSTFR) has been demonstrated using a low alumina cracking catalyst as adsorbent. It was demonstrated that catalytic conversion proceeded up to complete conversion and that a theoretical treatment can be used to control performance very well.

Control of reaction heat is conventionally approached by multibed reactors with intermediate quench and alternatively by the use of indirect heat exchange. A recent development (Makihara and others, 1987) is the 'superconverter' which features a long (20 metre) double-wall reactor in which heat is removed, allowing high conversion without raising the temperature adversely. This is being tested in a unit having full scale dimensions.

There is a growing body of literature (Fabbricino and others, 1984) suggesting that periodic 'dosing', such as pulsing of the reactor system with carbon dioxide, can cause a substantial improvement in catalytic activity in methanol synthesis.

Another promising 'engineering' approach involves the integration of gasification, methanol synthesis and generation of electricity using efficient combined cycle. Coal gasification is followed by catalytic methanol synthesis on a once-through basis to form methanol (Keller, 1985) with the unreacted gases proceeding to combustion in efficient turbines.

2.1.5 Higher oxygenates: C_1-C_6 alcohols, isobutanol, MTBE, TAME

Relevant thermodynamic considerations and reaction networks for CO hydrogenation have been referred to earlier. Early research in Germany led to processes for production of products containing higher oxygenates, then called Synthol products. These processes were termed Synol synthesis, oxyl synthesis, and isobutyl oil synthesis (Cornils and Rottig, 1982). From a catalyst viewpoint, it has been known since the 1930s that the addition of alkali to methanol synthesis catalysts promotes the formation of higher alcohols and other oxygenates, Table 1 (Natta, 1957). For this type of catalyst, best results were obtained at 440°C, 25 MPa. The most active promoters for the production of higher alcohols are Cs, Rb, and K. From a practical viewpoint, K is used commercially because of the high cost of Rb and Cs. The role of K as promoter in the selective synthesis of higher alcohols has been attributed by DiConca and others (1984) to its basic character which favours condensation of formaldehyde, in agreement with the earlier hypothesis proposed by Natta.

The manufacture of MAS, Metanolo ed Alcoli Superiorie, a mixture of methanol and higher alcohols has been carried by Snamprogetti in a plant having 15,000 t/y capacity. Synthesis conditions were 12–16 MPa, 350–420°C. The percentage

Table 1 Effect of alkaline promoters upon the performance of a ZnO-Cr_2O_3 catalyst employed in the synthesis of alcohols (Natta, 1957)

Fractions obtained in the distillation of product **	Catalyst activated with				
	Li	Na	K	Rb	Cs
Tops	0.9	0.6	0.4	0.5	0.8
CH_3OH	40.4	44.6	53.5	46.6	47.4
C_2	4.6	4.6	3.5	3.8	4.0
	45.9	49.8	57.4	50.9	52.2
C_3	0.5	0.9	0.8	1.6	1.0
Isobutylalcohol (primary)	8.1	12.5	10.3	15.2	15.6
C_5 (amyl alcohols)	0.6	0.9	1.1	1.7	1.3
Intermediates	0.3	0.5	0.9	1.6	1.1
C_6	0.5	1.2	1.0	1.3	1.6
C_7	0.8	1.3	1.2	2.3	2.0
Residue	0.5	2.5	2.3	4.1	4.5
	2.1	5.5	5.4	9.3	9.2
Intermediates 2.4 + distillation loss	1.7	1.7	1.7	2.5	2.4
H_2O	41.1	28.7	23.3	18.8	18.3
Yield, expressed in litres per hour per litre of catalyst	0.585	0.985	0.882	0.980	1.102

* The compositions of the catalysts, expressed in weight percentages, before the reduction of CrO_3 to Cr_2O_3, were the following:

$ZnO:CrO_3:Li_2O = 55.0:36.1:0.32$
$ZnO:CrO_3:Na_2O = 56.1:34.1:0.59$
$ZnO:CrO_3:K_2O = 55.5:35.6:0.96$
$ZnO:CrO_3:Rb_2O = 55.0:35.5:1.90$
$ZnO:CrO_3:Cs_2O = 54.5:33.7:2.20$

As it may be noticed, the alkali contents are equal in all catalysts, if measured in moles

** The concentrations of reaction products are expressed in weight per cent

Table 2 Typical composition of liquid products from synthesis gas over $Cu/ZnO/Al_2O_3$ catalyst at 0.5 H_2/CO ratio, 3300 GHSV, 285°C, 6.6 MPa (Elliott and Panella, 1986)

Compound	Wt%
Water	0.53
Methanol	76.59
Methyl formate	0.64
Ethanol	6.98
Methyl acetate	2.16
1-propanol	3.70
Butanone	0.27
Methyl propanoate	0.39
2-methyl-1-propanol	3.92
1-butanol	1.38
2-pentanone	0.46
2-pentanol	1.07
C_6 ketones	1.05
C_6 alcohols	0.41
C_7 ketones	0.70
C_8 ketones	0.21

composition of alcohols is C_1, 68–72; C_2, 2–3; C_3, 3–5; C_4, 10–15; C_5, 7–12. Blending octane number is $(R + M)/2$ = 106–121.

With the advent of much more active Cu catalysts, interest turned to their application for synthesis of higher oxygenates (Cornils, 1982). The Cu catalyst is capable of high selectivity to methanol. However, when a 'standard' catalyst is operated at 285°C and 6.6 MPa pressure, using a syngas H_2/CO ratio = 0.5, higher oxygenates are formed. A typical composition of liquid products is given in Table 2 (Elliot and Pannella, 1986). Although the main product is methanol under these conditions, significant amounts of higher alcohols are formed including isobutanol.

A detailed study was made of the effect on selectivity and activity by the addition of components to $Cu/ZnO/Al_2O_3/K$ catalysts (Hofstadt and others, 1983). They found that, at 350°C and 10 MPa, MnO favours the formation of ethanol, Cr_2O_3 favours propanol and ThO_2 favours butanol, *see* Table 3.

The effect of Cs and Rb was found to enhance higher oxygenates using a Cu/ZnO catalyst, Figure 13 (Vedage and others, 1983).

Interest in synthesis of isobutanol (2-methyl-1-propanol) is two-fold: it is useful as a gasoline blending agent (octane enhancer and methanol solvent) and, alternatively, for possible manufacture of MTBE. MTBE, methyltertiarybutyl ether, is made by reacting methanol with isobutylene.

Table 3 Effect of promoters on selectivity of Cu-ZnO-Al_2O_3-K catalysts (Hofstadt and others, 1983)

		Distribution of higher aliphatic alcohols, %							
Cat	Promoter*	C_2	C_3		C_4			C_5	$>C_5$
			2-	1-	2-	i-	1-		
B	-	23.1	2.5	33.1	2.0	31.4	1.9	4.0	2.5
B1	MnO	38.4	2.3	36.1	2.0	14.5	2.0	2.7	2.0
B2	Cr_2O_3	18.3	2.4	36.5	1.6	34.6	1.5	2.3	2.8
B3	ThO_2	11.9	2.2	25.9	4.0	42.9	4.3	5.6	3.2
B7	Cr_2O_3	18.2	2.5	37.4	1.5	34.1	1.4	2.2	2.7
D2	Cr_2O_3	18.0	2.5	38.1	1.4	34.0	1.3	2.1	2.6

C_2 = ethanol
C_3, 2- = propan-2-ol, 1- = propan-1-ol
C_4, 2- = butan-2-ol, i = 2-methylbutan-1-ol, 1-= butan-1-ol
C_5 = pentanols
$>C_5$ = higher aliphatic alcohols
* all catalysts contain 3% K and Al_2O_3

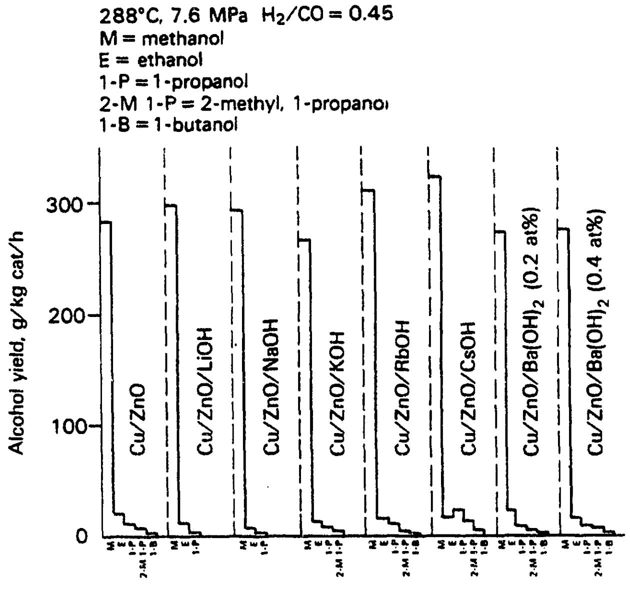
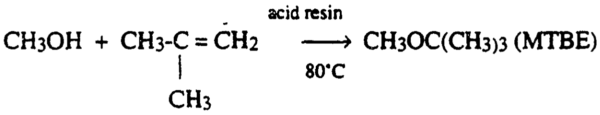
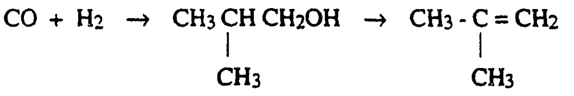


Figure 13 **A comparison of alcohol yields over impregnated CU/ZnO (30/70 mol%) catalyst** (Vedage and others, 1983)



$$CH_3OH + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[80^{\circ}C]{\text{acid resin}} CH_3OC(CH_3)_3\ (\text{MTBE})$$

Isobutylene can be made from isobutanol.



$$CO + H_2 \rightarrow CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2OH \rightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2$$

At present, by-product isobutylene is generally cheaper than isobutylene produced in this manner. However, it is of interest that MTBE can be manufactured wholly from syngas by a multistep route. This may be of commercial interest in special circumstances, such as cheap coal or gas, often in remote locations. It is significant that the use of MTBE, a synthetic fuel which is economically successful despite low oil prices, is growing rapidly worldwide, and its success is based on its high-octane performance values rather than its energy content.

It should be mentioned that TAME, tertiary amyl methyl ether, also a high octane gasoline additive which is manufactured from isoamylene (isopentene) and methanol, is also enjoying growing manufacture and use.

Actually, it is possible to synthesise isobutanol from syngas at fairly high selectivity using alkali-promoted ZnO catalysts, particularly when operated at high temperatures. Early work emphasised severe conditions, 30–40 MPa and >400°C (Natta, 1957).

With Cu/ZnO/Al_2O_3 catalysts promoted with K, relatively high yields of higher alcohols were obtained at <300°C and 10–13 MPa (Smith and Anderson, 1983). Further research showed that caesium is a particularly effective promoter for isobutanol manufacture with the Cu system, Table 4 (Klier and others, 1984, 1987). An extensive laboratory pilot plant study established the optimum parameters for catalysts for maximising isobutanol and other alcohols for use in gasoline (Talbot, 1983).

There are many opportunities for synthesis of chemicals from syngas, $H_2 + CO$, with the addition of a third reactive molecule. One example is OXO alcohols. Slyvinsky and others (1988) have shown that the addition of acetylenic

Table 4 **Product distribution over Cu/ZnO = 30/70 catalysts with varying concentrations of caesium salts** (Klier and others, 1984)

	Cu/ZnO		CsOH/Cu/ZnO (0.4/30/70)		CsOH/Cu/ZnO (0.8/30/70)		CsOOCH/Cu/ZnO (0.4/30/70)	
	Yield	Selectivity*	Yield	Selectivity	Yield	Selectivity	Yield	Selectivity
CO	2136.65	–	1757.35	–	2110.69	–	2015.85	–
CO_2	124.38	–	96.17	–	78.83	–	97.67	–
H_2O	–	–	–	–	–	–	0.32	–
CH_4	3.98	2.06	3.46	1.54	3.89	1.92	3.47	1.72
C_2H_6	1.90	1.06	0.54	0.26	0.37	0.19	0.57	0.30
CH_3OH	283.73	74.31	322.11	71.88	318.66	78.86	303.58	75.31
$HCOOCH_3$	6.16	1.72	7.94	1.89	8.74	2.31	8.04	2.13
C_2H_5OH	20.83	7.59	17.90	5.56	12.92	4.45	15.01	5.18
CH_3COOCH_3	11.13	3.78	8.04	2.33	4.45	1.43	6.68	2.15
C_3H_7OH	12.11	5.07	24.29	8.67	14.95	5.92	17.55	6.97
$(CH_3)_2CHCH_2OH$	5.33	2.41	14.82	5.72	9.01	3.86	12.11	5.20
C_4H_9OH	3.67	1.66	5.59	2.16	2.47	1.06	2.44	1.05
$C_2H_5COOCH_3$	0.53	0.21	–	–	–	–	–	–
$CH_3COOC_2H_5$	0.30	0.12	–	–	–	–	–	–
CO conversion %	14.11		17.54		14.27		14.89	

288°C, 7.6 MPa, $H_2/CO = 0.45$
Total flow rate = 8 l/h
yield in g/kg cat/h,
*selectivity in carbon atom per cent

compounds, as the third component, offers a means of obtaining aliphatic and aromatic alcohols, as well as diols, by reactions designated as 'initiated hydrocondensation of carbon monoxide'.

2.2 Catalysis not involving ZnO

This section is primarily concerned with catalytic research to test novel concepts. The discussion is organised as follows:

- liquid phase systems ;
- modified metal catalysts ;
- catalysis for C_2 oxygenates.

2.2.1 Liquid phase systems

Base catalysis
An entirely different liquid phase system for the manufacture of methanol consists of the synthesis of methyl formate, prepared by reacting methanol with CO in the presence of a homogenous alkali alkoxide catalyst at 80°C, and 3 MPa, followed by catalytic hydrogenation of the methyl formate to methanol at 180°C and 3 MPa. The reaction chemistry is shown below.

$$CH_3OH + CO \xrightarrow{NaOCH_3} HCOOCH_3,$$

$$HCOOCH_3 + 2H_2 \xrightarrow{\text{Cu catalysts}} 2CH_3OH$$

$$CO + 2H_2 \longrightarrow CH_3OH$$

Recent work has shown that the temperature and pressure required for hydrogenation on the formate can be reduced considerably. A pilot plant was reported to have been built in Germany in 1945 (Woodward, 1967). A recent economic evaluation has been made (Rao and DeRosa, 1987) which concluded that the LTMP (two-stage low temperature methanol process) is economically unattractive when cryogenic separation of syngas is required. However, suggestions were made concerning improvements which were regarded as possible.

Dual site catalysts
A liquid phase catalyst system is being developed at Brookhaven (Slegier and others, 1984) based on a dual-function concept of catalysis. One form involves the reaction of syngas using a catalyst consisting of nickel boride and molybdenum hexacarbonyl, Table 5 (Slegier and others, 1984).

The concept involves activation of CO at one site, metal carbonyl, and the activation of H_2 as a hydridic-reducing agent at a second site. Further catalyst development (O'Hare and others, 1986) is pointing to a new low temperature process, the development of which is made possible by a catalyst system (composition not disclosed) that lowers synthesis temperature from 257°C to about 100°C. The new catalyst operates in a liquid phase system which allows synthesis reaction to proceed at isothermal conditions making possible complete conversion of syngas to methanol in a single pass through the methanol synthesis reactor. Significant economic advantages are visualised. A favourable factor, when syngas is generated from methane, is that partial oxidation with air can be used, eliminating the need for an oxygen plant. The catalyst can operate in the presence of nitrogen. Specific technical information has not been made public. There have been reservations about the practical operation, for example its inactivation by CO_2 in syngas.

Table 5 Reactions of syngas employing a dual functional catalyst consisting of nickel boride and molybdenum hexacarbonyl (Slegier and others, 1984)

Run	Millimoles boride*	Temp, °C	Pressure, MPa	Time, hour	Yield, % MeOH†	Yield, % Methane†
1	1.39	150	2.0	4	4.2	–
2	1.42	160	2.0	4	5.4	–
3	1.43	170	2.0	4	7.3	–
4	1.42	180	2.0	4	22.0	–
5	1.39	190	2.0	4	31.0	–
6	1.45	195	2.0	4	33.0	–
7	1.39	200	2.0	4	42.8	51.5
8	1.46	225	5.1	4	49.8	70.2
9	1.42	195	4.6	4	41.6	–
10	1.46	200	5.1	4	48.2	38.2

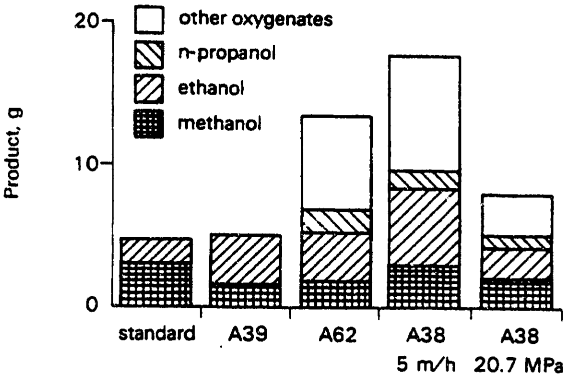
* 5 millimole molybdenum hexacarbonyl in each case
† Yield based on nickel. Stoichiometric yield = 37.5%, based on Ni_2B: $4(Ni_2B)_2H_3 + CO = 3CH_3OH + 8Ni_2B$

Metal complexes
Lapidus and Savelen (1984) reviewed the characteristic features of activation of CO and CO_2 by transition metal complexes. They concluded that in principle homogeneous systems can be developed which are superior to heterogeneous catalysts. They also concluded that the study of metal complex catalysts for reduction of carbon oxides can prove useful both for the development of new industrial catalysts for synthesis of hydrocarbons from mixtures of carbon oxides and hydrogen and for the improvement of existing catalysts.

Advances in catalytic theory and practice involving metal complexes has made such complexes a promising catalyst research subject. It has been found that ruthenium complexes used as catalysts can produce a mixture of C_1 to C_4 alcohols from syngas. Pressures of 40 MPa are required (Dombeck, 1983). The addition of novel ingredients to the catalyst is reported (Dombeck, 1985, 1986) to increase activity and selectivity to higher alcohols and make possible the lowering of the pressure to 200 MPa (Figure 14). In addition, related catalysts were found to promote methanol homologation.

The concept of bimetallic catalysts in which one metal is a good hydrogenation catalyst and the other metal active for carbonylation has been investigated (Whyman, 1986). A homogenous catalyst with a composition of 10/1 Ru/Rh was found to be very effective in converting syngas to C_2 oxygenates, particularly when an alkaline metal ion was used as promoter. Acetate esters were formed in an acetic acid medium. Pressures of 100 MPa were required.

Metal cluster chemistry has entered a period of exponential



3.75 mmol Ru, 15g Bu_4PBr at 34.4 MPa, 230°C and using a $H_2/CO = 1$ synthesis gas

Figure 14 Effect of several additives on a catalytic system (Dombeck, 1986)

growth during the past decade (Gates and others, 1987). Much of the driving force is the prospect of application of metal clusters as catalysts. Metal clusters are compounds containing more than one transition metal atom. $Co_2(CO)_8$ is a cluster. In the presence of hydrogen it is converted to $HCo(CO)_4$, famous as a hydroformylation catalyst, but not considered to be a cluster.

One outstanding example of cluster catalysis is found in the rhodium catalysed hydrogenation of CO to form ethylene glycol (Pruett, 1977). Under reaction conditions of 500°C and 120–200 MPa pressure, rhodium precursors are transformed into a mixture of anionic rhodium carbonyl clusters. The hydroformylation of olefins with $Rh_4(CO)_{12}$ is related reaction chemistry which gives some insight into the role of the anionic rhodium carbonyl clusters in catalytic reactions with CO.

The unique characteristics of clusters and opportunity to synthesise specific variations are believed to provide a bright future for cluster catalysts, particularly for multisite activation of a substrate leading to unusual products.

A different approach to homogeneous catalysts for methanol synthesis was explored using soluble Group VI metal ion complexes (Klingler and others, 1986). In this research hexamethylsilicon and hexabutyltin oxides were found to catalyse five fundamental reactions which form a catalytic cycle for methanol synthesis and water gas shift reactions. The facile formate ion disproportionation is a central feature of this chemistry.

Biocatalysis

The application of biocatalysis to assist in the use of coal has been investigated extensively, especially for sulphur removal (Couch, 1986). In addition, there has emerged the realisation that biocatalysis may find an application for conversion of syngas to liquid fuels. The biological production of fuels from coal-derived gas has been the subject of a recent review (Gaddy, 1986) and exploratory research (Barik and others, 1986; Clausen and Gaddy, 1986) as well as a preliminary evaluation of the technical and economic potential (Duthie, 1985, 1986).

The survey concluded that, theoretically, microorganisms acting on syngas, which can be made from coal, can produce many chemicals including methanol, ethanol, butanol, acetic acid, propionic acid, and acetone. Of these, only the organisms capable of producing acetate have been isolated and studied. It is noted that methane may be formed easily from CO by the action of methane-producing bacteria. The conversion of syngas to methane was demonstrated (Augenstein and others, 1977) but no advantage was seen over the use of conventional nickel catalysts which are highly selective for methane synthesis. It is noted that a methanotrop may be used to produce methanol or formaldehyde from methane. Table 6 lists microbial cultures capable of converting CO, CO_2, H_2, or acetates as primary substrates. However, in general, little in-depth information is available in the literature.

It has been suggested that sewage sludge, soil and so on, rather than pure cultures, be screened for CO and acetate conversion. Screening studies have shown the influence of some of the parameters, for example the importance of pH. Preliminary results showed slow CO conversion to alcohols, some 40% of CO converted going to alcohols, predominantly ethanol. These results are regarded as encouraging.

A technical and economic predictive estimate has been made. For the purpose of evaluating the potential of bioconversion, assumptions were made believed to be achievable (Bechtel, 1986). Capital and operating costs were estimated for ethanol production to be as low as 60 cents per gallon (all are US gallons in this report) using utility type financing, compared

Table 6 Summary of microbial cultures using CO, CO_2, H_2, or acetate as primary energy substrates* (Gaddy, 1986)

Organisms	Source	Energy substrate(s)	Major products
Desulphobulbus propionicus	estuarine sediment	acetate	propionate
Rhodopseudomonas capsulata	natural environment	acetate butyrate	$H_2 + CO_2$
Acetobacterium woodii	marine estuary	$H_2 + CO_2$	acetate
	rumen	carbon monoxide	acetate + CO_2)
Acetoanaerobium noterae	swamp sediment	$H_2 + CO_2$	acetate
Clostridium aceticum	sludge	$H_2 + CO_2$	acetate
Clostridium thermoaceticum	sludge	carbon monoxide	acetate + butyrate
Clostridium thermoautotrophicum	sludge	carbon monoxide $H_2 + CO_2$	acetate + butyrate

* partial list

with 106–128 ¢/gal reported as costs of fuel grade ethanol. Sensitivity to cost-determining parameters were established to help guide future research.

2.2.2 Modified metal catalysts

Molybdenum catalysts

Catalysts containing molybdenum can readily convert syngas to methane. However, alcohols can be synthesised employing properly formulated molybdenum catalysts operated under suitable conditions (Table 7). The nature of the support greatly influences the activity of supported MoS_2 in CO hydrogenation (Mauchausse and others, 1988). The most active catalysts have supports which are able to react with H_2S to form sulphide species thus decreasing the number of Mo-O-support inhibiting linkages.

A process to convert syngas to alcohols over a molybdenum catalyst is in an advanced development stage. Most versatile are catalysts based on poorly crystalline MoS_2 derived from the rapid heating of MoS_3 or an ammonium thiomolybdate salt. Alkali promoted catalysts result in, on a CO_2-free basis, 80–90% selectivity to alcohols containing 50–60% C_2-C_5 alcohols. When promoted with Co or Ni salts, and operated at 30–60% conversion, methanol can be reduced to 25–35% while retaining a total selectivity to oxygenates of >80%. With these doubly promoted catalysts, the parallel reaction of homologating to initially formed alcohols is significant. Relatively large deviations from the statistically predicted C_2 and C_3 fractions result from this secondary reaction (Murchison and others, 1987).

Molybdenum sulphide catalysts have been characterised by electron microscopy, XPS, X-ray powder diffraction and catalytic performance. The incorporation of caesium was found to enhance conversion selectivity (Klier and others, 1986, 1987).

A systematic laboratory pilot plant study (British Coal, 1987) of molybdenum sulphide catalysts for conversion of syngas examined the effect of support, Mo and K loading, temperature, H_2/CO ratio, pressure, flow rate, and time on steam. Carbon used as a support was found to be superior to Al_2O_3 or SiO_2. A 20% MoS_2 – 10% K_2CO_3/C catalyst, provided for a straight line increase in CO conversion from 270°C, an increase in alcohol yield between 170 and 350°C, followed by constant production at 350°C and a gradual increase in C_1-C_3 products, Figure 15.

Detailed results of tests using a 1:1 H_2:CO ratio over a range of temperatures are shown in Table 8.

The variation of yields of various alcohols and hydrocarbons is shown. The temperature for maximum yield of desirable

Table 7 Catalytic activities and principal products formed over MoS_2 catalysts from synthesis gas. (Klier and others, 1985)

Catalyst*	Surface area m^2/g	Temp, °C	Pressure, MPa	H_2/CO	GHSV, h^{-1}	% CO conversion	Principal products†	Researcher
MoS_2	23.5	350	0.1	3.1‡	4000-6500	0.5-0.8§	>97% CH_4	McMaster Univ
MoS_2	63	255	8.3	0.92	3140	5.0	55.6% CH_4 43.6% C_2+HC 0.8% CH_3OH	Lehigh Univ
3% KOH/MoS_2	2.2	350	2.05	1.97	179	52	96.3% C_5+HC	EXXON
4% KOH/MoS_2	27	262	8.21	0.76¶	676	16.5	42.5% CH_3OH 32.7% C_2H_5OH 10.6% CH_4	Dow Chemical
10% K_2CO_3/66% MoS_2/20% clay	-	255	10.45	1.02**	3171	16.3	53.2% CH_3OH 24.9% C_2H_5OH 12.6% CH_4	Dow Chemical
10% K_2CO_3/MoS_2	60	255	8.3	0.92	3140	9.5	57.7% CH_3OH 17.4% C_2H_5OH 17.1% CH_4	Lehigh Univ
17.4% KOH/MoS_2	-	300	2.75	1.00	12,000	4.4	35.5% CH_3OH 36.6% C_2H_5OH 19.0% CH_4	Union Carbide

* wt%

† carbon atom %; CO_2-free basis

‡ similar results obtained with a H_2/CO = 1 synthesis gas

§ after 45 hr of testing; initial activity was approximately 60% higher

¶ contained 20 ppm H_2S

** contained 50 ppm H_2S

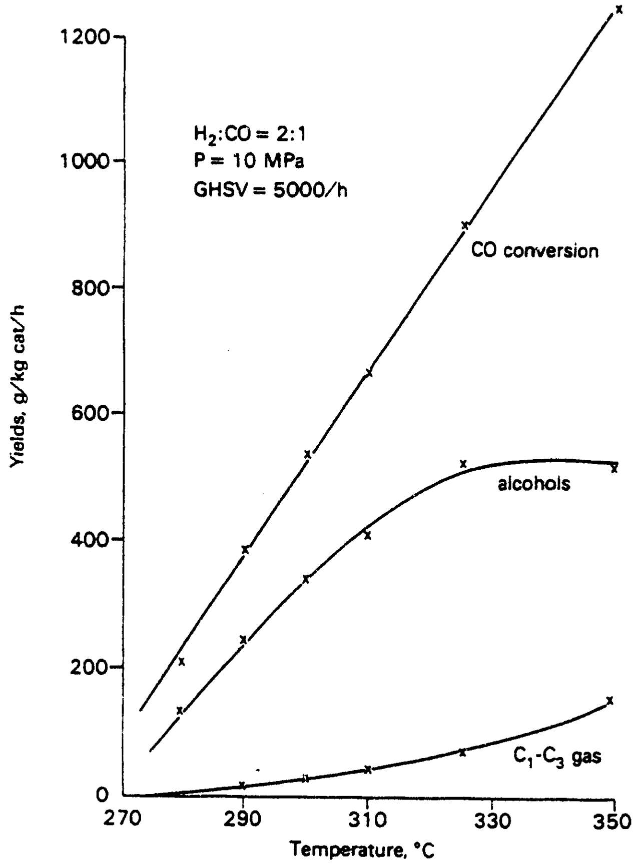


Figure 15 Yields as a function of temperature, MoS_2 catalyst (British Coal, 1987)

products was found to be 310°C. Optimum efficiencies appear to be at a CO conversion rate of 650 g/h/kg catalyst. Efficiencies at 300°C were 49% in CO and 39% in H_2 consumption, 55% in CO_2 produced, 75% in gas made on a weight basis. These low efficiencies were caused by high hydrocarbon gas production.

Alkali-promoted Mo catalysts have also been investigated for alcohol synthesis from syngas. Selectivity to alcohols as opposed to hydrocarbons is greatly influenced by the precursor and K salts (Tatsumi and others, 1985, 1986, 1987). Further, the sequence of impregnation is important (Tatsumi and others, 1986). The remarkable effect of KCl on increasing alcohol production compared to K_2CO_3 for SiO_2-supported catalysts may be partly due to its ability to prevent Mo species from interacting with SiO_2. Further, the addition of alkali metal halides to Mo/SiO_2 was found to increase activity and selectivity with increased processing time. Over Mo-KF/SiO_2 the alcohols comprised 70% by weight of the total product on a CO_2-free basis. However, the KCl-promoted catalyst gave the highest CO conversion (Tatsumi, 1987). It was suggested that the presence of K effectively prevents the complete reduction of Mo to metal, resulting in increased production of alcohols (Muramatsu and others, 1987).

Table 8 Conversion of syngas over a MoS_2/carbon/K_2CO_3 catalyst*: effect of temperature upon yields and selectivities (British Coal, 1987)

Operating conditions						
Temp, °C	275	290	300	310	320	330
Pressure, MPa	10.1	10.1	10.1	10.1	10.1	10.1
GHSV, l/h/l cat	3106	3196	3080	3046	3095	3056
H_2:CO	1	1	1	1	1	1
Recoveries, %	105.3	107.9	104.7	102.9	104.8	104.1
Conversions, /h/kg cat						
CO, g	263.2	473.9	687.3	893.5	1170.6	1513.6
CO, mols	9.4	16.9	24.5	31.9	41.8	54.1
CO, wt% of CO fed	6.8	11.9	17.8	23.5	30.3	39.6
H_2, g	15.6	28.1	43.8	61.1	76.1	95.8
H_2, mols/mol CO	0.8	0.8	0.9	1.0	0.9	0.9
Yields, g/h/kg cat						
C_1	16.9	29.3	50.4	79.1	116.1	128.5
C_2	0.0	7.8	7.3	20.2	33.0	37.1
C_3	0.0	0.0	0.0	9.9	19.4	18.1
C_{4+}	0.0	0.0	0.0	0.0	12.8	11.9
CO_2	104.3	195.5	330.6	464.8	677.5	1087.3
MeOH	79.1	141.6	161.6	184.3	181.5	145.5
EtOH	57.6	92.0	127.7	140.0	135.4	108.1
PrOH	18.2	28.5	47.2	58.3	69.8	61.9
H_2O	2.8	7.2	6.2	-2.0	1.3	10.9
Total	278.8	502.0	731.0	954.6	1246.8	1609.4
Selectivities, wt% of CO						
C_1	6.4	6.2	7.3	8.9	9.9	8.5
C_2	0.0	1.7	1.1	2.3	2.8	2.4
C_3	0.0	0.0	0.0	1.1	1.7	1.2
C_{4+}	0.0	0.0	0.0	0.0	1.1	0.8
CO_2	39.6	41.3	48.1	52.0	57.9	71.8
MeOH	30.0	29.9	23.5	20.6	15.5	9.6
EtOH	21.9	19.4	18.6	15.7	11.6	7.1
PrOH	6.9	6.0	6.9	6.5	6.0	4.1
H_2O	1.1	1.5	0.9	-0.2	0.1	0.7
H_2	-5.9	-5.9	-6.4	-6.8	-6.5	-6.3
Total	100.0	100.0	100.0	100.0	100.0	100.0
Selectivities, CO_2 free, wt%						
C_1-C_4	9.7	12.1	14.4	22.3	31.8	37.5
MeOH	45.3	46.2	40.4	37.6	31.9	27.9
EtOH	33.0	30.0	31.9	28.6	23.8	20.7
PrOH	10.4	9.3	11.8	11.9	12.3	11.9
H_2O	1.6	2.4	1.5	-0.4	0.2	2.1
Total	100.00	100.00	100.00	100.00	100.00	100.00

* 19% MoS_2/SS610 Carbon (5% K_2CO_3)

The addition of Ni to Mo-KCl/SiO_2 greatly enhanced alcohol production in CO hydrogenation and improved selectivity to C_{2+} alcohols, Table 9 (Tatsumi and others, 1986). Almost all the oxygen leaves the reaction as CO_2 rather than H_2O, due to the activity of the Mo catalysts for the CO shift reaction. The formation of a Ni-Mo alloy was confirmed for a used catalyst by observation of corresponding X-ray diffraction lines, with the Mo content of the alloy estimated to be 30 wt% from the lattice spacing.

The hydrogenation of carbon dioxide over alkali-promoted

Table 9 Performance of Mo-M (Fe, Co, Ni)-K/SiO_2 catalysts*

Catalyst			CO	CO_2	Alcohol		C_{2+}/C_1 ratio	
Mo	M	K	conv, %	yield %,	STY†	Sel‡	Alcohol	HC
5	-	0.84	0.44	0.14	2.9	66	0.97	1.2
5	5Fe	0.84	0.64	0.13	2.6	33	3.4	1.2
5	5Co	0.84	0.52	0.14	3.1	46	4.2	1.5
5	5Ni	0.84	2.9	1.7	16	48	2.1	1.4
5	5Ni	1.63	1.8	0.74	6.9	56	2.0	1.3
10	-	1.63	0.52	0.15	3.6	71	1.4	1.8
-	10Ni	1.63	0.28	0.14	0.44	21	0.38	0.79

* Reaction conditions;
523 K, 1.6 MPa ($CO/H_2=1$), W/F = 10 g cat h/mol
† space-time yield, g/kg-cat h
‡ selectivity in carbon atom per cent

Mo/SiO_2 catalyst to form C_1-C_5 alcohols was demonstrated (Tatsumi and others, 1985). MoS_2 catalysts containing large amounts of alkali are capable of converting syngas to C_1-C_4 alcohols. Bifunctionality has been attributed to the alkali activation of CO and MoS_2 dissociatively activation of H_2 (Santiesteban and others, 1988). The addition of Ni to Mo-K/SiO_2 was found by Tatsumi and others (1988) to be effective for enhancing alcohol production, ascribed to the formation of a Mo-Ni alloy.

Fe, Co, Ni catalysts for alcohols

While Fe, Co, and Ni have long been known for their catalytic capability to hydrogenate CO to methane, it has been found possible to utilise catalysts containing these metals for the synthesis of alcohols. Indeed the standard alkali-promoted iron FT catalyst produces significant amounts of alcohols. Oxygenates are enhanced if this type of catalyst is modified by nitriding and reaction conditions are adjusted to augment oxygenates formation (Anderson, 1984; Schulz and others, 1988).

Early patents on alkalised Co catalysts for production of oxygenates from syngas provided the basis for operation of the so-called 'Synthol' process in Germany.

Recently it has been disclosed (Courty and others, 1982; Grandvallet and others, 1984) that Co catalysts can be used to produce C_1-C_6 alcohol mixtures when certain rules are followed during preparation of the catalyst. Only certain precursor materials possessing certain phase composition and crystallographic structure lead to catalysts which are active in higher alcohol synthesis. The main steps in preparation of a copper-cobalt-aluminium zinc mixed oxide catalyst have been described (Grandvallet and others, 1984) to obtain well dispersed Cu-Co bimetallic catalyst. This type of catalyst has been characterised and tested for methanol decomposition at atmospheric pressure and a mechanistic picture given for the functioning of the catalyst.

The IFP process being developed (Courty and others, 1982, 1984, 1987) is described as based on Cu and Co as being the key components, associated with at least one other metal as well as alkali. This permits formation of 20–50% C_2 alcohols.

While cobalt and nickel catalysts are well known for their capability to hydrogenate CO to hydrocarbons, they can be modified to enhance their capability to synthesise alcohols (Sugi and others, 1985). The formation of C_2 oxygenates was found to be increased by modification of Co/SiO_2 by Ru or Re and alkaline earth metals. X-ray photoelectron spectroscopy (XPS) measurements suggest that cobalt is kept in a moderate oxidation state by the synergistic effect of the transition metal and alkaline earth, and further, that the formation of C_2 oxygenates occurs on a partially reduced cobalt site (Kaneda and others, 1985). Additional information is provided for modification of cobalt catalysts for the enhancement of C_2 oxygenates in CO hydrogenation.

Nickel catalysts are capable of producing higher alcohols such as ethanol and propanol when catalysts are prepared by coprecipitation of Ni with titanium or manganese oxide and further promoted with copper and sodium. It was observed from temperature programmed desorption (TPD) measurements that the amount of associatively adsorbed CO on copper is remarkably increased when Na is added to the catalyst (Uchiyama and others, 1985). A coprecipitated Ni-TiO_2 catalyst produced higher alcohols along with methanol, and a coprecipitated Ni-ZnO catalyst selectively produced methanol, while a coprecipitated Ni-Al_2O_3 catalyst produced hydrocarbons, mainly methane (Hayasaka and others, 1988).

Platinum group metals

Palladium. Since palladium is well known for its ability to hydrogenate CO to CH_4, it was rather a surprise when it was reported (Poutsma and others, 1978) that palladium catalysts produced sizeable amounts of methanol when operated at conditions under which methanol is thermodynamically possible. Modest amounts of methyl formate and ethylene glycol were also observed. Since that time, many varied studies have established the importance of the support (Ryndin and others, 1981), Pd particle size (Ichikawa and others, 1984), and an understanding of intermediates active in the catalytic chemistry (Ponec, 1982). There is considerable support for the belief that the presence of Pd ions is somehow essential for methanol synthesis. Pd compounds wholly in ionic form are not active in converting syngas to methanol.

Hydrogenation of CO to form methanol, ethanol, and acetaldehyde was investigated at atmospheric pressure over alkali doped Pd and Rh catalysts on various supports. During reaction, surface formate or acetate ions were detected by infrared spectroscopy (Naito and others, 1984). No such species were detected in undoped samples. Using tracer techniques, it was demonstrated that active sites for oxygenated compound formation contain some surface oxygen and that alkali metal cations are effective in preserving such surface oxygen.

In a study on Pd/MgO/SiO_2 catalysts it was possible to detect formyl species by a chemical trapping method (Hindermann and others, 1984). Moreover, a correlation was found between concentration of formyl surface complex and methanol activity of the catalyst, which has given rise to a mechanism in which the reaction takes place on oxidised palladium in the neighbourhood of the support or promoter. Chemical trapping was also used by Vedage and others (1984) to elucidate the accelerating effects of H_2O on hydrogenation over Cu/ZnO.

Although the copper catalysts provide for 99% selectivity to methanol, there is still a need for an improved methanol catalyst. Pd may be able to provide the basis for a catalyst which can operate with more activity and stability (Kikozono and others, 1981).

Platinum. The role of the support for Pt-based catalysts for selective formation of methanol was determined by Meriaudeau and others (1984) who determined that catalysts such as Pt-ThO_2 act as bifunctional catalysts and that for catalysts such as Pt-SiO_2 or -Al_2O_3, the mechanism is probably via a formate intermediate.

Rhodium, ruthenium, iridium. In addition to methanol, much attention has been devoted to catalysts for the synthesis of higher alcohols from syngas, particularly with Rh catalysts. Supported rhodium catalysts have received greatly increased attention during the past decade, not only with a view to developing catalysts for the production of oxygenated products by CO hydrogenation, but also because of the excellent opportunity to study the fundamental relationship between catalyst structure and performance. Interest has been heightened by the finding that activity and selectivity to oxygenates can be greatly influenced by the support (reviewed by Bell, 1987) and by added constituents which act as promoters (Dai and Worley, 1986; Chuang and others, 1985; Goodwin and Wender, 1985).

The interpretation of surface chemistry of CO hydrogenation over supported rhodium catalysts has been controversial (Poels and Ponec, 1983). Various concepts have been proposed to account for the observations (Kawai and Ichikawa, 1985). Early work (Ellgen and others, 1979; Wilson and others, 1981) established the dramatic effect of small quantities of Mn, Mo, W, Fe on the activity of Rh/SiO_2 catalysts. It was postulated that the promoter forms a mixed oxide with Rh which decreases the rate of CO dissociation and thus favours the increased selectivity to oxygenates.

Basic supports were reported (Katzer and others, 1981) to favour formation of oxygenates, but no clear correlation between basicity of the support and activity has been established (Bell, 1987). Rare earth oxides such as lanthanum have also been found to be effective in enhancing rhodium for syngas conversions (Underwood and Bell, 1987; Bond and Richards, 1986). A strong interaction was found between Ru and Al_2O_3, shown in the influence on activity for CO hydrogenation over Ru/Al_2O_3. When the catalyst is strongly reduced, CO conversion activity increased. XPS showed that the Ru is electronegatively charged (Okada and others, 1984).

The oxidation state of Rh has been assigned a major role in determining activity and selectivity (Sachtler, 1984; Poels and Ponec, 1983; Poels and others, 1984; Lee and others, 1986, 1987). A great deal of data has been developed concerning the necessity of Rh^{1+} for formation of oxygenates, but this still remains controversial. Data accumulated in the last decade (Lee and others, 1986, 1987) indicate that Rh^{m+} species promote methanol synthesis, perhaps by being centres of synthesis and that Rh^{m+} species are not necessary for, but may promote, formation of higher alcohols.

The concept of requiring an 'ensemble' of metal ions has been advanced with the belief that a certain minimum size is necessary to provide the several sites necessary for dissociation of CO and H_2 chemisorption. Small ensembles favour oxygenates since less dissociative chemisorption occurs on them.

It was found that the dispersion of Rh in Rh/SiO_2 has a strong influence on activity and selectivity for hydrogenation of CO (Arakawa and others, 1984). With decreasing dispersion, turnover frequency of CO conversion does not change significantly up to 0.5. CH_3OH is produced selectively at high dispersion. C_2 oxygenated compounds are produced favourably for dispersions 0.25–0.45. CH_4 formation decreased monotonously with decreasing dispersion (less methane at high dispersion) (Figure 16). However,

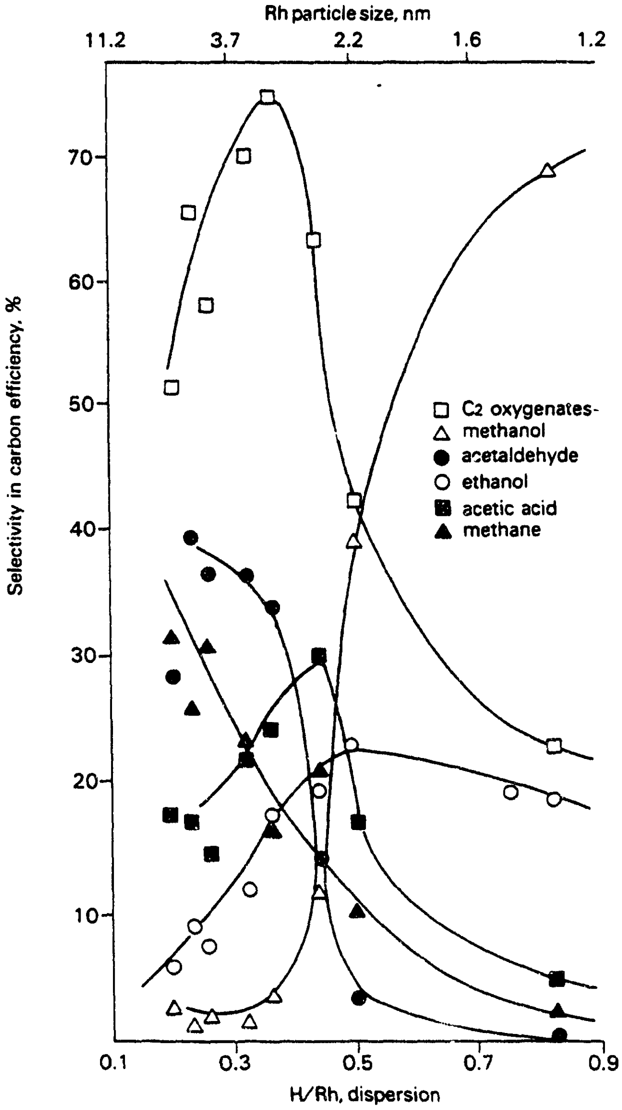


Figure 16 Relationship between dispersion and selectivity (Arakawa and others, 1984)

Table 10 Hydrogenation of CO over silica-supported molybdenum-iridium catalysts (Kuwahara and others, 1985)

Catalyst no	Metal loading, wt%		GHSV h^{-1}	CO conv, %	Carbon atom selectivity, %									CO_2
					Hydrocarbons					Alcohols				
	Mo	Ir			C_1	C_2	C_3	C_4	C_5	C_1	C_2	C_3	C_4	
I*	3.2	0	62	0.61	22	8.0	3.6	1.3	0	0	0	0	0	65
II*	0	6.5	62	0.60	42	7.6	4.2	2.2	0.7	15	2.0	0.9	0	25
IIIA*	2.5	5.0	6000	3.0	28	7.5	4.0	1.7	0.8	23	11	3.3	1.0	18
IIIB	2.4	6.2	2000	3.8	26	6.4	3.5	1.2	0.7	22	11	3.7	1.2	23
IV†	2.5	6.4	2000	8.2	24	5.6	2.9	1.2	0.6	23	9.4	2.6	0.9	28
V‡	2.3	6.9	2000	3.4	25	6.3	3.2	1.1	0.6	24	10	3.7	1.5	24
VI§	2.4	6.4	2000	0.65	27	7.9	4.3	2.4	1.0	19	12	4.0	1.4	19

Conditions: $CO:H_2:Ar=3:6:1$, 2.13 MPa, 220°C

* results obtained after 4 h on stream, 240°C

† Ir-doped Mo/SO_2

‡ Mo-doped Ir/SO_2

§ after impregnation, the catalyst was calcined in air at 500°C for 3 h and reduced in H_2

differences in activity have been attributed to differences in morphology of the particles (Kip and others, 1988).

Crystal size effect for Ru/Al_2O_3 was also found for hydrogenolysis of butane (Lin and others, 1986).

Attention has been focused on the activity of bimetallic catalysts for CO hydrogenation. Along this line it was found that catalysts containing both Ir and Ru are effective in formation of oxygenated compounds. The addition of Li brought about improvements in both activity and selectivity (Hamada and others, 1984). The promotion effects for an Ru/Al_2O_3 catalyst have also been reported by Mori and others, 1986. Fukushima and others, 1985, found that the addition of Fe to Ir/SiO_2 improves yield and selectivity towards methanol (90% carbon efficiency) owing to suppression of methanation.

Kuwahara and others (1985) found that Mo-Ir catalysts are even more effective than Ir-Ru, even through Mo or Ir catalysts have little activity alone. $Mo\text{-}Ir/SiO_2$ catalyst prepared by coimpregnation was about 500 times as active as Mo/SiO_2 or Ir/SiO_2. Alcohols with up to four carbon atoms were formed in experiments at 220–240°C and 2.1 MPa pressure (Table 10).

In a study of bimetallic catalysts, Niemantsverdriet and others (1988) conclude that for $FeIr/SiO_2$ the active sites for methanol formation contain noble metal and iron cations. Ichikawa and others (1988) found cluster-derived bimetallic catalysts prepared from SiO_2-supported Rh_4Fe carbonyl clusters exhibit markedly higher activities and selectivities towards oxygenates which mainly consist of ethanol and methanol.

Multimetallic catalysts such as $Rh\text{-}Ti\text{-}Fe\text{-}Ir/SiO_2$ have been investigated by Arakawa and others (1985). Ethanol was produced at more than 50% selectivity from syngas over $Rh\text{-}Ti\text{-}Fe\text{-}Ir/SiO_2$ tested at 50 MPa and 260°C (Table 11). This multi-promoted catalyst was specially developed to enhance ethanol production. The performance of Rh/SiO_2 catalysts altered by individual metals was investigated, followed by the approach of using multimetals. From X-ray diffraction line broadening, Rh crystalline size was estimated to be 3.3 nm. Changes in XRD pattern and diffraction patterns indicate major changes in crystallite behaviour with individual modifiers and combinations. Most interesting is that peaks due to Rh crystallites are not observed in the case of catalysts containing TiO_2 additive except for $Rh\text{-}Ti\text{-}Fe\text{-}Tr/SiO_2$.

Arakawa and others (1988) suggest the concept of two classes of promoters for Rh/SiO_2, those which increased CO

Table 11 Reaction behaviour of promoted Rh/SiO_2 catalyst (Arakawa and others, 1985)

	Selectivity, %								
Catalyst	CO conv	MeOH*	EtOH*	AcH	AcOH*	C_2-oxy	CH_4	C_{2+}	CH_4/C_{2+}
Rh/SiO_2	2.9	2.3	6.5	34.2	34.9	75.5	18.4	2.3	8.2
Rh-Ir (1:0.5)/SiO_2	3.1	2.3	17.5	31.2	25.8	74.5	20.3	1.4	14.3
Rh-Ti (1:1)/SiO_2	12.2	9.1	22.5	6.8	13.7	43.2	32.7	9.2	3.6
Rh-Fe (1:0.3)/SiO_2	5.9	11.7	39.0	1.7	7.3	48.0	32.8	2.0	16.4
Rh-Ti-Fe (1:1:0.3)/SiO_2	14.3	3.4	42.2	2.9	12.0	57.0	30.6	3.3	9.3
Rh-Ti-Fe-Ir (1:1:0.3:0.5)/SiO_2	12.5	3.7	50.7	1.8	12.5	65.0	21.5	2.6	8.3

Each catalyst contains 4.7 wt% of Rh. Number in a parenthesis shows an atomic ratio of additives to Rh. Data were obtained at a time on stream of 2 h. * denotes the sum of neat product and ester. C_2+ denotes the sum of hydrocarbons other than CH_4. Reaction conditions; catalyst charge: 1.0g, reaction pressure: 5.1 MPa, reaction temperature:260°C, flow rate: 100 ml/min, syngas ratio (H_2/CO):1.

conversion based on acceleration of CO dissociation and those which improve selectivity based on the control of electronic state and ensemble of Rh particle. By the combination of additives, efficient multi-promoted catalysts were designed. Ethanol and acetic acid were produced with more than 50% selectivity over Rh-Ti-Fe-Ir/SiO_2 and Rh-Mn-Li/SiO_2 respectively. A high CO/H_2 ratio, for example 9, is essential for selective synthesis of acetic acid.

It has been suggested that the modifier affects the bonding of CO to the metal (van den Berg and others, 1985) in what might be called an electronic effect. Lowering the heat of bonding to the metal, weakening the CO bond or assisting in tilting the CO so that to some extent both ends of the CO molecule are attached to the surface have all been discussed. Infrared studies have generally shown that promoters cause a lowering of the C-O bond strength and increase Rh-CO bond strength.

Ichikawa and others (1984) concluded that Mn, Ti, and Zr additions promoted considerable CO dissociation on Rh metal and also stabilised surface oxygen and C_2-oxygenated precursors to improve the yield of C_2 oxygenated products. In contrast, Fe suppressed CO dissociation and enhanced reactivity of Rh for the hydrogenation of C_2 oxygenate precursor to ethanol as well as associative CO into methanol. Addition of Mo to Rh/ZrO_2 catalysts maintains good CO dissociation properties and, at the same time, favours CO insertion and formation of C_{2+} oxygenates (Carimate and others, 1988).

A comprehensive mechanism has been proposed (Sachtler and Ichikawa, 1986) in which a 'dual site' model was deduced involving dissociative chemisorption of CO and H_2, the formation of CH_x adsorbed groups and a chain reaction on an ensemble of Rh atoms. Liu and others (1988) have shown by chemical trapping techniques that the main reaction-pathway involves ketene as an intermediate in formation of ethanol over promoted Rh/SiO_2 catalysts.

It should be noted, by the way, that the formation of CH_x is required for synthesis of higher oxygenates. Since CH_x can proceed to form methane and higher hydrocarbons, the avoidance of hydrocarbon formation in higher alcohol synthesis is difficult, more so than in methanol synthesis.

Recently it has been discovered that when relatively large amounts of molybdena or vanadia are incorporated into supported rhodium catalysts, the activity for CO hydrogenation increased more than ten-fold and selectivities to oxygenates are also augmented significantly (Jackson and others, 1986; Sudhakar and others, 1987; Foley and O'Toole, 1987; Kip and others, 1987).

As noted in Table 12 (Bhore and others, 1988) the Mo/Al_2O_3 catalyst has very low activity and does not form oxygenates. The dramatic influence of incorporating a large amount of molybdena in Rh/Al_2O_3 catalyst is to increase CO conversion, water gas shift reaction, selectivity to oxygenates and C_1 oxygenates as a percentage of oxygenates. Other effects are: absence of aldehydes, low acetic acid and esters, and high ether formation.

Table 12 Syngas conversion by Rh/Mo/Al_2O_3 catalysts: effect of catalyst composition on product distribution (Bhore and others, 1988)

Catalyst	3% Rh	3% Rh/ 7.5%Mo	3%Rh/ 2% Na	15% Mo
Temp, °C	250	250	275	250
GHSV, (h^{-1}	3000	36000	820	3000
CO Conv, %	5.7	5.3	6.1	1.8
of CO Conv, % to CO_2	1	25	7.3	50
of CO converted, % Converted to: (CO_2 free basis)				
Hydrocarbons	72	34	62	100
CH_4	61	26	56	60.9
C_2H_6	4	6	4	29.4
C_3H_6	5	2	1.6	9.7
C_4H_{10}	2	0	0	
Oxygenates	28	66	38.6	0
MeOH	2	16	1.9	
MeOMe	1	26	0	
MeCHO	2	0	9.4	
EtOH	11	7	8.8	
MeOAc	3	1	3.5	
HOAc	0	0	2.5	
EtCHO	0.4	0	2.4	
n-PrOH	2.7	1	0	
MeOEt	3	15	0	
EtOAc	3	0	10.1	
C_1 oxy	5	47	3	
C_2 oxy	21	17	33	
CH_4 + C_1 oxy	61+5=66	26+47=73	56+3=59	

A comparison of the kinetics of CO hydrogenation reactions over Rh/Al_2O_3 with and without added MoO_3 established that the hydrogenation capability of the former is not inhibited by CO as it is for the latter. From these and other evidence, a dual site mechanism has been proposed (Figure 17) in which

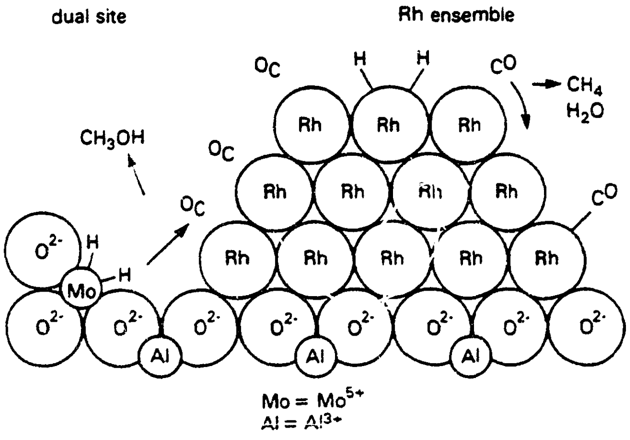


Figure 17 Proposed structure/reactivity scheme, rhodium-molybdena-alumina catalyst (Sudhakar and others, 1987)

CO is activated by Rh and H_2 by MoO_{3-x} with migration (spillover/reverse spillover) of hydrogen to the activated CO complex. Increased hydrogenation capability is a consequence of separate activation of CO and H_2. This concept is believed to be of value in the design of more effective catalysts of this type.

Alloy catalyst for alcohol synthesis

Catalysts derived from rare earth/copper intermetallic precursors have been found (Jennings and others, 1987) to exhibit extraordinarily high activity for methanol synthesis by CO hydrogenation. Methanol synthesis was observed at temperatures as low as 100°C. A stable activity of 25 moles of methanol per kilogram of catalyst per hour was obtained for a catalyst derived from $CeCu_2$. In situ XRD studies revealed that the formation of certain intermediate hydride phases is critical to the formation of the active catalyst. Both intermetallic and rare earth hydrides are involved. XRD and transmission electron microscopy (TEM) analysis showed that discharged catalysts contain large crystallites of Cu (40–80 nm) and the corresponding lanthanide oxide. Methanol activity does not appear to correlate with copper crystallite size, and BET N_2 isotherms gave total surface area of less than 5 m^2/g.

It was also shown that these catalysts are irreversibly deactivated when exposed to low concentrations of CO_2. These findings strongly suggest that the reaction mechanism which obtains here is quite different from that which operates with conventional $Cu/ZnO/Al_2O_3$ catalysts.

In other work, a better understanding of alloy surfaces for CO hydrogenation was provided by Szymanski and others (1984) who found that alloying Pt with Zr increased selectivity to methanol, especially on a ZrO_2 support.

2.2.3 Catalysis for C_2 oxygenates: ethanol, acetic acid

Ethanol from methanol

The manufacture of ethanol from syngas by a multistep process, first synthesising methanol, then adding CO and H_2 to form ethanol, has the important advantage that each step is now well known and proceeds with high selectivity.

The invention by scientists at Monsanto of a process for manufacture of acetic acid by insertion of CO into the methanol molecule, using a rhodium- or iridium-iodine catalyst, has been an outstanding success worldwide. This has led to the concept of the manufacture of ethanol from methanol by adding the further step of hydrogenating the acetic acid to ethanol.

In the Ensol process (Humphries and Glasgow, Monsanto, BASF), the chemical reactions are:

$$H_2/CO \longrightarrow CH_3OH \xrightarrow{CO} CH_3CO_2H \xrightarrow[-H_2O]{H_2} CH_3CH_2OH$$

Alternatively, the Davy-McGee process (Marten and Camps, 1986) involves hydrogenation of methyl acetate as follows:

$$H_2/CO \longrightarrow CH_3OH \xrightarrow[-H_2O]{CO} CH_3CO_2CH_3 \xrightarrow{H_2} CH_3CH_2OH + CH_3OH$$

The homologation or reductive carbonylation of methanol to yield ethanol plus acetaldehyde and acetates has been much studied, but has not yet been commercialised (Comils and Rottig, 1982).

$$CH_3OH + 2H_2 + CO \xrightarrow[RuCl_3.I_2]{Co_2(CO)_8} CH_3CH_2OH + H_2O$$

Cobalt catalysts, first used, are still the best catalysts in their activity and selectivity. Rhodium produces acids and esters together in addition to ethanol.

A very significant discovery in methanol homologation has been the rate enhancement associated with the addition of iodide or iodine. MeI is formed which enters into the reaction cycle. A selectivity to acetaldehyde of greater than 60% can be obtained at 68% conversion. For the production of ethanol, ruthenium has been found to be the best cocatalyst since all aldehyde is hydrogenated to ethanol (Wender and Seshadri, 1984). For comparison, it should be noted that methanol carbonylation to acetic acid proceeds with 99% selectivity. There is an opportunity for improvement in methanol homologation selectivity.

Acetic acid from syngas

Homogeneous catalyst systems have found important industrial applications in the manufacture of acetic acid and acetic anhydride from syngas. The reactions involved in the Tennessee Eastman Company integrated productions of chemical from coal are shown below. The conversion of methyl acetate to acetic anyhydride represents a novel application of a homogeneous rhodium-iodine catalyst (Larkins, 1986).

$$2H_2 + CO \xrightarrow{Cu\text{-}ZnO} CH_3OH$$

$$CH_3OH + CO \xrightarrow{Rh} CH_3COOH \text{ (acetic acid)}$$

$$CH_3OH + CH_3COOH \xrightarrow{H^+} \underset{\text{(methyl acetate)}}{CH_3COOCH_3} + H_2O\,,$$

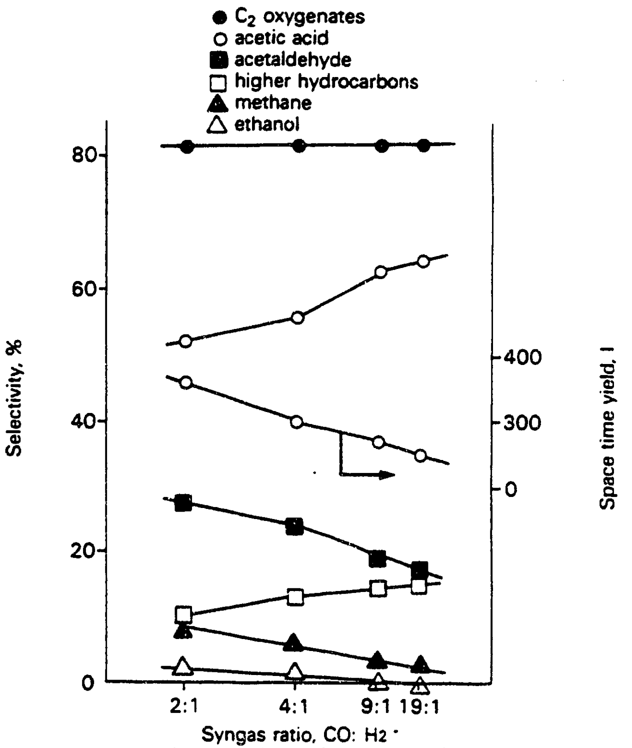
$$CH_3COOCH_3 + CO \xrightarrow{Rh+I_2} \underset{\text{(acetic anhydride)}}{(CH_3COO)_2O}$$

$$(CH_3COO)_2O + \text{cellulose} \longrightarrow \text{cellulose acetate} + \underset{\text{(recycled)}}{CH_3COOH}$$

The efficient manufacture of acetic acid directly from syngas offers the possibility of a route for the manufacture of ethanol which is better than the multistep processes which have been discussed.

Commodity chemicals such as acetic acid and ethylene glycol, as well as C_1-C_4 alcohols, useful as gasoline components, can be generated directly from synthesis gas by the application of 'melt' catalysts. These melt catalysts generally comprise ruthenium carbonyls, oxides and so on, dispersed in low melting point (mp <150°C) quarternary phosphonium salts. Optionally, a second transition metal derivative may be added to ensure improved yields of particular products. Ruthenium, cobalt, and halogen are key elements of the catalyst to produce acetic acid directly from syngas (Knifton, 1986, 1987). For example, as shown in Table 13, a liquid product containing 76 wt% acetic acid plus 1.1% propionic acid were produced at 48.8 MPa.

The synthesis of acetic acid from syngas over supported multimetal catalysts has been investigated (Nakajo and others, 1986). It was found possible to produce acetic acid with more than 63% selectivity over Rh-Mn-Zr-Li/SiO_2 catalysts at 300°C and 10 MPa pressure of syngas having a CO/H_2 ratio of 9. There is a striking influence of CO/H_2 ratio on the selectivity to acetic acid shown in Figure 18.



reaction conditions 10.4 MPa 300°C
Rh:Mn:Zr:Li=1:⅓:⅛:⅔ atomic ratio

Figure 18 Influence of syngas ratio on reaction behaviour over 3wt% Rh-Mn-Zr-Li/SiO_2(Nakajo and others, 1986)

In further work (Nakajo and others, 1987), a striking effect was found on acetic acid selectivity for high pressure hydrogenation of CO by treatment by H_2S of the catalyst Rh-Ir-Mn-Li/SiO_2 (Table 14). The role of treatment by H_2S on CO catalytic chemistry was studied by FTIR, ESCA, and chemisorption. ESCA measurements showed that the electronic state of Rh particles was not much influenced by the H_2S treatment. From FTIR measurements, it was determined that the bridged-species almost disappears with H_2S treatment, leaving linear-CO species. It was found that the amount of CO chemisorbed decreased with H_2S treatment. These results suggest that H_2S treatment reduces the amount of bridged-CO species which contributes to increase in CO

Table 13 Carboxylic acids from synthesis gas (Knifton, 1986)

Catalyst precursor	Product composition (mmol)*							liquid yield, %
	CH_3COOH	C_2H_5COOH	CH_3COOMe	CH_3COOEt	CH_3COOPr	H_2O	CH_4	
Ru(acac)$_3$-CoI$_2$	110	1	2	9	2	20	53	66
RuO$_2$2CoI$_2$†	33	5	0.2	4	2	7	22	24
Ru$_3$(CO)$_{12}$-CoI$_2$‡	58	0.4	3	9	2	10	18	41
Ru$_3$(CO)$_{12}$-CoI$_2$	116	5	4	34	6	10	37	84
RuO$_2$-CoBr$_2$	132	2	32	81	20	25	156	204
RuO$_2$-CoCl$_2$	50	7	39	66	11	382	678	358§
RuO$_2$-CoCO$_3$	60	2	31	47	9	225	374	299¶
Ru$_3$(CO)$_{12}$-Co$_2$(CO)$_8$	34		2	5		6	1	29
RuO$_2$-Co$_2$(CO)$_8$-I$_2$	113	3	6	23	6	19	122	108
RuO$_2$-CoI$_2$-I$_2$	20			1	0.3	1	15	11
RuO$_2$-CoI$_2$-4MeI							24	<2
CoI$_2$								<2
Ru$_3$(CO)$_{12}$‡			23	16	3	14	141	192

Operating conditions: 48.8 MPa; 220°C; 18 hr; CO/H_2, 1:1
Reaction charge: Ru, 4.0 mmol; Co, 4.0 mmol; Bu_4PBr, 10.0 g quaternary salt
* Analysis of gas and liquid samples by glc; CH_3COOEt and CH_3COOPr fractions contain small quantities of C_2H_5COOMe and C_2H_5COOEt respectively, liquid products may also contain smaller quantities of MeOH, EtOH, PrOH, MeOOCH, and $(CH_2OH)_2$
† Reaction charge: Ru, 4.0 mmol; Co, 8.0 mmol
‡ Run time, 6 h
§ Product also contains: MeOH, 150 mmol; EtOH, 136 mmol; PrOH, 29 mmol; liquid product comprises two phases
¶ Product also contains: MeOH, 107 mmol; EtOH, 104 mmol; PrOH, 23 mmol
** Product also contains: MeOH, 244 mmol; EtOH, 110 mmol; PrOH, 11 mmol

Table 14 Influence of H_2S treatment of the catalyst on the reaction behaviour (Nakajo and others, 1987)

H_2S/Rh atomic ratio	CO conv %	Selectivity in carbon efficiency, %					STY† of CH_3COOH g l^{-1} h^{-1}
		CH_3COOH	CH_3CHO	C_3+* oxygenates	CH_4	C_2-C_6 hydrocarbons	
0.000	6.4	55.4	19.1	9.5	3.2	11.1	450
0.004	4.5	63.9	20.4	5.3	3.0	5.9	359
0.006	3.0	67.2	20.2	4.2	2.8	3.8	260
0.011	1.9	69.4	19.9	3.4	2.8	2.3	171

Catalyst: 7.0 wt%Rh(1)-Ir(1/8)-Mn(1/48)-Li(1/16)/SiO_2
Catalyst charge: 10 ml
Reaction conditions; temperature: 300°C, pressure 9.8 MPa, GHSV: 10000 h^{-1}, CO/H_2: 9/1
* sum of C_2H_5CHO, C_3H_7CHO, and C_2H_5COOO
† space time yield

conversion as well as higher hydrocarbon formation. Thus chain propagation is suppressed and acetic acid selectivity increased.

2.3 Catalytic decomposition of methanol for fuel use

Syngas can be made available as a fuel by the catalytic decomposition of methanol or catalytic reaction of methanol with steam. There is a gain in fuel efficiency if waste heat is used to carry out the conversion of methanol to syngas. Investigation of the use of syngas as an engine fuel dates back at least to 1970. The heating value of the syngas is greater than the methanol from which it was derived. Conversion of methanol to syngas is endothermic. When waste exhaust heat is used which is available on board an automobile (or in a power plant) to decompose methanol, greater efficiency can be achieved: 15% when methanol is steam reformed and 20% when it is dissociated (Yoon and others, 1985). However, engine tests have shown a fuel consumption benefit at the same equivalence and compression ratio is actually about 3–7% (Mills and Ecklund, 1987).

A catalytic methanol dissociation reactor is not very proficient at providing good transient response. Experimental development now is focused on a composite system using dissociated methanol and very lean mixtures at light to medium loads, and liquid methanol with lean to stoichiometric mixtures as the load increases to full output.

The use of catalysts to enhance fuel-use efficiency presents opportunities of considerable potential. This is a research area which has been relatively neglected.

2.4 Commentary

This chapter has discussed advances in catalysis for conversion of syngas to oxygenates. ZnO-containing catalysts have been extensively investigated. The morphology of Cu-ZnO-Al_2O_3 catalysts has been established. Alumina acts to stabilise catalytically favourable forms consisting of ternary platelets of Cu-ZnO-Al_2O_3 and binary Cu-ZnO, in both of which there is an intimate dispersion of Cu in ZnO. It has been established that the precursors used in catalyst preparation are of critical importance. Significant also is the finding that activity for methanol synthesis is directly proportional to copper metal surface area. Further, reaction chemistry studies have established that the pathway to methanol for this catalyst type is through CO_2 and not through CO. However, additional investigation has shown that Cu^{1+} is also involved and that the oxidation state of the copper is dependent on gas phase composition, particularly CO_2 and H_2O content, which controls the Cu/Cu^{1+} redox couple. Thus, recent reaction mechanism and catalyst characterisation studies have established to a great extent the reaction network pathways, including the important water gas shift reaction, and the critical role played by the copper in its different oxidation states. It is believed that this scientific knowledge can act as a guide and as an inspiration for the design of new and improved catalysts.

There has been considerable progress in the development of liquid slurry catalyst systems for methanol synthesis. There is considerable optimism that the heat control provided by this type of system can provide for more economical manufacture. There are opportunities for further improvements, such as catalysts which operate with higher stability. A novel concept which has been demonstrated is the integrated catalytic synthesis and separation of product methanol. The technology for manufacture of C_1-C_6 alcohols has been improved and demonstrated commercially. There is still an important need to decrease methane formation which occurs at the elevated temperatures used in higher alcohol synthesis. Relatively high amounts of isobutanol are produced and there are indications, such as by incorporation of caesium in the catalyst, as to how isobutanol selectivity can be increased. Isobutanol is of interest not only as an octane enhancer in gasoline, but also because of its potential in the manufacture of MTBE. Total manufacture of MTBE is possible from syngas. It is noted that the worldwide manufacture of MTBE, which involves synthetic methanol, represents a very important advance in synfuels technology and commercialisation.

Non-ZnO catalysts studies have been a particular active and fruitful research field. Complexes of transition metals, notably ruthenium, have been discovered which, in homogenous systems, are capable of alcohol synthesis from syngas. These are regarded as promising for improved control of activity and selectivity. Recently it has become recognised that enzymes, themselves metal complex catalysts, have the capacity to convert syngas selectivity to C_2 oxygenates, specifically ethanol and acetates. Biocatalysis, long famous for high selectivity and activity at low temperature, offers a new, or at least little explored, direction for research. There is a special interest in ethanol as a fuel. The technology for its production from syngas has developed along three lines: homologation reactions (better selectivity needed), multistep synthesis via CO insertion into the methanol molecule followed by hydrogentation (high selectivity demonstrated, commercial plants proposed), or by direct synthesis using supported-metal catalysts. Much improved Group VIII metal catalysts have been synthesised utilising the concept of multimetal combinations which combine to enhance activity and selectivity. These have been shown to convert syngas to alcohol mixtures with >50% selectivity to ethanol or, alternatively, to >50% to acetic acid. Even higher selectivity (76%) to acetic acid has been achieved using a novel 'melt' catalytic system containing ruthenium carbonyls dispersed in low-melting phosphonium salts. For supported metal catalysts, the control of product formation by metal particle size appears to be an important finding. Selectivity to methanol of 75% was observed for Rh of 1.2 nm size and 75% to C_2 oxygenates for 11.2 nm size. This has been attributed to reaction control by multiple active site interactions which depend on ensemble size. It is important to note that the understanding of supported transition metal catalysts has advanced greatly in respect to influence on activity and selectivity by choice of support, metal combinations, added chemical modifiers. As a consequence, a modified cobalt catalyst has been developed which is being considered for industrial installation. The search for special alloy catalysts has uncovered a remarkable combination of Ce and Cu which convert sbygas to methanol at a high activity a the very low temperature of 100°C. Unfortunately, this catalyst is deactivated by CO_2. Special attention is directed to molybdenum-containing catalysts. Those based on MoS_2 have been studied extensively and optimised for synthesis of oxygenates. Their performance has been established under detailed pilot plant tests under varied process conditions. Additionally, it has been discovered that catalysts, typified by $Rh\text{-}MoO_3\text{-}Al_2O_3$, have unusually high activity and improved selectivity to oxygenates. The concept of dual sites, with one site activating CO and the other activating H_2, opens the way for enhanced design of improved catalysts.

Finally, it has been pointed out that the use of catalysts to increase fuel use efficiency presents opportunity of considerable potential.

3 Hydrocarbon fuels from syngas

In this chapter, key features in the long development of FT catalytic technology are summarised. Then recent research on catalysts which do not contain zeolites is presented. Catalysts which contain zeolites are then discussed, beginning with the technology of the methanol-to-gasoline process and proceeding to research on direct conversion of syngas to high octane gasoline. This is followed by a review of catalysts to improve process engineering, specifically FT operated to produce a high wax content product, followed by selective cracking to liquid fuel; FT operated in the slurry phase; and variations of operating conditions to improve selectivity. FT chemical reactions and the relationship between catalyst structure and performance are then discussed. The next section reviews recent research on selective conversion of syngas to isoparaffins or to low molecular weight olefins. Finally, there is a summary of the Koelbel-Engelhardt process involving the conversion of CO and H_2O to hydrocarbons.

3.1 Development of catalytic background

The development of technology for the catalytic conversion of syngas to hydrocarbon fuels has been the subject of thorough reviews. However, these reviews stress past accomplishments and generally do not address new and emerging catalytic developments to be discussed in this report. None the less, past experiences do provide critical information. It has been said that a broad jump into the future can benefit from a good running start. Early reviews are valuable in pointing out catalytic concepts which have been tried (Storch and others, 1951; Pichler, 1952; Anderson, 1956; Emmett, 1956), information derived from their extensive industrial application in Germany and South Africa (Hoogendoorn, 1977; Dry, 1981, 1982, 1986, 1987; Frohning, 1980; Frohning and others, 1982), their overall status (Wender and Seshadri, 1984; Haag and others, 1987). Some reviews providing insight into progress in catalytic phenomena (Mills and Steffgen, 1973; Vannice, 1976, 1987; Ponec, 1978; Lee and Ponec, 1987; Falbe, 1967, 1970, 1977, 1980, 1982; Keim, 1983, 1986; Fahey, 1987). Other reviews have specifically addressed the methanol-to-gasoline MTG process (Chang, 1983; Voltz and Wise, 1976).

The development of catalysts for conversion of syngas to hydrocarbon fuels began in 1902 with the discovery of Sabatier and Sanders that Ni promotes formation of methane. In 1910 Mittasch, Bosch and Haber had discovered that iron modified by alkali can convert nitrogen and hydrogen to ammonia. By 1923 Fischer and Tropsch had found that while Fe catalyses the conversion of syngas to methane, a mixture of alcohols and higher hydrocarbons is formed when Fe is modified by alkali addition. The Synthol process (not to be confused with the Sasol Synthol process, Cornils and Rottig, 1982) was commercialised that year in Germany producing mixed alcohols, as was the process for making synthetic methanol. It should be noted that selection and control of pressure and temperature, H_2/CO ratio in the syngas feed (lower H_2/CO gives higher wax formation) and avoidance of impurities, contributed to successful catalyst performance. Worldwide interest was aroused and considerable catalyst and process development was carried out, notably in Great Britain.

During the period 1935–45, which includes World War II, employing a cobalt catalyst, the FT process was used to produce gasoline in Germany, reaching 10,000 BPD in 1944. A considerable research effort was made to develop Fe-based catalysts to replace costly Co, but Fe catalysts were not commercialised. Following the war, operation of the German plants was discontinued because of the availability of less costly petroleum. Several significant catalytic discoveries were made. It was found that ruthenium is particularily capable of making high yields of wax products. Also, the isosynthesis process was found by Fischer and Pichler (reviewed by Cohn, 1956), with high selectivity to isoparaffins, particularly isobutane, using ThO_2 catalysts and operated at relatively high temperature. It was in this period also that Otto Roelen, in related chemistry, discovered the OXO reaction.

Following the war, Koelbel pioneered a development programme using a liquid catalyst slurry system which provided better heat control and so allows higher syngas conversion. Also, with Engelhardt, he invented the KE process in which CO reacts catalytically with steam to produce hydrocarbon products. The 1950s was a period of intense research. In the US the Bureau of Mines established a wide technology base including thermodynamic correlation for syngas reactions, recognition of the important kinetic influence in determining chain length distribution of higher hydrocarbons and alcohols (Anderson, 1983), and establishment of the catalytic performance of a wide variety of catalytic compositions including the use of nitrided iron catalysts. An oil-recycle reactor FT plant was placed in operation in Louisiana, MO, using Fe catalysts. However, this plant was shut down after brief operation due to the discovery of large petroleum reserves, as was the Hydrocol plant built by industry in Brownsville, Texas. This latter plant used an iron catalyst modified by 1% alkali in a fluid bed mode for heat control.

However, responding to the special circumstances in South Africa, the FT process has been installed in a major way beginning in 1955 when SASOL I, an 8000 BPD plant was placed in operation, followed by SASOL II (50,000 BPD) in 1980 and SASOL III of similar size in 1983. These plants utilise an alkalised iron catalyst, SASOL I in the lower temperature fixed-bed Arge process and the higher temperature entrained-fluid-bed Synthol process (Figure 19) in SASOL I, II and III.

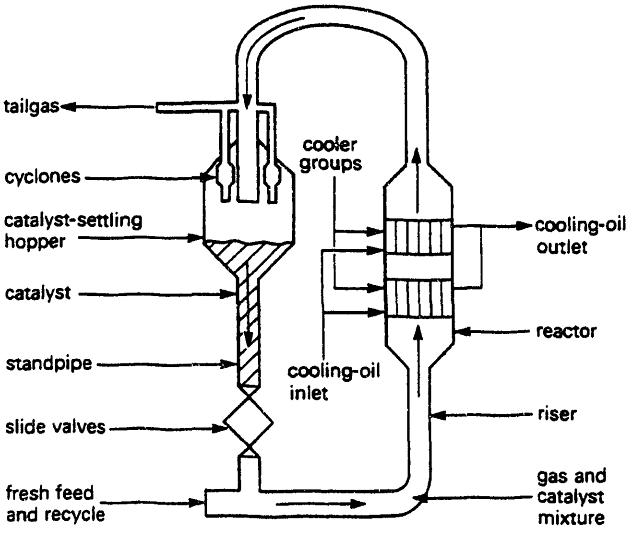


Figure 19 Schematic diagram of entrained fluidised-bed FT reactor

A significant new industrial development was the installation in 1986 of the MTG process in New Zealand, producing 14,500 BPD, corresponding to one third of their gasoline needs. This process has been regarded as the first new catalytic system in 50 years for conversion of syngas to gasoline, involving a new type of catalyst in which methanol, manufactured from syngas, is converted with high selectivity into high octane gasoline using a catalyst containing ZSM 5 molecular sieve.

It should be mentioned that from the 1970s, when the oil crisis was experienced, until 1986 when oil prices were greatly lowered, was a period of intensive research for synfuels production from coal. Synfuels reseach has largely been discontinued, particularly by industry. During this period, research focused on surface science of catalysts, catalytic mechanisms as influenced by catalyst structure, combination catalysts of group VIII metals with zeolites, catalysts for slurry reactors, and catalysts for process schemes developed to avoid high methane formation. In addition to FT slurry reactors, new process schemes have involved conversion of syngas either to olefins which are polymerised to fuel liquids or to high wax products which are hydrocracked to liquid fuels. Attention also focused on catalysts capable of utilising cheaper syngas of lower H_2/CO ratios produced by advanced high temperature gasifiers (H_2/CO of 0.5 vs 2.0 for low temperature gasifiers).

While much has been learned since 1902, relatively few catalysts are utilised and, with the exception of ZSM 5, the catalysts are essentially those discovered 50 years ago, Ni for methane, alkalised Fe, Co, Ru for FT, and those containing ThO_2 for isosynthesis. During this period there has been great developments involving a wide array of catalysts for petroleum refining and petrochemicals. Are there new opportunities in catalysis for converting syngas to liquid hydrocarbon fuels? This is now addressed. As Antoine de Saint Exupery said in his book, *Wind, Stars, Sea and Sand*, 'When it comes to the future, our task is not to forsee it, but to enable it to happen.'

3.2 Non-zeolite catalysts

Fe, Co, Ni, and Ru are considered to be the active metals in FT catalysts. The catalyst used in Germany consisted of Co-ThO_2-MgO-kieselguhr (silica) in 100:5:8:200 parts by weight (Frohning and others, 1982). The catalyst in the Sasol units are alkalised (K) Fe. The catalyst for the Arge unit is prepared by precipitating iron hydroxide into silica gel. The catalyst for the Synthol units is made by melting iron oxide and additives and then grinding to a powder, in a manner similar to the preparation of iron synthetic ammonia catalysts.

Extensive research has established that Fe is less active in hydrogenation than Co and so produces more olefins and alcohols. Ru is noted for its capability to produce higher molecular weight hydrocarbons. Fe is well known for its water-gas-shift (WGS) activity, but neither Co nor Ru are active. For catalysts without WGS activity, the oxygen in the CO is rejected as water, so that a syngas having a H_2/CO ratio of 2 is required in making olefins or alcohols and an H_2/CO use ratio slightly larger than 2 in making paraffins. For catalysts that promote the WGS reaction, the oxygen in CO is mainly rejected as CO_2. The water formed in the FT reaction reacts with the CO to form additional H_2. Consequently, low H_2/CO ratio syngas can be used with these catalysts, with a practical minimum of about 0.6.

Higher selectivity to desired products is the primary objective in seeking improved catalysts. Catalysts having higher activity and stability are additional goals. In addition to CO hydrogenation ability, the capability of accelerating the water gas reaction is also desired. This makes possible the utilisation of more economical syngas having lower H_2/CO ratios. Comils and others (1984) have described the important aspects of developments for selective synthesis via the FT process. The coupled dependency of catalyst composition, preparation, pretreatment, and synthesis conditions were stressed. The effect on selectivity of each of these factors was illustrated.

Selectivity sought in FT reactions usually emphasises higher yields of high octane gasoline, although in certain circumstances high yields of diesel fuel of good cetane number can be of prime importance. Recently, there has been new interest in production of C_2-C_4 olefins used either to make liquid fuels or used as chemical feedstocks. Further, there has been new emphasis on formation of isoparaffins as being more desirable for environmental reasons than aromatics for octane enhancement.

From the viewpoint of catalyst composition, the capabilities of metals for CO hydrogenation were established by 1925. Further progress in the last 50 years to obtain improved selectivity and catalyst stability has been achieved by the use of promoters, support selection and preparational conditions. The concept of adding chemical constituents, 'promoters', to more or less conventional catalysts has been widely tried and discussed. In addition, a number of innovative ideas for improved catalyst preparation have been investigated.

Nitrides, carbides, carbonitrides, borides have been shown to be active for FT. Nitrided iron catalysts show improved stability against deterioration caused by oxidation and free carbon deposition. They preferentially catalyse synthesis of alcohols and low boiling hydrocarbons (Anderson, 1983, 1984). The nitrided catalyst was more active and produced less gaseous hydrocarbons than the corresponding reduced catalyst, Table 15.

Table 15 Tests of reduced and nitrided catalysts at high space velocity and temperature* (Anderson, 1984)

Atom ratio, N:Fe	0	0.40
Gas composition, H_2:CO	1.3	1.0
Space velocity, h^{-1}	2300	2820
Temperature, °C	316	288
Contraction, %	51	48
Yield, wt% of total hydrocarbons		
C_1	10.3	8.6
C_2	14.8	13.7
C_3	20.4	16.6
C_4	16.8	14.2
Condensed products		
Up to 204°C	26.2	36.3
Heavy oil	7.2	9.5
Wax	4.3	1.1

* Operating pressure, 2.53 MPa

Iron nitride catalysts have been characterised recently using modern techniques (Delgass, 1986; Schulz and others, 1988). Metal borides have also been examined, although catalytic tests were not promising (Bartholomew, 1986).

Raney Fe-Mn has been shown to be two to four times as active as similar catalysts made by coprecipitation (Hanson and others, 1987; Chen and others, 1986).

Bimetallic clusters which have been sulphided, such as $C_{5\text{-}8}Mo_2Fe_2S_{1.8}$, were demonstrated to be sulphur-tolerant CO hydrogenation catalysts (Curtis and others, 1988).

The concept of *epitaxial* deposition has been used to prepare a novel non-magnetic Fe on Cu 111 and Cu 110. The Fe has remarkable electronic properties and interesting preliminary catalytic properties for syngas conversion (Cooper and Montano, 1986). Spinel $MgAl_2O_4$ has been tested as a support for Ce-Co (Kondoh and others, 1986).

Alloys have also been investigated. Alloys of Fe, Co, and Ni on a support were shown to generally enhance catalytic activity and suppress methane formation (Aria, 1987). Also, special porous and amorphous $Ni_{67}Zr_{33}$ alloys have been prepared and are being tested for catalytic properties (Shimogaki and others, 1985).

It has been shown that the *particle size* of supported Ru is important (Abrevaya and others, 1986, 1988). Small particles, 1 nm, produced significant proportions of higher hydrocarbons, and large single crystals, 11 nm, gave mainly methane (Lin and others, 1985, 1986, Figure 20).

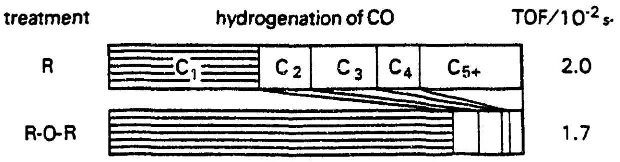


Figure 20 **Selectivities and turnover frequencies for hydrogenation of CO over 2.5% Ru/Al_2O_3 prepared from $Ru_3(CO)_{12}$ at 260°C, 0.1 MPa, H_2/CO=2** (Lin and others, 1986)

The concept of *partial poisoning* provides a powerful means of improving catalyst selectivity, interpreted in terms of ensemble control (Rostrup-Nielsen and Alstrup, 1988). Stengen and Sattenfield (1985) and Matsumoto and Sattersfield (1987) reported decreased methane formation by sulphur poisoning of a fused magnetite FT catalyst. Along this line, Tong and McCarty (1987) examined Fe catalysts treated with a sub-monolayer of chemisorbed sulphur. They found that the treated catalysts had a threefold reduction in methane selectivity relative to the untreated fused iron, when tested in 2:1 H_2/CO syngas at 300°C and atmospheric pressure. The C_2 olefin selectivity approached 100%. McCarty and Wilson (1986) also demonstrated the improvement in selectivity with Fe treated with low levels of sulphur, *see* Figure 21.

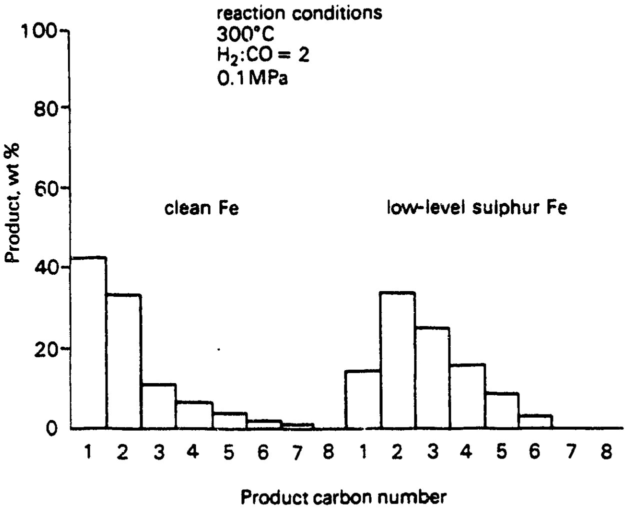


Figure 21 CO hydrogenation over clean versus low-level sulphur-treated Fe (McCarty and Wilson, 1985)

It has been found that *physically mixed catalysts*, as distinguished from chemically mixed catalysts, can hydrogenate coal to produce methane (Echigoya and Niiyama, 1982). Interparticle spillover is believed to provide for a remarkable acceleration in this conversion of coal to methane. This concept may have application in formation of liquid hydrocarbons.

3.3 Zeolite-containing catalysts

Zeolites are porous crystalline solids which have well defined pore systems and large internal surface areas. The diameters of their pores are similar to that of hydrocarbon fuel molecules. This has led to the application of zeolites in catalysts as 'shape selective' components since only certain size or shape molecules can enter and leave the internal porous structure. The most common forms of zeolites are alumino-silicates which can act as strong acids. The structure of ZSM 5 is shown in Figure 22. The 5.6 nm pore opening is formed by a ring of 10 oxygen ions. The crystal structural arrangement is depicted by lines drawn between the center of oxygen ions. The pores can also be visualised as tubes whose three dimension interconnections are also shown.

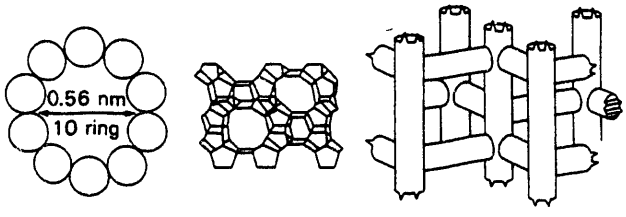


Figure 22 Structure of ZSM 5 zeolite

3.3.1 Methanol to gasoline and related processes

The methanol to gasoline (MTG) process represents a new approach to the conversion of syngas to gasoline involving the application of a new type of catalyst. This two-step process provides for gasoline of high octane quality at high selectivity. Syngas is first converted to methanol which, in a second step, is converted nearly quantitatively to high octane gasoline over a catalyst containing the molecular sieve ZSM 5, Figure 23. Invented by scientists at Mobil (first disclosed by Meisel and others, 1976) the technology was developed under the joint technical direction and financial sponsorship (30/70) of Mobil and US DoE (Mills, 1977). The MTG process has been installed in New Zealand using a fixed-bed mode, producing 14,500 BPD gasoline, one third of the New Zealand needs. The syngas is produced from off-shore natural gas. The process development has been described in detail (Voltz and Wise, 1976) as has the chemistry (Chang, 1983; Chang and Silvestri, 1977, 1979).

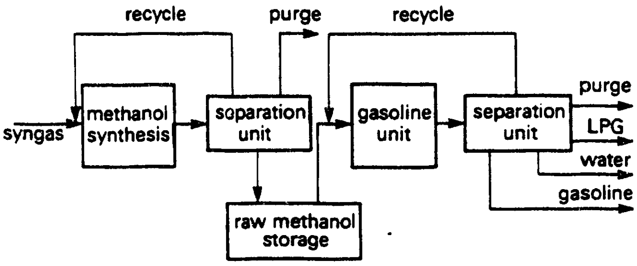


Figure 23 Two-stage methanol to gasoline (MTG) process

Operation of the MTG in the fluid-bed mode has been tested in a 100 BPD plant in Germany (Socha and others, 1986). The products distributions obtained with the two modes are shown in Table 16.

Much research has been devoted to understanding the scientific aspects of the MTG reaction chemistry, to develop alternative or improved catalysts, to process simplification, to changing process conditions to maximise olefin production, to use of the MTG catalyst to upgrade products from conventional FT operation, and to development of a hybrid slurry FT/MTG process. The reaction mechanism has been particularly related to the unique properties of ZSM 5 zeolite (Chang, 1983; Ono, 1983, 1987; Haag and others, 1987). Catalysts have been investigated in which Al in the ZSM 5 crystal framework has been replaced by other ions. The introduction of Zn or Ga is said to increase selectivity to aromatic compounds (Ono, 1987).

Technology has been developed for integrated gasoline synthesis by modifying three process steps, syngas production, oxygenate synthesis, and MTG, in order to be able to operate all steps at the same pressure and the last two steps in one single synthesis loop, without isolation of the synthesised methanol. The TIGAS (Topsoe Integrated Gasoline Synthesis) process (Topp-Jorgensen and Dibbern, 1986) utilises combined steam reforming and autothermal reforming for syngas production and uses a multifunctional catalyst system, to produce a mixture of oxygenates instead of only methanol. The front end and the oxygenate synthesis can operate at the same relatively low pressure. When the MTG is integrated into the oxygenate synthesis, producing both methanol and dimethyl ether, the operating conditions are

Table 16 Typical process conditions and product yields for MTG processes (Haag and others, 1987)

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 outlet 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)	93	97

relatively mild. The integrated concept results in a simple flow scheme, Figure 24, and lower investment costs.

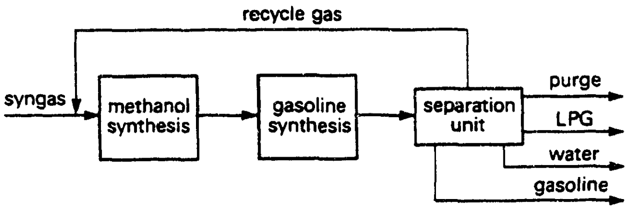


Figure 24 Topsoe integrated gasoline synthesis (Topp-Jorgensen and Dibbern, 1986)

Alternatively Lurgi has developed a direct heat exchange MTG reactor concept, Supp (1985).

3.3.2 Direct conversion of syngas to liquid fuel

Early in the development of the two-step MTG process, it was recognised that it would be preferable to develop a process in which syngas is converted to gasoline in one step. A combination methanol synthesis/shape selective catalysts was deemed to offer a promising approach. However, results were disappointing in that too much methane is formed. A basic problem is that favourable pressure/temperature regimes differ considerably for operation of the two different catalysts. Since that time, a wide variety of catalytic approaches has been tried to develop catalysts which can directly convert syngas to liquid fuels of high octane (Denise and others, 1984)

Suppression of methane formation during syngas conversion has been sought by modifying a combination transition metal/zeolite catalysts (Melson and Zuckerman, 1988). For a Co/SiO_2-ZSM 5 catalyst, the addition of Cu lowered methane and increased C_{5+} yield from 72% to 76% (Rao and others, 1986).

The promotional effects of cations on zeolite supported FT catalytic metals has been tested by Goodwin and Wender (1986), Oukaci and others (1986, 1987), who found that the olefin to paraffin ratios are highest when the larger alkali ions have been exchanged into the zeolite, while selectivity to isoparaffins is enhanced by smaller alkali ions.

There is a strong conviction in the scientific community that zeolites possess great potential as support for metals active in FT. Combination catalysts of Co/special zeolites/promoters have been developed which demonstrate improved activity and selectivity (Miller and others, 1986, 1987) specifically lower methane and higher C_{5+} and reduced sensitivity to H_2/CO ratio, Table 17.

Table 17 Support effects on Co/X_{11} catalysts* (Miller and others, 1986)

Catalyst support Conversion	γ-alumina 45.6	TC-103 42.8	TC-133 49.6	TC-123 48.0
C_1	6.7	5.3	5.4	3.6
C_2-C_4	10.2	9.7	8.5	4.7
C_5 -350°F	29.8	23.0	24.7	22.4
C_5 350-650°F	35.9	31.5	33.7	34.9
C_5 650°F+	16.6	30.4	27.2	34.4
C_{5+}	83.1	85.0	86.2	91.7
C_4 Olefin/paraffin	1.8	2.1	2.0	2.7

* Conditions: 240°C, 1:1 H_2:CO, 2.07 MPa, 300 GHSV
TC: modified molecular sieve

In other work, the nature of surface intermediates was measured by Wolf (1986). Ru/zeolite A catalysts were prepared by Rossin and Davis (1986) who found that during synthesis reaction the Ru did not migrate to the surface of the zeolite. Bimetallic Pt-Mo supported on Y zeolite was investigated by Borg and others (1986). Zuckerman and Melson (1986) tested the concept of preparing catalysts containing Ru and Fe using cluster $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ supported on ZSM 5, establishing structure/activity correlations for bifunctional reaction capabilities.

Niwa and Murakami (1987) used a chemical vapor deposition method to put on an ultra thin layer of SiO_2 on zeolites. Because of the fine-controlled pore-opening size, high shape selectivity was observed. Conversion of methanol was shifted to lower molecular weight product molecules, an effect seen also in the aromatics.

Variation in zeolite character has been extensively investigated. Yashima (1987) reported on reforming of hydrocarbons produced from syngas, finding that the yield of aromatics is increased with increase in the concentration of Al in HZSM 5, which is in turn related to increased acidity.

A very different concept involving molecular sieves has been tried by Foley (1986). An innovative catalyst was prepared consisting of a particle, the outside shell of which is a carbon molecular sieve, and the interior a FT catalyst. The shell is designed to let syngas molecules into the interior catalyst for conversion to hydrocarbons, but not to let out larger, undesirable molecules. These are converted to lower molecular weight products which then are allowed to escape. These catalysts did indeed show improved products distribution relative to those obtained with usual FT catalysts.

3.4 Reaction chemistry, catalyst structure/performance

The reaction chemistry of CO hydrogenation is controlled by both thermodynamic and kinetic factors. Thermodynamics impose equilibria constraints, expressed in terms of free energy values of product molecules, Figure 5. Methane is always the preferred product. Thermodynamic considerations also provide insight into the important influence of pressure on reaction equilibria as has been discussed by Anderson (1984).

Catalysts, on the other hand, control reaction kinetics. They have the ability to provide selectivity in product formation through their capacity to accelerate those reactions which form desired products. The FT process consists of a complex combination of reactions. The rate of each reaction can be altered by the catalyst. From a variety of research studies including isotopic tracers and the relatively new technique of trapping surface complexes (Williams and others, 1986) the following reactions, as shown in Figure 25, are believed to represent FT reaction chemistry (Dry, 1987).

As mentioned earlier, the dissociation of the CO molecule on the catalyst surface is a key initial reaction effecting selectivity, particularly the direction towards alcohols or hydrocarbons. It should also be noted that oxygenated products, particularly alcohols, are postulated to be formed in a termination step whereby a surface alkyl group migrates to an undissociated CO molecule on the catalyst surface. However, with Cu catalysts, methanol synthesis has been shown to proceed through CO_2 as discussed earlier.

A further fundamental reaction chemistry concept related to the determination of product carbon chain-length distribution. The mechanism of chain growth by incremental CO addition leads to a product distribution described mathematically by the ASF equation. A consequence is illustrated in Figure 9. Much effort has been expended to circumvent the constraints of the ASF equation, and to thus make a more desirable distribution of products. A particular objective is to make less methane than provided for by ASF.

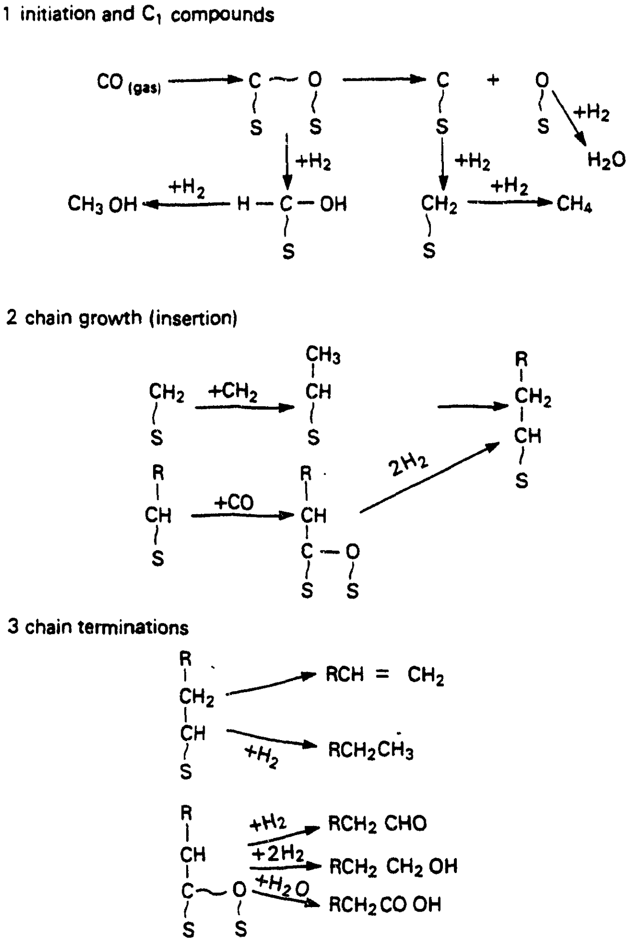


Figure 25 Mechanism of FT process (Dry, 1987)

The fundamental dynamics of CO hydrogenation over heterogeneous catalysts (Tamaru, 1978) have been discussed at various symposia. Mention can also be made of special kinetic techniques, namely transient kinetics (Zhang and Biloen, 1985) and PSRA, pulse surface reaction analysis (Takahashi and others 1986; Murakami, 1987).

Mechanism studies of hydrocarbon formation from methanol over ZSM 5 catalysts has determined that the reaction pathway proceeds through the formation of dimethylether, then small molecule olefins and on to larger paraffins and aromatics, Figure 26. Carbenium ion chemistry is involved including hydrogen transfer.

3.5 Catalysts to improve process engineering

3.5.1 FT to high wax/crack to liquid fuels

The Shell Middle Distillate Synthesis process, SMDS, is a two-stage process based on the development of a catalyst which converts syngas into long-chained hydrocarbon waxes

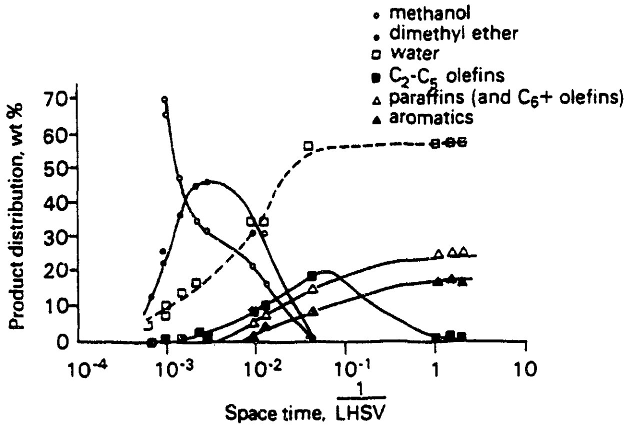


Figure 26 Reaction pathway for methanol conversion to hydrocarbons over ZSM 5 at 371°C (Chang and Silvestri, 1977)

which can be hydroconverted and fractionated into naphtha for gasoline, kerosine for jet fuel, and gas oil for diesel (van der Burgt and others, 1985). The decrease in formation of less valuable C_1 + C_2 gases in favour of waxes in the FT synthesis is shown in Figure 27. Thermal efficiency from natural gas is 60%. A fixed-bed reactor has been selected for the FT reaction and a trickle flow reactor for hydrocracking. Product carbon number distributions obtained with Fe, Co, Ru-type catalysts have been established for $\alpha = 0.7$ to $\alpha = 0.93$ by Sie and others (1988). They calculated the distribution of C_{10} and of $C_{10\text{-}20}$ products from the two-stage concept are 64 and 36 respectively for $\alpha = 0.8$, and 20 and 80 for $\alpha = 0.95$.

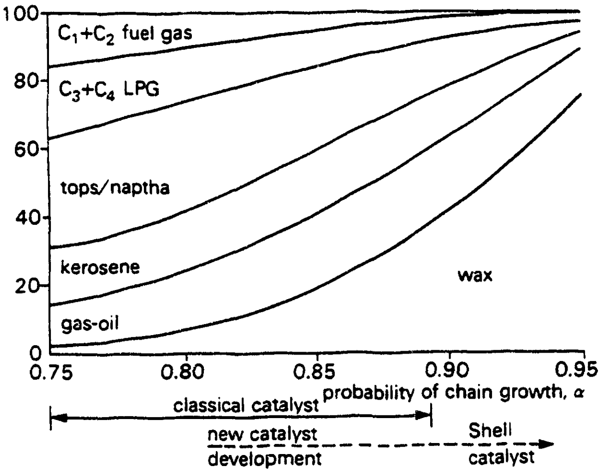


Figure 27 Product distribution for FT synthesis as a function of alpha (van der Burgt and others, 1985)

In related work, UOP has characterised FT wax and the potential for its upgrading (Humbach and Schoonover, 1985; McArdle and others, 1986; Shah and others, 1987). Further, Satterfield (1985, 1986) has established detailed information on the basic kinetics in terms of the ASF distribution relating to high wax formation in FT operation. Evidence is accumulating that on most if not all FT iron catalysts there are two ASF chain growth probabilities (Huff, Satterfield, 1984). The dominating distribution in most cases shifts about C_{10}. The C_{10+} product typically is about double the amount that would be expected by simple extrapolation of data obtained in the C_{10} region. Hanlon and Satterfield (1988) conclude that the 'double-alpha effect' is not caused by olefin incorporation nor is it a two-site catalyst effect associated with K-promoted and non-K-promoted sites. Control of this effect would provide an additional way of improving selectivity.

When conducting FT for high wax formation, it is fundamental that the formation of methane is minimised. Utilisation of FT catalysts designed for high wax/low methane, coupled with the excellent new catalytic technology for selective wax cracking, is believed to provide for very promising improved FT technology.

3.5.2 FT synthesis in the slurry phase

In their excellent review, Frohning and others (1982) discuss variation in FT process engineering in order to improve heat control. These variations include operation with entrained or fluid bed catalyst circulation, liquid phase or staged techniques, or hot gas recycle.

A slurry FT reactor operates with a finely divided catalyst suspended in an oil reactor medium. Using a precipitated Fe catalyst, the slurry reactor has been demonstrated to yield high single-pass H_2+CO conversion with low (0.6) H_2/CO ratio gases. It has the advantage of producing high C_{3+} product yields and utilises a simple reactor design. Koelbel and Ralek (1980, 1984) have provided an excellent review from inception of the concept to 1970. Recently, a variety of catalyst have been tested for use in the slurry reactor mode. Carroll and others (1986) found that cobalt catalysts prepared from the carbonyl were preferable to those made from the nitrate. Kikuchi (1987) has developed ultra-fine particles composed of Fe-Co-Ni or pure Fe for liquid phase FT synthesis. These catalysts are more active than precipitated catalysts having the same composition. The hydrodynamics of three phase slurry reactor systems have been extensively studied in order to engineer appropriate catalytic reactors for optimum performance (O'Dowd and others, 1985; Bukur, 1985, 1986; Stern and others, 1985; Fujimoto, 1987; Kuo and others, 1985). Heat transfer properties have also been studied (Saxena and Shrivastava, 1986). In addition, it has been found that catalytic performance can be enhanced by reductive pretreatment of the catalyst with CO rather than H_2 (McDonald, 1986).

A second concept involving slurry reactor catalysis consists of a combination of a slurry phase FT followed by upgrading of the FT products over the MTG catalyst (Poutsma, 1980; Kuo and others, 1985; Haag and others, 1987). Two modes of FT operation were established, characterised as low wax and high wax. The wax can be further upgraded to make gasoline plus diesel. Typical selectivities are shown in Table 18. These different modes were obtained by varying the catalyst and process conditions. This combination process is regarded as a significant improvement over classical FT.

3.5.3 Variation in synthesis conditions to improve selectivity

Selectivity in FT synthesis can be significantly altered by

Table 18 High reactor-wax mode hydrogen selectivities for the two-stage slurry FT/ZSM-5 pilot plant (Haag and others, 1987)

Product type	Yield, wt% After FT	After ZSM-5*
C_1	3.3	3.4
C_2=/C_2	1.8/0.7	1.1/0.7
C_3=/C_3	2.8/0.8	0/3.2
C_4=	2.5	0
i-C_4/n-C_4	0/0.9	(1.0)/0.7
C_5-C_{11}	22.4	39.6
C_{12+} (liquid)	9.7	1.0
Reactor wax	50	51.3
Oxygenates	5.1	–
Gasoline properties		
RVP, psi		10
PONA, vol%		60/14/7/19
R+O		92

* after alkylation
= indicates olefin

Table 19 Products from SASOL Fischer-Tropsch reactors (Haag and others, 1987)

Operating conditions and product selectivity, wt%	SASOL I Arge	 Synthol	SASOL II Synthol
Catalyst, alkali promoted Fe	Precipitated	Fused	Fused
Catalyst circulation rate, Mg/h	0	8000	-
T, °C	220-255	315	320
p, MPa	2.5-2.6	2.3-2.4	2.2
Fresh feed H_2/CO, molar	1.7-2.5	2.0-3.0	–
Recycle ratio, molar	1.5-2.5	2.0-3.0	–
H_2+CO conversion, mol%	60-68	79-85	–
Fresh feed, km^3/h	20-28	70-125	300-350
Diameter x height, m	3x17	2.2x36	3x75
C_1	5.0	10.0	11.0
C_2=	0.2	4.0	
C_2	2.4	6.0	7.5
C_3=	2.0	12.0	
C_3	2.8	2.0	13.0
C_4	3.0	8.0	
C_4	2.2	1.0	11.0
C_5-C_{12}	22.5	39.0	37.0 (C_5-191°C)
C_{13}-C_{18}	15.0	5 .0	11.0 (191-399°C)
C_{19}-C_{21}	6.0	1.0	3.0
C_{22}-C_{30}	17.0	3.0	(399-521°C)
C_{30}	18.0	12.0	0.05 (>521°C)
Nonacid chemicals	3.5	6.0	6.0
Acids	0.4	1.0	–

= indicates olefin

varying operating conditions such as temperature, pressure, and H_2/CO syngas ratio. The effect of temperature was evident in the differences in products from the Arge unit operated at 240°C and the Synthol unit operated at 315°C, Table 19.

The increase in temperature of synthesis also is evident in the MTG process which has been tested for olefin production when operated at higher synthesis temperatures.

Dry (1986) has proposed FT operation at higher pressures in a fixed bed fluid mode which would have advantages of smaller size and in the case of Fe catalysts would result in lower carbon deposition and so lead to longer catalyst life.

It is known that decreasing the syngas feed H_2/CO ratio results on a shift to higher molecular weight products as illustrated by increasing α value (Cornils, 1984), Figure 28.

The effect of lower H_2/CO ratios has also been demonstrated for Ru catalysts (Karn and others, 1965), Figure 29.

Other variations in operating conditions have been tested. Concentration cycling has been studied to try to improve selectivity (Gulari, 1986). Chaffee and others (1986) obtained unusual product distributions by control of CO/H_2/H_2O mixture composition over a Co,MgO,ThO_2/SiO_2 catalyst. A different concept was tested by recycling alkenes during CO hydrogenation, Niiyama and Nakamura (1987; Nakamura and others, 1988), who found enhanced gasoline yields, Figure 30.

3.6 Selective conversion to hydrocarbon types

Special attention has been given to catalysts which produce preferred classes of compounds, particularly isoparaffins or low molecular weight olefins. Relevant research utilising both zeolite and non-zeolite catalysts is discussed.

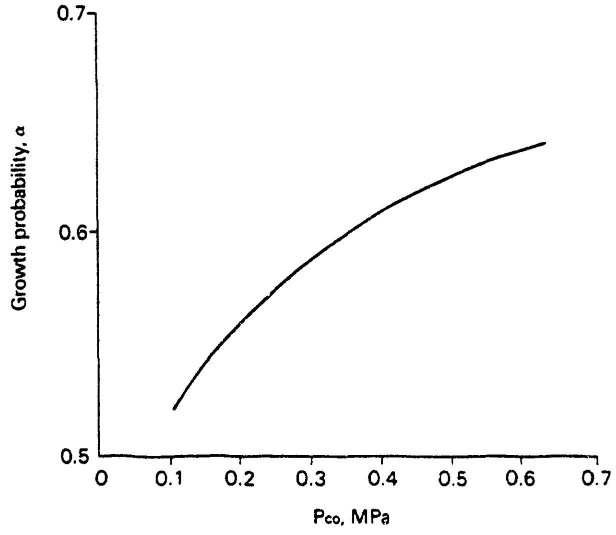


Figure 28 Dependence of growth probability on partial pressure of CO at 250°C (Cornils and others, 1984)

gas composition, H_2:CO	4:1	3:1	2:1	1:1
temperature, °C	224	222	225	239
conversion, %	82	77	66	40
usage ratio	3.9	2.5	2.2	1.9

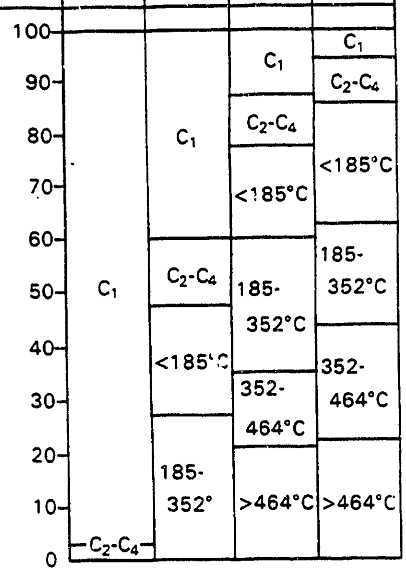


Figure 29 Effect of H_2:CO ratio at 2.2 MPa over a 0.5% Ru on alumina catalyst (Karn and others, 1965)

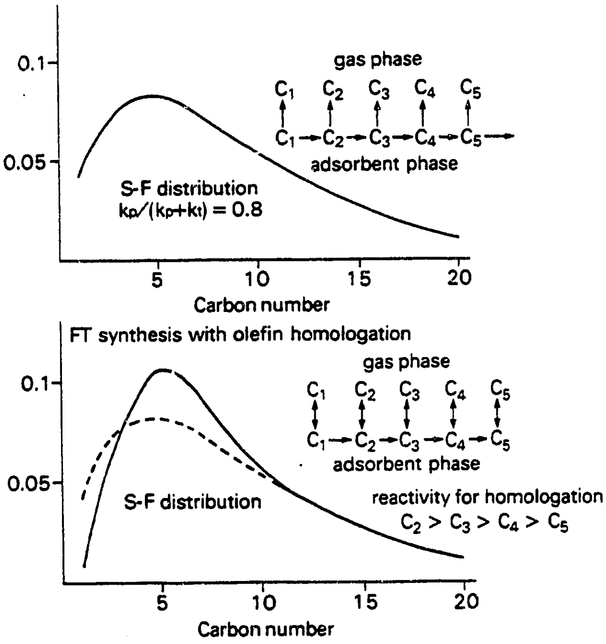


Figure 30 Anderson-Shulz-Flory distribution of hydrocarbons expected in FT synthesis and its change when olefin homologation is superimposed (Niiyama and Nakamura, 1987)

3.6.1 Isoparaffin synthesis

There is particular interest in the synthesis of isoparaffins. Originated in Germany, the conversion of syngas to hydrocarbons having a high content of isoparaffins, especially isobutane and isobutene, has been termed the Isosynthesis Process, reviewed by Cohr (1956). The Isosynthesis Process differs from the usual FT process in that it is conducted at considerably higher temperature and pressure and uses as catalyst a difficultly reducible oxide, particularly ThO_2. The activity is increased by the addition of 20% alumina and the addition of 3% K, based on Al_2O_3, gave a further increase in iso-C_4 compounds. Product distribution does not follow the ASF distribution pattern. At temperatures below 400°C, alcohols are the main products. At temperatures above 500°C, low molecular weight hydrocarbons predominate. Interest in Isosynthesis has revived (Shah and Perrotta, 1976; Chang and others, 1979). A laboratory pilot study conducted by Talbot (1983), established process variable/product distribution relationships. Tseng and Eckerdt (1987) and Silver and others (1986) concluded that over ZrO_2, isosynthesis propagation is via insertion of CO into an aldehyde. Fujimoto and others, 1985, determined the activity and selectivity to isoparaffins over Ru catalysts regulated by a wide range of promoters. Chaffe and others (1986) established unusual product distribution using a 24% Co, 2.5% MgO, 1.4% ThO_2/kieselguhr catalyst.

Another approach for application of metal/zeolite catalysts is to produce higher yields of isoparaffins, as reported by Fraenkel and Gates (1980). Later work showed that the higher-than-usual isoparaffins appear to be transitory. Possibly the metal migrates out of the zeolite with time of operation. Iwasawa (1987) using ZSM 5 coated with $Zr(OC_2H_5)_4$ to deposit ZrO_2, reported the catalyst to be very selective in producing isopentane from methanol, Table 20.

Considerable success in selective formation of isoparaffins was also achieved using bimetallic Ru-Pt supported on zeolites (Fujimoto and others, 1985; Tatsumi, 1986). Tominaga (1987) found the best catalyst in terms of high CO conversion and high selectivity to gasoline (70%) and rich in branched chain components was a 2% Ru 2% Pt/HY zeolite. Alloy formation was confirmed to be responsible for the enhanced CO conversion. Non-ASF product distribution and i/n ratios higher than thermodynamic equilibria were deduced to be due to acid catalysed secondary reactions of isoalkanes. A similar catalyst supported on DAHY was fairly resistant to deactivation during operation. Shul and others (1986) investigated the durability of zeolite-supported Ru-Pt bimetallic catalysts for isoalkane synthesis from syngas. Iwasawa (1987) using Pd-supported on ultra thin lanthana-coated ZSM 5 was able to obtain hydrocarbons of which 71% was C_3, 96% being propane. Fujimoto and others (1985) produced >80% selectivity to C_3-C_4 paraffins using a hybrid catalyst comprising a methanol synthesis catalyst and Y-type zeolite. An H-silicalite support for Rh-Ti-Fe-Ir was found to convert syngas to ethylene with a 45% selectivity (Arakawa and others, 1986).

3.6.2 Olefin synthesis

Development of new FT catalysts has also focused on increased activity and enhanced selectivity to lower molecular weight olefins. Interest has stemmed, on the one hand, for producing chemical feedstocks as well as for conversion to

Table 20 Selectivities and activities in the CO/H_2 reactions (Iwasawa, 1987)

			Selectivity, %									
Catalyst	T/°C	CO conv, %	C_1	C_2	$C_{2=}$	C_3	$C_{3=}$	C_4	$C_{4=}$	C_{5+}	CO_2	Me_2O
ZSM5/ $(ZrO_2)_{0.7}$	300	0.07	61.7	14.1	3.9	9.4	3.1	7.8	0.0	0.0	0.0	0.0
	350	0.13	61.4	10.9	7.3	9.2	3.9	0.0	0.0	0.0	0.0	0.0
	400	0.23	62.6	10.4	10.2	8.5	3.6	0.0	0.0	1.4	0.0	0.0
ZSM5/ $(ZrO_2)_1$	300	0.04	72.8	11.9	5.1	6.8	3.4	0.0	0.0	0.0	32.1	0.0
	350	0.75	35.1	10.7	3.7	9.9	1.6	21.8	0.6	16.7	24.7	0.2
	400	0.31	49.5	15.9	3.2	9.3	1.59	17.2	0.5	3.0	34.4	0.2
ZSM5/ $(ZrO_2)_2$	270	0.11	63.3	16.0	3.1	13.7	3.1	0.8	0.0	0.0	34.4	0.2
	320	0.40	61.5	11.3	7.6	10.4	2.8	5.1	1.3	0.0	34.7	0.2
	370	0.59	60.7	13.4	9.9	11.1	2.7	2.1	0.1	0.0	31.6	0.1

= indicates olefin

liquid fuels (Sheldon, 1983; Falbe, 1982; Keim, 1986). Snel (1987) provided a critical review showing selectivity to olefins may be influenced by several effects: classified as basicity, catalyst dispersion, electron-withdrawal ligand, and several support interaction effects. Improved selectivities have been observed for K-promoted Fe (for references in the rest of this paragraph, *see* Venter and others, 1986), Fe promoted with Ti, V, Mo and Mn oxides, catalysts promoted by sulphur, bimetallic and coprecipitated Mn-Fe catalysts, and carbon-supported catalysts. In recent years, various researchers have reported that the introduction of manganese in FT catalysts increases olefin selectivity. Most of these studies were conducted with bulk Mn-Fe catalysts prepared by coprecipitation or initial alloying, although various organometallic compounds have been used as precursor. A promising method of obtaining highly dispersed supported catalysts is the use of an organometallic mixed-metal cluster as metal precursor. This method has the advantage of intimate metal contact between the zero-valent metals in known molecular ratio. Venter and others (1986, 1987a,b) studied the preparation, characterisation and catalytic behaviour or carbon-supported Fe/Mn/K cluster-derived catalysts with special emphasis on those giving unusually high selectivities to light weight olefins. Their best catalysts, KMnFe2/S and KMnFe/C produced a hydrocarbon product containing, for example, 31% C_2H_4, 39% C_3H_6, 20% C_4H_{10}, and 11% CH_4. Kim and others (1986) also investigated the influence of Mn as a promoter for C_2-C_4 olefin production, finding that the olefin/paraffin ratio increased from 1.1 to 5.3 as the Mn content was increased from 0% to 10.6%. Raney Mn-Fe was particularly effective. Barrault and others (1984) stressed the importance of the nature of the precursor in controlling catalyst properties. From the mixed oxide, $Fe_xMn_yO_z$, a catalyst was made which produced a product with 75% C_2-C_4 of which 70% were olefins. Hnatow and others (1984) established the effect of alkali in promoting precipitated Fe catalysts in improving 1-alkene selectivity. Gustafson and Wehner (1986) concluded that the addition of Pd to Fe supported on ZnO results in an increase in activity; selectivity to alpha olefins remains high. Pd may increase the dispersion of the Fe and kinetic studies showed that Pd may assist in activation of H_2. Hagiwara and others (1986) studied hydrogenation of CO to light olefins over chlorine-containing magnetite catalysts in slurry phase. Selectivity to C_2-C_4 olefins was 48%. CH_4 was suppressed to 11%. Attention is also drawn to high olefin selectivity resulting from partial poisoning by sulphur (Tong and McCarty, 1987).

Research on olefin synthesis using zeolite catalysts has also been productive. The MTG process can be altered to maximise olefin production (the MTO process) by increasing space velocity, decreasing MeOH partial pressure and increasing reaction temperature (Soto and Avidan 1985; Haag and others 1987). Yields reported for the MTO process are C_1-C_3 paraffins, 4 wt%; C_4 paraffins, 4%; C_2-C_4 olefins, 56%; C_{5+} gasoline, 36%. Hoelrich and others (1983) reported C_2-C_4 selectivities as high as 80% as did Supp (1985). It has been possible to convert olefins to gasoline plus diesel fuel in >95% yield, by the Mobil MOGD process. Further, because of the catalyst shape selectivity, the majority of products are methyl branched olefins (Haag and others, 1987).

The conversion of syngas to hydrocarbons has also been developed by Dow using Mo-based catalysts. The catalyst is Mo on a carbon support, promoted with 0.5–4 wt% K. These carbon-supported catalysts convert syngas to high yields of ethane, the most desirable cracking stock to ethylene. The advantages of these catalysts is that they avoid liquids altogether and are sulphur tolerant. The major disadvantage is the high methane yield. Furthermore (Pedersen and others, 1980), ethane selectivity from syngas is significantly greater than ASF predictions over related catalysts, Mo or V plus Fe, supported on alumina or titania, in the presence of H_2S.

Peuchert and Linden (1984) reported on a series of Co catalysts on ZSM 5, silicalite, mordenite, and silica. Pronounced changes were observed in selectivity for CO hydrogenation. The Co/silicalite catalyst markedly suppressed methane formation, and showed high olefin selectivity in the C_2/C_4 fraction. Inui and Miyamoto (1987) found that a Fe-Mn-Ru/zeolite composite catalyst was very effective in converting syngas to C_2/C_4 olefins. Among the synthesised silicates, Fe-silicate having the pentasil structure exhibited very high performance in converting light olefins to high octane gasoline. Ga and Pt/Ga-silicate were active and selective for the conversion of light olefins to aromatics

(68%). In other studies, Misono and others (1987) found that Ru supported on intercalated montmorillonite produced C_4-C_{10} hydrocarbons with 80% selectivity. The shape selectivity of acid catalysed secondary reactions was seen to be an important factor.

3.7 Koelbel-Engelhardt synthesis

Systematic research on the role of the water-gas shift reaction led in 1949 to the development of a new process hydrocarbon synthesis from CO and steam, referred to as the Koelbel-Engelhardt or KE process (Koelbel and Ralek, 1984). The reaction

$$3\,CO + H_2O \rightarrow -CH_2- + 2\,CO_2$$

occurs on iron, nickel, and ruthenium catalysts. The process makes possible hydrocarbon synthesis without the production of hydrogen and is suitable for use with hydrogen-free or hydrogen-poor, CO-rich gases such as producer gas or blast furnace gas. The primary products of the KE process consist of mainly unbranched aliphatic hydrocarbons which, depending on reaction conditions, can be primarily olefins. In principle, all catalysts that are active for the FT reaction and are oxidation resistant under KE conditions, are active for KE synthesis. Iron catalysts are particularily valuable, but cobalt and nickel catalysts also catalyse the reaction. Under high pressure, ruthenium catalysts produce longer hydrocarbon chains. Considerable catalyst research has been directed to increasing activity, life, and selectivity. Nitriding the iron catalyst hinders CO decomposition. Addition of alkali salts suppress methane formation. The process was developed in both the fixed-bed and slurry reactor modes, with latter preferable. In 1953, a slurry phase demonstration plant began operation in Germany and was operated successfully for two years, producing about 11.5 tonnes of product a day. However, economic interest diminished with the decrease in CO content in exit gases in the modern steel industry. Nevertheless, the simultaneous operation of KE and FT reactors can be advantageous. The successful operation of the KE demonstration plant using CO and water may have made its greatest contribution to the enhancement of recent growing interest in slurry phase FT reactors and catalysts designed for their optimum operation.

3.8 Commentary

In summary, this chapter has pointed out a number of recent significant advances in catalytic technology for conversion of syngas to liquid hydrocarbon fuels. Some are improvements in classical FT technology. These represent opportunities for additional improvement through research. One promising technique is the catalytic conversion of syngas to a low methane, high wax product which is selectively hydrocracked to liquid fuels, particularly middle distillates. It is reported that this type of process is being considered for installation in Malaysia starting with natural gas. The overall energy efficiency is estimated to be 60%. A second advanced technology employs a slurry catalyst system, with process advantages derived from superior heat control. A special development along this line is a combination of slurry FT followed by processing over a catalyst containing zeolite ZSM 5. Of the product, 71% is gasoline having an octane rating of 90 research and 83 motor. Many of the recent outstanding catalytic advances have been made possible by the relatively recent discovery of new zeolite catalysts and their capabilities. A major industrial accomplishment is the MTG process which has been installed in New Zealand. The TIGAS process represents a simplification with lower capital investment costs. There is a need to provide further simplification by developing multifunctional catalysts which at one temperature, are capable of converting syngas through a transitory methanol and then to gasoline and diesel fuel.

Higher selectivity in synthesising liquid fuels has been achieved by use of novel catalyst systems. Iron catalysts in the carbonitride form have shown higher gasoline yields (36% vs 26%) compared with conventional catalysts. Raney-type alloys of Fe-Mn are two to four times as active as catalysts of the same composition prepared by conventional coprecipitation methods. It has been demonstrated that the use of ruthenium of small crystal size, 1 nm diameter, gave greater selectivity to higher hydrocarbons; larger particles, 11 nm, gave mainly methane. This points out opportunities for control of selectivity by use of the concept of metal ensemble size, and fundamentally in the adjustment of multiple sites which are catalytically interacting. This may be a factor in the finding that partial poisoning of metal catalysts by sulphur can bring selectivities of C_2-C_4 olefins synthesis to over 50%, much higher than the ASF distribution. Partial poisoning has been found to be a very powerful technique for selectivity control in a variety of catalytic applications. There have been additional examples in selective synthesis of C_2 hydrocarbons, including notably the use of MoS_2. Selectivity in the synthesis of isoparaffins has also been improved greatly, particularly involving the use of zeolite catalysts. A Ru-Pt/HY catalyst has produced iso/normal hydrocarbons greater than thermodynamic equilibria and greater than ASF predictions, the iso/normal C_4 ratio being 10. It should also be pointed out that important new understandings of the catalytic chemistry has been achieved, particularly the key steps of dissociative CO chemisorption and CO insertion reactions. This has been matched by a new understanding of the coupled dependency of catalyst composition, preparational techniques, pretreatment and synthesis conditions. This knowledge can contribute greatly to effective future catalyst research.

4 Scientific design of catalysts

There is a growing belief that catalytic technology is being transformed from an art to a science, with the possibility of the scientific design of catalysts of greatly improved capabilities.

4.1 Surface science

The development of advanced instrumental techniques such as FTIR (Fourier transform infrared spectroscopy), XPS (X-ray photoelectron spectroscopy), EXAFS (extended X-ray absorption fine structure), NMR (nuclear magnetic resonance), SIMS (secondary ion mass spectrometry) to identify a few, now provides the means of determining the surface structure of catalysts and surface complexes on an atomic scale never before possible (Kelley, 1987). This is believed to provide the means for placing catalysis on a new scientific basis. This in turn promises an understanding which, it is believed, will make possible the synthesis of catalysts designed to catalyse specific reactions, catalysts which would not have been achieved by a trial-and-error method. Surface science research reports and discussion relevant to catalysis are found in the proceedings of the quadrennial International Congresses on Catalysis, biennial meetings of the Catalysis Society of North America, reports of various European meetings on catalysis and journals which deal with surface science. An instructive review pertinent to syngas reactions is given by Davis and Somorjai (1985). Other papers deal with specific topics, for example with SMSI (strong metal support interaction) (Uchijima and Kunimori, 1987) and surface carbon formation (Butt and Stan, 1985). It is beyond the scope of this review to discuss, much less to evaluate, this complex and emerging fundamental research area, other than to point out that significant advances are continuing and that surface science offers a major opportunity for design of greatly improved catalysts.

4.2 New scientific approaches

In addition to the relatively new instrumental approach to catalyst research, and to increasing understanding of catalysis by enzymes, man-made enzyme mimics, and homogeneous molecular catalysts, there are other new approaches which have promise. Computer-assisted graphics is a powerful tool used in complex biological systems. Visual models of catalyst structures and reactant molecules are constructed to help guide synthesis of desired geometric shapes and dimensions, goal of molecularly engineered catalyst design (Cusumano, 1987). New perspectives on catalysis from surface science emphasise the coupling of measurements of reaction kinetics at elevated pressures with an ultrahigh vacuum system for surface analysis (Goodman and Houston, 1987). A kinetic modeling approach to design of catalysts has been proposed by Dumesic and others (1987) which allows estimation of catalyst performance from reaction mechanism considerations and serves to direct the catalyst designer towards experiments which are likely to yield the catalyst properties sought.

Another concept of catalyst design is based on pulse surface reaction rate analysis (PSRA) which has been used in which has been used in which the dynamics of both CO adsorbed and CH_2 produced were simultaneously measured over Ru/Al_2O_3 catalysts (Mori and others, 1986). This technique has been used to design promoted Ru/Al_2O_3 catalysts (Mori and others, 1986; Takahashi and others, 1986). A related proposal is to design catalysts using artificial intelligence (Murakami, 1981).

Further scientific studies can contribute to new and improved catalysts. Possible examples are superconductive materials with unusual catalytic properties or advances in photo-assisted catalysis or electrocatalysis.

5 Economic considerations

It is appropriate to consider the factors which make up the costs of synfuels and also the cost decreases which successful research could make possible.

5.1 Cost of synfuels

A comprehensive assessment of synfuels has been made by Teper and others (1984), Figure 31. A major advantage in this

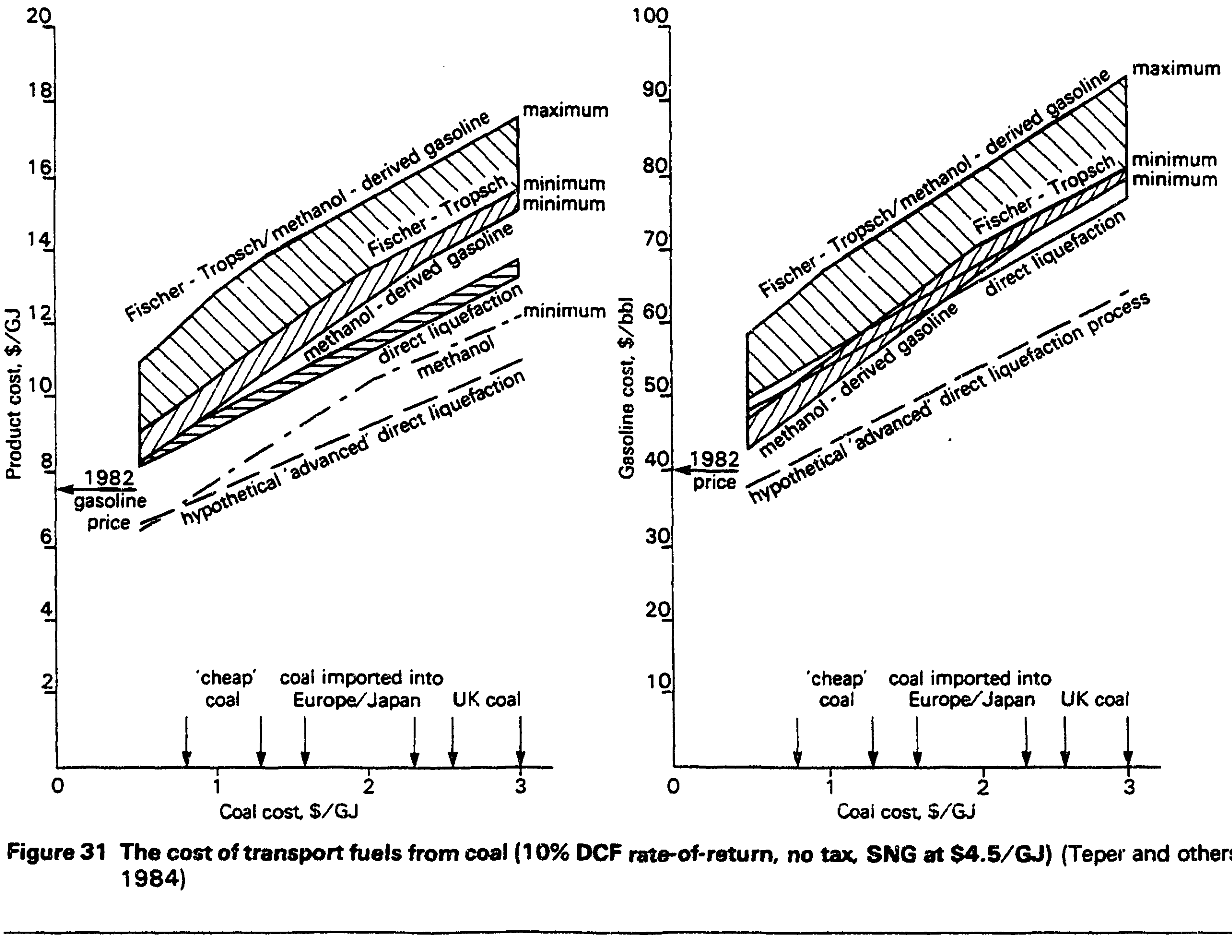


Figure 31 The cost of transport fuels from coal (10% DCF rate-of-return, no tax, SNG at $4.5/GJ) (Teper and others, 1984)

in-depth assessment, is the application of a single standard basis for comparisons.

Salmon (1986) has provided detailed economics of production of methanol from coal and natural gas. The general conclusion was reached that methanol from coal is approaching competitiveness with methanol from natural gas, providing that favourable financing arrangements and guarantees can be obtained and that the price of natural gas is above $4/million Btu level.

The elements which make-up coal conversion economics have been summarised by Mills and Knudsen (1979), Table 21. The high cost burden contributed by plant investment charges is emphasised. Thus, improved energy efficiency can improve economics only a small amount relative to catalyst improvements which can reduce capital costs.

Table 21 Coal conversion economics (Mills and Knudsen, 1979)

	M$ annual	$/GJ	$/tonne
Capital charges 11.5%	144	1.60	77
depreciation (5.0%)			
maintenance (4.0%)			
ins and taxes (2.5%)			
Coal at $27.5/tonne	125	1.42	66
Operating cost	16	0.19	9
Manufacturing cost	285	3.21	152
Federal tax	125	1.42	66
Profit at 10% after tax	125	1.42	66
Annual sales	535		
Selling price		6.05	284

Basis: Plant site 7.1 Mm^3 (250 Mft^3) gas or 5700 tonnes (42,000 bbl) oil/day; plant investment $1.25 x 10^9; thermal conversion efficiency 67%

General reviews include the evaluation of alcohols as motor fuels assessed from an overall viewpoint by the Swedish Motor Fuel Technology Co (1986). The economic impact of new developments in methanol technology has been reported by Dybkyjaer and Hansen (1985). A ranking of synthetic fuels from indigenous resources for road transport in the United Kingdom has been provided by Langley (1987).

It should be noted that on the basis of conventional economics, synfuels are about twice as expensive as petroleum, currently priced at about $18 per barrel.

5.2 Value of attaining research objectives

It is fair to say that presently developing improved technology is expected to improve economics 5–10% in some instances and perhaps 30% or so overall. These represent large savings in costly synfuels plans but in general do not provide synfuels which are as cheap as today's petroleum on a calorific value basis. However, beyond the direct comparison of fuel values on an energy basis are their quality or engine performance values, measured by octane value for gasoline, cetane value for diesel, and alcohol performance in high compression engines. Other considerations include environmental benefits. Perhaps most instructive is the success of MTBE – a synfuel which is growing rapidly world-wide, whose success is based on its high performance as octane enhancer, economically preferred over other methods of achieving needed octane.

In order to assess the value of potential improvements in catalytic technology, it is instructive to consider the relative cost elements which have been summarised by Dry (1986):

Synthesis gas production58%
(Coal gasification 53%, CH_4 reforming 5%)
FT synthesis18% (plant 15%, catalyst 3%)
Product separation12% (cryogenic 4%, oxygenates 4%)
Refinery 10%
Diverse 2%

Dry noted that the advantage of a big improvement in FT selectivity is that the costs of both the product separation and the refining sections are lowered.

An overview of the improvement in hypothetical 'advanced liquefaction costs is provided by the IEA assessment of costs in Figure 31.

Gray (1984) and Gray and Tomlinson (1985) have provided an estimate of the potential for economic improvements in indirect liquefaction. Specific estimates on the value of improvements have been provided by Gray and others (1980), The Impact of Developing Technology on Indirect Liquefaction; El Sawy and others (1984), A Techno-Economic Assessment of the Mobil Two-Stage Slurry FT/ZSM-5 Process; Tomlinson and others (1985), The Impact of Water-Gas Shift Requirements on the Economics of Indirect Liquefaction Processes; and El Sawy and others (1986), Development of a Techno-Economic Model for the Evaluation of Research Opportunities in FT Synthesis. It was concluded that the elimination of the shift requirement would result in a gasoline cost savings of 5%. The cost savings in advanced synthesis systems such as slurry/ZSM 5 two-stage process are in the range of 12–15%. The advantage of increased catalyst activity is illustrated in Figure 32, which depicts a family of curves which represent progressive reduction in the unit cost of refined FT products with increasing level of catalyst selectivity at different levels of catalyst activity (CA = m^3 syngas converted per g Fe per hour in slurry operation).

Calculation for wax upgrading indicates that wax hydrocracking offers the least unit cost of refined FT products compared to both the conventional and non-conventional refining schemes. This is due to the lower capital and higher output of the wax hydrocracking unit as compared to that of the FCC unit.

The economic impact of an improved methanol catalyst has been estimated to be 10% (Grens and others, 1983). Greater improvements were seen by Short (1987) for a catalyst which

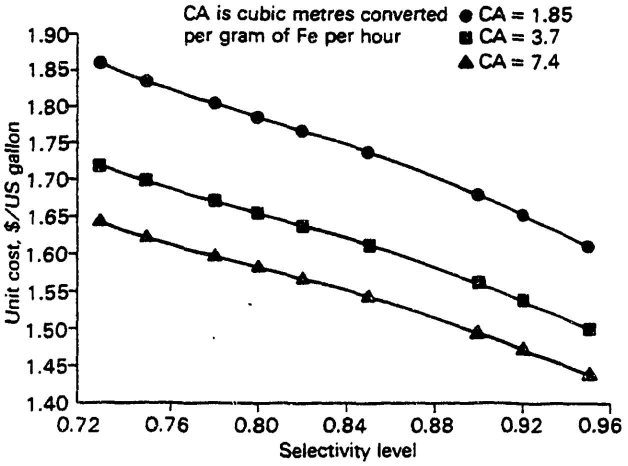


Figure 32 Change in unit product cost with change in selectivity level (El Sawy and others, 1986)

can operate at 120°C and a pressure conventional for gasification.

In order to scope the potential for biosynthesis in indirect liquefaction of coal, Bechtel (1986) provided an evaluation of technical and economic potential. It was concluded that costs for ethanol could be 60–80 ¢/gal compared with fuel use ethanol of 100–130 ¢/gal and gasoline of 40– 80 ¢/gal.

The above review of economics is believed to illustrate the range of economic improvements which are on the horizon through developments which are in progress. It should be emphasised that improved catalysts have an overall economic effect not only on the FT synthesis step, but also on decreasing the cost of reactors used for the synthesis (that is, more active catalysts mean smaller reactors or fewer of them) and also on simplification of product upgrading required to produce specification fuels. Also, sulphur resistant catalysts reduce syngas cleanup requirements. Catalysts capable of processing low H_2/CO ratio gases eliminate the shift reaction. It is the sum of all these improvements that lead to the overall 20–30% reduction in product costs.

Furthermore, it is the *fuel performance value*, not just fuel energy content, which determines the economic value of a fuel. Specifically, it is the value of high octane enhancement by synthetic fuels in blends, compared to other manufacturing costs of achieving required octane values, which provides economic improvements. This is particularly important with phase-down and elimination of lead in gasoline.

The potential for new research directions is great – catalysts which are much more selective to high performance fuels (for example, direct conversion of syngas to MTBE), much more active catalysts resulting in lower plant costs, catalysts which satisfy radically new process concepts (coal simultaneously gasified and converted to gasoline or methanol).

6 Assessment and recommendations

The technical status for the catalytic conversion of syngas to synthetic liquid fuels has been reviewed with emphasis on recent research results. Significant advances in various investigations have been summarised at the end of Chapter 2 for oxygenate fuels and Chapter 3 for hydrocarbon fuels. A synopsis of the scientific design of catalysts was presented in Chapter 4. Chapter 5 provided guidelines for evaluating the economic importance of research accomplishments. General improvements in catalytic technology which are needed for more efficient conversion of syngas to liquid fuel are summarised below, followed by specific recommendations for new directions for catalytic research.

Catalytic improvements which could contribute significantly to more economical manufacture of synthetic liquid fuels are:

1. catalysts which have higher selectivity to molecular species which are useful as high performance fuels. For hydrocarbons, this means conversion, preferably in one step, to high-octane gasoline components, namely isoparaffins and aromatics, or to olefins which can be converted to liquid fuels. For oxygenates, this means octane-enhancing ethanol or higher mixed alcohols, or special value molecules such as MTBE.
2. catalysts which eliminate or greatly reduce methane formation, particularly in the FT process or higher alcohol manufacture.
3. catalysts which provide for operation of process modes which are engineered to improve plant investment and operating costs. An example is the catalytic slurry system which can control heat release and decrease requirements for syngas recycle.
4. catalyst systems capable of providing for process integration for better energy efficiency.
5. catalysts with higher stability, resistant to deactivation by carbon deposition or by sulphur or halides.

Specific recommendations for research are as follows. It is recognised that some represent possible improvements in technology already under development while others are of a longer term nature. For those under development the thought is that a further advance could be very valuable in justifying their industrial installation. For the mid- and longer-term projects, it is expected that these have the potential for even greater improvements.

6.1 Research for near-term applications

Slurry FT/ZSM 5. A better knowledge is required of the essential reactions in each stage of the combination slurry phase FT/ZSM 5 process to provide improved catalytic integration of the two steps for optimum performance.

Wax and crack. Research should be carried out to find catalysts which synthesise a high wax hydrocarbon product having a narrower and hence improved molecular weight distribution.

MTG process. A multifunctional catalyst should be sought which, at a single temperature in a single reactor, is capable of conversion of syngas to methanol and thence to high octane hydrocarbons, with low methane yield.

Methanol. There should be a search for a very active catalyst for synthesis of methanol which can be used at a temperature of about 150°C. This research should be integrated with engineering studies to design plants with lower investment costs.

Slurry synthesis. A determination is needed of the reasons for loss of catalyst stability in slurry operation for synthesis of hydrocarbons or of alcohols, and improved catalysts and procedures established which provide for some stable operation.

C_1-C_6 alcohols. A concerted effort should be made to find ways to lower methane formation.

Methanol homologation. More selective catalysts should be sought for direct conversion of methanol to ethanol using syngas.

Methanol fuel use. Improved catalytic systems should be found to increase energy efficiency in use of methanol fuels.

6.2 Research for the mid-term

These recommendations are based on exploratory research results and new concepts such as: biocatalysis, partial poisoning, metal ensemble size control, metal complexes, supported and modified multimetals, molybdenum-group VIII metal combinations, dual sites, melt catalytic systems, alloys, epitaxial depositions and a wide range of ideas on zeolite-containing catalysts.

Biocatalysis for conversion of syngas to liquid fuels offers an essentially new research approach which merits support.

There is great merit in developing the technique of partial poisoning of metal catalysts with sulphur or other agents, and so restrict unwanted reactions and improve overall selectivity.

The effect of metal particle size needs to be better understood and techniques for control of particle size established, with the objective of determining if the selectivity observed can be put to practical use.

The use of metal-organic complexes, including metal clusters, is recognised as offering the potential for unusually high selectivity attained by control of geometric and electronic factors through choice of metal and ligands. The investigation of transition metal complexes is recommended.

A goal should be to establish the practical technology for synthesis of isoparaffins and isoalcohols, building on the promising information already established and overcoming loss of selectivity during operation.

Synthesis of very high yields of low molecular weight olefins have been reported using several different types of catalysts. It should be a prime research objective to follow up on these leads and to develop practical catalysts for selective olefin synthesis.

Research is needed to find a catalyst which controls chain growth synthesis beyond a certain stage by finding catalytic chemistry which avoids the polymerisation type mechanism or limits it from proceeding beyond a certain stage.

Modification of supported metals is a field of great potential, with opportunities in the use of special supports, chemical modifiers, and utilising multimetal components.

Dual function catalysts which activate hydrogen and carbon monoxide on separate sites offer a new means for control of catalytic performance and warrant research to understand and improve on performance.

Sulphide catalysts should be studied. A special objective should be to improve MoS_x and related catalysts so that they produce less low molecular weight hydrocarbons.

Melt catalysts are in an exploratory phase and proffer opportunities for synthesis of particular molecules of interest as fuels or fuel precursor. This is a new research direction.

The chemistry of the water gas shift reaction should be better established, particularly in respect to the synthesis reaction and for preparation of catalysts with improved balance of functions able to utilise syngas with low H_2/CO ratios.

Epitaxial deposition offers a means of providing novel metals characteristics not found otherwise. These can have unusual chemical and therefore catalytic properties.

Unusual inorganic structures such as layered smectites, new zeolites with different pore structures, and new ceramic solids, carbonitrides or ion implantation systems, are research topics for improved catalytic properties.

Combinations of zeolites and metals offers one of the most challenging opportunities for new catalytic capabilities. One particular objective is to keep the metal from migrating from the zeolite pores. Other ideas include new types of zeolites in which Fe replaces Al, ship-in-a-bottle techniques, encapsulating carbon molecular sieves, and others.

6.3 Research for the long-range

Fundamental research is essential to achieve new and improved catalysts. In summary, such research is concerned with establishing reaction mechanisms, in understanding the surface science of catalysis and catalyst structure-performance relationships, as well as searching for new techniques for scientific design of catalysts.

The dynamics of catalytic reactions are fundamental to the essential performance of catalysts. A major research commitment should be the identification of catalytic mechanisms. This can provide, as it has so successfully in the past, the scientific knowledge and particularly as a source of new ideas for catalytic improvements which otherwise would not have been achieved.

New advanced instrumental capabilities to examine catalyst surfaces on an atomic scale has revealed new understandings of catalyst structure and surface complexes. Catalyst characterisation by new instrumental techniques as well as classical methodology have great promise for the scientific design of new and improved catalysts and research on structure/performance should be pursued vigorously.

The ability to visualise by computer-assisted graphics the geometric parameters of catalysts in relationship to their chemical structure and reactant molecules can provide for the synthesis of catalysts having new and precise capabilities.

A scrutiny should be made of scientific discoveries which could contribute to novel high performance catalysts. Examples could be in discoveries in superconductivity materials or in fields leading to electro-assisted or photo-assisted catalysis. These should be investigated, at least on an exploratory basis.

It has long been known that those experienced in catalyst preparation have been successful in making improved catalysts through an integrated application of their experience. It should now be possible to put catalyst synthesis on the basis of the application of artificial intelligence and other computerised techniques.

6.4 Conclusions

The purpose of this report is to present and discuss new research ideas and experimental results for the catalytic conversion of syngas to synfuels so as to assist in judgements in their technical and practical merits and to provide possible justification for future research projects. It is believed that there are excellent near and longer term opportunities for improved technology for improvements in the economics of indirect coal liquefaction. Improved catalysts can provide

- greater selectivity to higher value high-performance fuels;
- decreased plant costs;
- higher thermal efficiency.

It has been estimated that catalysts having improved capabilities for syngas conversion have the potential to improve the economics of synthetic liquid fuels manufacture by 10% to about 30%. Better catalysts can provide economic savings not only in the conversion reaction step, but they can also be advantageous by a combination of simplification of product upgrading, elimination of shift reaction requirements, and lessening of needs for syngas purification. Beyond these advantages, the selective synthesis of products which are of high performance value as fuels, notably octane rating enhancement, can contribute to economic benefits far beyond their value based on their heats of combustion.

7 References

Abrevaya H, Targos W M, Robota H J, Cohn M J (1986) Development of selective ruthenium catalysts for Fischer-Tropsch synthesis. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 83-104 (1986)

Abrevaya H, Targos W M, Robota H J, Cohn M J (1987) Development of selective ruthenium catalysts for Fischer-Tropsch synthesis. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 18-27 (1987)

Abreveya, H, Targos W M, Robota H J, Cohn M J (1988) Metal particle size effects in FT synthesis with supported Ru catalysts. In: *Catalysis 1987*, Amsterdam, The Netherlands, Elsevier, pp 97-114 (1988)

Anderson R B (1956) Kinetics and mechanism of Fischer-Tropsch synthesis. In: *Catalysis*. Princeton, NJ, USA. Van Nostrand-Reinhold, vol. 4, pp 1-372 (1956)

Anderson R B (1983) Chain growth and iron nitrides in Fischer-Tropsch synthesis. In: *Heterogeneous catalysis*. Washington, DC, USA. *American Chemical Society Symposium Series*; **222**; 389-402 (1983)

Anderson R B (1984) *The Fischer-Tropsch synthesis*. New York, NY, USA, Academic Press, 301 pp (1984)

Andrew S P S (1981) Theory and practice of the formulation of heterogeneous catalysts. *Chemical Engineering Science*; **36** (9); 1431-1445 (1981)

Arai H, Egudri K, Ishihara T, Horiuchi N (1987) Hydrogenation of carbon monoxide over supported alloy catalysts. In: *Studies on utilization of coal through conversion*. Ministry of Education, Science and Culture, Japan, SPEY-16, pp 205-210 (1987)

Arakawa H, Fukshima T, Ichikawa M, Natsushita S, Takeuchi K, Maatsuzaki T, Sugi Y (1985) Selective synthesis of ethanol over Rh-Ti-Fe- Ir/SiO_2 catalyst at high pressure syngas conversion. *Chemistry Letters Japan*; 881-884 (1985)

Arakawa H, Takeuchi K, Matsuzaki T, Suge Y (1984) The effect of metal dispersion on the activity and selectivity of Rh/SiO_2 catalyst for high pressure CO hydrogenation. *Chemistry Letters Japan*; 1607-1610 (1984)

Arakawa H, Kiyozumi Y, Suzuki K, Takeuchi K, Matsuzaki T, Sugi Y, Fukushima T, Matsushita S (1986) Selective synthesis of ethylene from syngas over hybrid catalyst system. *Chemistry Letters Japan*; 1341- 1342 (1986)

Arakawa H, Hamaoka T, Takeuchi K, Matsuzaki T, Sugi Y (1988) Selective synthesis of ethanol over multipromoted Rh/SiO_2 catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry*. Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 602-609 (1988)

Augenstein D C, Wise D L, Wentworth R L, Galliher P M, Lipp D C (1977) *Investigation of converting the products of coal gasification to methane by the action of microorganisms*. FE-2203-17, Springfield, VA, USA, National Technical Information Service, 138 pp (Jan 1977)

Barik S, Clausen E C, Gaddy J L (1986) Production of fuels from coal derived gases. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA. US DoE Pittsburgh Energy Technology Center, pp 92-105 (1985)

Barrault J, Renard C, Yu L T, Gal J (1984) Selective hydrocondensation of CO into light olefins on iron-manganese oxide catalysts. In: *Proceedings 8th international congress on catalysis*. Berlin, FR Germany, Verlag Chemie, pp 101-112 (1984)

Bartholomew C (1986) Metal boride catalysts for indirect liquefaction. In: *University coal research projects*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 51-52 (1986)

Bechtel National Inc. (1986) *Indirect liquefaction of coal via biosynthesis. Preliminary evaluation of technical and economic potential*. DE87002324, Springfield, VA, USA, National Technical Information Service, 105 pp (Oct 1986)

Bell A T (1987) Supports and metal support interactions. In: *Catalyst design*. New York, NY, USA, Wiley, pp 103-109 (1987)

Berg F G A van den, Glezer J H E, Sachtler W M H (1985) The role of promoters in CO/H_2 reactions; effects of MnO and MnO_2 in silica- supported rhodium catalysts.

Journal of Catalysis; **93**; 340-352 (1985)

Bew D G (1981) Economic aspects of catalytic processes. In: *Catalysis and chemical processes.* New York, NY, USA, Wiley, pp 64-87 (1981)

Biloen P, Sachtler W M H (1981) Mechanism of hydrocarbon synthesis over Fischer-Tropsch catalysts. In: *Advances in catalysis*, New York, NY, USA, pp 165-216 (1981)

Bhore N A, Sudhaker C, Bischoff K B, Manogue W H, and Mills G A (1988) Syngas conversion by $Rh/Mo/Al_2O_3$ catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry* Ottawa, Ontario, Canada, Chemical Institute of Canada pp 594-601 (1988)

Bond G C, Richards D G (1986) Lanthanum oxide promoted Rh/TiO_2 and $Rh/Pt/TiO_2$ catalysts for alcohol formation from syngas. *Applied Catalysis*; **28**; 303-319 (1986)

Borg F, Gallezot P, Massardier J, Perrichon V (1986) Pt-Mo bimetallic catalysts supported on Y zeolite. IV Activity and selectivity in CO hydrogenation reactions *C_1 Molecule Chemistry*; **1**; 397- 405 (1986)

Bowker M, Houghton H, Waugh K C (1981) Mechanism and kinetics of methanol synthesis on zinc oxide. *Journal of the Chemical Society Faraday Transactions 1*; (77); 3023-3036 (1981)

Bowker M, Houghton H, Waugh K C (1983) Temperature programmed reaction studies of the interaction of methyl formate and ethanol with polycrystalline zinc oxide. *Journal of the Chemical Society Faraday Transactions 1*; (72); 2573-2582 (1983)

Bowker M, Hyland J N K, Vandervell H D, Waugh K C (1984) Gaseous promoter effects in methanol synthesis on zinc oxide. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, Vol **II**, pp 35-46 (1984)

British Coal (1987) Synthesis of chemical feedstocks and intermediates. Private communication (1987)

Broden G, Rhodin T N, Bruckner C, Benbow R, Hurych Z (1976) Synchrotron radiation study on chemisorptive bonding of CO on transition metals – polarization effect on Ir (100) *Surface Science*; 59; 593-611 (1976)

Bukur D B, Petrovic D, Daly J G (1985) Hydrodynamics of FT synthesis in slurry bubble cap reactors. In: *Proceedings indirect liquefaction contractors review*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 479-512 (1985)

Bukur D, Rosynek MP (1986) Development and process evaluation of improved FT slurry catalysts. In: *Proceedings indirect liquefaction contractors review*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 142-143 (1986)

Burgt M J van der, Klinken J van, Sie S T (1985) The Shell middle distillate synthesis process. In: *5th synfuels worldwide symposium*, Washington, USA, 11-13 Nov 1985. New York, NY, USA, McGraw-Hill Publications (Nov 1985)

Butt J B, Stair P C (1985) Surface studies of carbide formation in iron synthesis catalysts. In: *University coal research projects*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 68-69 (1985)

Carimati A, Girelli A, Marengo S, Martinengo S, Zanderighi L, Zerlia T (1988) Support doping and promotion by metal additives in synthesis gas conversion over rhodium-zirconia catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry*. Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 706-713 (1988)

Carroll W E, Cilen N, Withers H P (1986) FT slurry catalysts for selective transportion fuel production. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 83-94 (1986)

Chaffee A L, Ekstrom A, Lapszewica J, Loeh H (1986) Hydrocarbons from CO, H_2 - H_2O Mixtures. Unusual product distributions and mechanitic implications. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 138-141 (1986)

Chang C D (1983) Hydrocarbons from methanol. *Catalysis Reviews - Science and Engineering*; **25** (1); 1-118 (1983)

Chang C D, Silvestri A J (1977) The conversion of methanol and other O-Compounds to Hydrocarbons Over Zeolite Catalysts. *Journal of Catalysis*; **47**; 249-259 (1977)

Chang C D, Lang W H, Silvestri A J (1979) Synthesis gas conversion to hydrocarbons. *Journal of Catalysis*; **56**; 268-273 (1979)

Chaumette P, Courty Ph, Barbier J, Fortin T, Lavalley J C, Chauvin C, Kiennemann A, Idriss H, Sneeden R P A, Denise B (1988) Carbonates, a key for selecting methanol synthesis catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry*. Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 585-593 (1988)

Chen K R, Hanson F V, Nag N K, Oblad A G (1986) The hydrogenation of CO over Raney iron-manganese catalysts. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 95-108 (1986)

Chinchen G C, Denny F J, Parker, D G, Short G D, Spencer M S, Waugh K, Whan D A (1984) The activity of $Cu\text{-}ZnO\text{-}Al_2O_3$ methanol synthesis catalysts. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 178-188 (1984)

Chinchen G C, Denny P J, Jennings J R, Spencer M G, Waugh K C (1988) Synthesis of methanol. Part I. Catalysts and kinetics. *Applied Catalysis*; **36**; 1-65 (1988)

Chini P, Martinego S, Garlaschelli G (1972) Hydroformylation of propene under null conditions using dodecacarbonyltetrarhodium. *Journal of the Chemical Society, Chemical Communications*; **12**; 709-710 (1972)

Chuang S C, Goodwin J G, Wender I (1985) The effect of alkali promotion on CO hydrogenation over Rh/TiO_2. *Journal of Catalysis*; **95**, 435-446 (1985)

Clausen E C, Gaddy J L (1986) Biological production of liquid fuels from coal derived gases. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 112-125 (1986)

Clausen E C, Gaddy J L (1987) Biological production of liquid fuels from coal derived gases. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 279-313 (1987)

Cohn M (1956) The isosynthesis. In: *Catalysis Vol IV*, New York, NY, USA, Reinhold, pp 443-472 (1956)

Cooper B R, Montano P A (1986) Sulfur effects in multimetallic Fischer Tropsch catalysts. In: *University coal* *research projects.* Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 72-74 (1986)

Cornils B. Rottig W (1982) Higher alcohols from synthesis gas. In: *Chemical feedstocks from coal.* New York, USA. Wiley and Sons, pp 467-481 (1982)

Cornils B, Frohning D, Morkaw K (1984) Catalyst development for selective synthesis via the Fisher Tropsch process. In: *Proceedings 8th international congress on catalysis.* Berlin, FR Germany, Verlag Chemie, II pp 23-34 (1984)

Couch G R (1986) *Biotechnology and Coal.* London, United Kingdom, IEA Coal Research ICTIS/TR38, 56 pp (1986)

Courty P, Arlie J P, Convers A, Mikitenkop P, Sugier A (1984) C_1-C_6 alcohols from syngas. *Hydrocarbon Processing*; 105-108 (Nov 1984)

Courty P, Durando D, Freund E, Sugier A (1982) C_1-C_6 alcohols from syngas on copper-cobalt catalysts. *Journal of Molecular Catalysis*; **17**; 241-254 (1982)

Courty P, Forestiere A, Kawata N, Ohno T, Raimbault C, Yoshimoto M (1987) Production of C_1-C_6 alcohols from synthesis gas. In: *Industrial chemicals via C_1 processes.* Washington, DC, USA. *ACS Symposium Series*; **328**; 42-60 (1987)

Curtis M D, Penner-Hahn J, Baralt O, Schwank J, Thompson L (1988) Surface chemistry and CO hydrogenation activity of sulfided bimetallic clusters. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 869-874 (1988)

Cusumano J A (1987) Molecular engineering of catalytic materials. In: *10th North American meeting of the Catalysis Society*, San Diego, USA, Paper A27 (1987)

Dai C H, Worley S D (1986) Effects of potassium on carbon monoxide methanation over supported rhodium films. *Journal of the Physical Society*; **90** (18); 4219-4421 (1986)

Davis S M, Somorjai G A (1985) Molecular ingredients in heterogeneous catalysis: new horizons for high technology. *Bulletin de la Societe Chimique de France*; **3**; 271-287 (May 1985)

Delgass W N, Hummel A A, Wilson A P, Hummel K E (1986) Iron nitride catalysts for synthesis reactions. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (2) 207-214 (1986)

Denise B, Harmon C, Sneeden R P A (1984) Hydrocondensation of CO on composite bifunctional catalysts. In: *Proceedings 8th International Congress on Catalysis.* Berlin, FR Germany, Verlag Chemie, II, pp 93-112 (1984)

DiConca M, Riva A, Trifiro F, Uaccari A (1984) The zinc-chromium oxide potassium promoted catalyst for higher alcohols synthesis. In: *Proceedings 8th international congress on catalysis*, Berlin, West Germany, Verlag Chemie, II pp 173-183 (1984)

Dombek B D (1983) Homogeneous catalytic hydrogenation of CO : ethylene glycol and ethanol from synthesis gas. In: *Advances in Catalysis 32* New York, NY, USA, Academic Press, pp 325-416 (1983)

Dombek B D (1985) Optimum fuel alcohol mixtures from syngas. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 239-263 (1985)

Dombek B D (1986) Optimum fuel alcohol mixtures from syngas. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 86-100 (1986)

Dry M E (1982) Catalytic aspects of industrial FT synthesis. *Journal of Molecular Catalysis*; **17**; 133-144 (1982)

Dry M E (1981) The Fischer-Tropsch synthesis. In: *Catalysis and Technology*, Berlin, FR Germany, Springer Verlag, I Chapter 4 (1981)

Dry M E (1986) Recent developments in SASOL FT technology. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (2); 288-292 (1986)

Dry, M E (1987) Chemicals produced in a commercial Fischer-Tropsch process. In: *Industrial chemicals via C_1 processes.* Washington, DC, USA. *ACS Symposium Series*; **328**; 18-33 (1987)

Dumesic J A, Milligan B A, Greppi L A, Balse V R, Sarnowski K T, Beal C E, Kataoka T, Rudd, D F (1987) A kinetic approach to the design of catalysts : formation of a catalysts design advisory program. *Industrial and Engineering Chemistry Research*; **26**; 1399-1407 (1987)

Duthie R (1986) *Indirect liquefaction of coal via biocatalysis: preliminary evaluation of technical and economic potential.* US DoE report DE-AC22-85PL80013 (Oct 1986)

Duthie R (1985) Indirect liquefaction of Coal Via Biosynthesis. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 91-105 (1985)

Dybkyjaer I, Hansen J B (1985) New developments in methanol technology. *Chemical Economy and Engineering Review Japan*; **17** (5); No. 188 (1985)

Echigoya E, Niiyama H (1982) Hydrogenation of coal to methane by the use of physically mixed catalysts. In: *Research on effective use of energy: Reports of special project research under grant in aid of the Ministry of Education, Science and Culture, Japan.* Tokyo, Japan, Ministry of Education, Science and Culture, pp531-536 (1982)

Ellgen P C, Bartley W J, Bhasis M M, Wilson T P (1979) Rhodium-based catalysts for the conversion of synthesis gas to two-carbon chemicals. In: *Hydrocarbon synthesis from carbon monoxide and hydrogen. Advances in Chemistry Series*; **178**; 147-157 (1979)

Elliot D J, Pennella F (1986) Ester and ketone formation from synthesis gas over Cu/ZnO/Al_2O_3 catalysts. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 39-45 (1986)

El Sawy A, Gray D, Neuworth M, Tomlinson G (1984) *A techno- economic assessment of the Mobil two-stage slurry Fischer-Tropsch/ZSM-5 process* DE85003890 DOE/DP/00789-T99, Springfield, VA, USA, National Technical Information Service, 173 pp (1984)

El Sawy A, Gray D, Talib A, Tomlinson G (1986) Development of techno-economic model for the evaluation of research opportunities in Fischer-Tropsch systems. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 152-176 (1986)

Emmett P H (1956) *Catalysis-hydrocarbon synthesis, hydrogenation and cyclization*, New York, NY, USA, Reinhold, 570 pp (1956)

Fabbricino L, Hudgins R R, Silverston P L (1984) Periodic dosing of methanol synthesis over a copper zinc mixed catalyst. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 202-209 (1984)

Fahey D R (1987) Industrial chemicals via C_1 processes. Washington, USA, *ACS Symposium Series*; **328**; 261 pp (1987)

Falbe J (1967) *Syntheses mit Kohlenmonoxyd (Syntheses with carbon monoxide).* Berlin, Germany. Springer-Verlag, 212 pp (1967)

Falbe J (1970) *Carbon Monoxide in Organic Synthesis.* Berlin, Germany. Springer-Verlag, 219 pp (1970)

Falbe J (Ed) (1977) *Chemierohstoffe aus Kohle (Chemical feedstocks from coal).* Berlin, Germany. G. T. Verlag, 445 pp (1977)

Falbe J (1980) *New syntheses with carbon monoxide.* Berlin, FR Germany, Springer-Verlag, 465 pp (1980)

Falbe J (Ed) (1982) *Chemical feedstocks from coal.* New York, USA. Wiley and Sons, 647 pp (1982)

Foley H (1986) Novel carbon molecular sieves for wax suppression in the Fischer-Tropsch reaction. In: *Indirect liquefaction contractors meeting*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 17-35 (1986)

Foley H C, O'Toole M P (1987) Bimetallic catalysts for the reaction of carbon monoxide and hydrogen and method of making the catalyst. *US patent 4,684,618* (4 Aug 1987)

Fraenkel D, Gates B C (1980) Shape-selective Fischer-Tropsch synthesis catalyzed by zeolite-entrapped cobalt clusters. *Journal of the American Chemical Society*; **102**; 2478-2480 (1980)

Frohning C D (1980) Hydrogenation of the Carbon Monoxide. In: *New synthesis with carbon monoxide.* Berlin, FR Germany, Springer-Verlag, pp 309-371 (1980)

Frohning C D, Koelbel H, Raleic M, Rottig W, Schnur F, Schulz H (1982) Fischer-Tropsch Process. In: *Chemical feedstocks from coal.* New York, USA, Wiley and Sons, pp 309-432 (1982)

Fujimoto K (1987) Reaction engineering of the slurry phase Fischer-Tropsch synthesis. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science and Culture, Japan, SPEY-16, pp 199-204 (1987)

Fujimoto K, Adachi M, Tominaga H (1985) Direct synthesis of isoparaffins from synthesis gas. *Chemistry Letters Japan*; 783-786 (1985)

Fujimoto K, Saima H, Tominaga H (1985) Selective synthesis of isoparaffins from synthesis gas. *Bulletin of the Chemical Society of Japan*; **58** (10); 3059-3060 (1985)

Fukushima T, Ishii Y, Onda Y, Ichikawa M (1985) Promoting role of Fe in enhancing activity and selectivity of MeOH production from CO and H_2 catalysed by SiO_2-supported Ir. *Journal of the Chemical Society, Chemical Commununications*; 1752-1754 (1985)

Gaddy J L (1986) *Biological production of fuels from coal-derived gases. Topical report no. 1, a review of the literature.* US DoE report DE- AC22-85PC80012 (Mar 1986)

Gates B C, Guczi L, Knozinger H (1987) *Metal clusters in catalysis. Studies in Surface Science and Catalysis 29.* Amsterdam, The Netherlands, Elsevier, 648 pp (1987)

Gherardi P, Ruggeri O, Trifiro F, Vaccari A, Del Piero G, Manara G, Notari B (1983) Preparation of Cu-Zn-Al mixed hydroxycarbonates precursor of catalysts for synthesis of methanol at low pressure. In: *Preparation of catalysts, III* Amsterdam, The Netherlands, Elsevier, pp 723-731 (1983)

Ghiotti G, Buccuzzi F (1987) Chemical and physical properties of copper- based catalysts for CO shift reaction and methanol synthesis. *Catalysis Reviews - Science and Engineering*; **29**; 151-182 (1987)

Goodman D W, Houston J E (1987) Catalysis: new perspectives from surface science. *Science*; **236**; 403-409 (24 April 1987)

Goodwin J G, Wender I (1985) Promotion effects on the synthesis of higher alcohols. In: *University coal research projects*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 63-65 (1985)

Grandvallet P, Courty P, Freund E (1984) Characterization and catalytic properties of copper-cobalt-aluminum-zinc mixed phases for higher alcohol synthesis. In: *Proceedings 8ih international congress on catalysis*, Berlin, FR Germany, Verlag Chemie II, pp 81-100 (1984)

Gray D (1984) Potential economic improvements in indirect liquefaction. *American Chemical Society, Division of Fuel Chemistry, Tutorial* (Aug 1984)

Gray D, Tomlinson G (1985) *A baseline technology assessment of methanol as an automotive fuel. Workshop on automative use of methanol-based fuels*, Washington, DC, USA, National Science Foundation, 45 pp (1985)

Grens J, Borg I, Stephens D, Colmenares C (1983) *Economic impact of an improved methanol catalyst.* UCRL 53436 Springfield, VA, USA, National Technical Information Service, 7 pp (July 1983)

Gulari E (1986) Rate and selectivity enhancement in FT synthesis. In: *University coal research projects*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 66-68 (1986)

Gustafson B L, Whener P S (1986) Selective production of alpha olefins from synthesis gas over ZnO supported Pd-Fe bimetallics. *American Chemical Meeting, Division of Fuel Chemistry, Preprints*; **31** (3); 109-115 (1986)

Haag W O, Kuo J C, Wender I (1987) Gasification for synthesis of fuels and chemicals. In: *Coal gasification: Direct application and synthesis of chemicals and fuels.* US DoE report DE/ER--0326, DE8800129 Springfield, VA, USA, National Technical Information Service, pp 117-197 (1987)

Hagiwara H, Sano T, Okado H, Saito K, Okabe K, Hosoya T, Takaya H, Bando K (1986) Conversion of synthesis gas to light olefins utilizing ZSM-5 type zeolite catalysts modified with alkaline earth metals, *Sekiyu Gakkaishi*; **29** (2); 174-177 (1986)

Hamada H, Kuwahara Y, Kintaichi Y, Ito T, Wakabayashi K, Iijima H, Sanon K (1984) Selective synthesis of C_2-oxygenated compounds over Ir-Ru bimetallic catalysts. *Chemistry Letters Japan*; 1611-1612 (1984)

Hanlon R T, Satterfield C N (1988) Reactions of selected 1-olefins and ethanol during the Fischer-Tropsch synthesis. *Energy and Fuels*; 2 (2); 196-204 (1988)

Hanson F V, Chen K R, Kim C S, Oblad A G, Tai W P (1987) The hydrogenation of CO over coprecipitated and Raney Fe-Mn catalysts. In: *10th North American meeting of the Catalysis Society*, San Diego, USA, Paper A41 (1987)

Hayasaka T, Ohbayashi Y, Uchiyama S, Kawata N (1988) Production of higher alcohols from synthesis gas over coprecipitated nickel catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 513-520 (1988)

Herman R G, Simmons G W, Klier K (1981) Catalytic synthesis of methanol from CO/H_2 III the role of alumina and ceria in the Cu/ZnO system. In: *New horizons in catalysis, 7A.* Amsterdam, The Netherlands, Elsevier, pp 475-489 (1981)

Himelfarb P B, Simmons G W, Klier K (1984) Microstructure of $Cu/ZnO/Al_2O_3$ methanol synthesis catalysts studied by scanning and transmission electron microscopy and diffraction methods. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 233-239 (1984)

Hindermann J R, Kiennemann A, Chakor-Alami A, Kieffer R (1984) Synthesis of methanol from CO and H_2 on $Pd\text{-}MgO\text{-}SiO_2$. Correlation between activity and concentration of formyl species. In: *Proceedings 8th international congress on catalysis,* Berlin, FR Germany, Verlag Chemie II, pp 163-171 (1984)

Hnatow P, Konig L, Schliebs B, Gaube J (1984) Development of FT iron catalysis of improved 1-alkene selectivity. In: *Proceedings 8th international congress on catalysis,* Berlin, FR Germany, Verlag Chemie II, pp 113-122 (1984)

Hoelderich W, Eichorn H, Lehnert R, Marossi L, Mross W, Reinke R, Rappel W, Echlimper L (1983) Aluminosilicate and borosilicate zeolites and their use in the conversion of methanol to olefins In: *Proceedings 6th international zeolite conference,* Butterworths, Guildford, United Kingdom, pp 545-555 (1983)

Hofstadt C E, Schneider M, Bock O, Kochoefl K, (1983) Effect of preparation methods and promoters on activity and selectivity of $Cu/ZnO/Al_2O_3$ catalysts in aliphatic alcohol synthesis from CO and H_2. In: *Preparation of catalysts III.* Amsterdam, The Netherlands, Elsevier, pp 709-721 (1983)

Hoogendoorn J C (1977) Gas from coal for synthesis of hydrocarbons. In: *Proceedings of the ninth synthetic pipeline gas symposium.* Chicago, IL, USA, American Gas Association, pp 301-313 (1977)

Huff G A, Satterfield C N (1984) Evidence for two chain growth probabilities on iron catalysts in the Fischer-Tropsch synthesis. *Journal of Catalysis*; **85**; 370-379 (1984)

Humbach J, Schoonover M W (1985) FT wax characterization and upgrading. In: *Proceedings indirect liquefaction contractors meeting,* Pittsburgh, USA, Pittsburgh Energy Technology Center, pp 29-38 (1985)

Ichikawa M, Fukushima T, Shikakura K (1984) The role of Fe, Mn, and Ti oxide additions in modifying C_2-oxygenate formation catalyzed by SiO_2 supported Rh-containing catalysts in a $CO\text{-}H_2$ conversion. In: *Proceedings 8th international congress on catalysis.* Berlin, FR Germany, Verlag Chemie II, pp 69-80 (1984)

Ichikawa M, Fukuoka A, Kimura T (1988) Selective CO hydrogenation to C_1-C_2 alcohols catalysed on Fe-containing Rh, Pt, Pd bimetal carbonyl cluster-derived catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 569-576 (1988)

Ichikawa S, Poppa H, Boudart M (1984) The effect of particle size on the reactivity of supported palladium. *ACS Symposium Series*; **248**; 439-451 (1984)

International Energy Agency (1985) *Synthetic liquid fuels. An IEA seminar* Paris, France, OECD, 152 pp (1985)

Inui T, Miyamoto A (1987) Development of shape-selective metallosilicates and their application to syngas conversion to liquid hydrocarbons. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan, SPEY-16, pp 175-181 (1987)

Iwasawa Y (1987) Surface design of CO hydrogenation catalysts and their reaction mechanisms. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan, SPEY-16, pp 211-216 (1987)

Jackson S D, Brandeth B J, Winstanley (1986) Carbon monoxide hydrogenation over group VIII metals supported on tungsten and molybdenum trioxides. *Applied Catalysis*; **27**; 325-333 (1986)

Kaneda K, Mori T, Kobayashi M, Imanaka T, Teranishi S (1985) The enhanced formation of C_2 oxygenates in the hydrogenation of CO over modified cobalt catalysts. *Chemistry Letters Japan*; 1315-1318 (1985)

Karn F G, Schultz J F, Anderson R B (1965) Hydrogenation of carbon monoxide and carbon dioxide on supported ruthenium catalysts at moderate pressures. *Industrial and Engineering Product Research and Development*; 4; 265-269 (1965)

Karwacki E J, Anwalt M R, Brown D M (1984) An investigation of the chemical states of copper in methanol catalysts and their relevance to activity maintenance. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 210-216 (1984)

Kawai M, Uda M, Ichikawa M (1985) The electronic state of supported Rh catalysts and the selectivity for hydrogenation of carbon monoxide. *Journal of Physical Chemistry*; **89**; 1654-1656 (1985)

Katzer J R, Sleight A W, Gajardo P, Michel J B, Gleason E F (1981) The role of the support in CO hydrogenation selectivity of supported rhodium. *Faraday Discussions of the Chemical Society*; **72**; 121- 133 (1981)

Keim W (1983) *Catalysis in C_1 chemistry.* Boston, USA, Reidel, 312 pp (1983)

Keim W (1986) Synthesis gas: feedstock for chemicals. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 12-15 (1986)

Keller A (1985) The coproduction of methanol and electrical power from coal. *Energy Progress*: 5 (3); 131-135 (1985)

Kelley M J (1987) Surface sensitive analytical techniques. *ChemTech*; **17** (1); 30-33; (2) 98-105; (3) 170-174; (4) 232-240; (5) 294-299; (8) 490-495; (10) 632-635 (1987)

Kikuchi E (1987) Development of catalysts for liquid phase FT synthesis. In: *Studies on utilization of coal through conversion.* Ministry of Education, Sciences, and Culture, Japan, SPEY-16, pp 193-198 (1987)

Kikuzono Y, Kagamis S, Naito S, Onishi T, Tamaru K (1981) Selective methanol formation from atmospheric CO and H_2 over novel palladium catalyst. *Chemistry Letters, Japan*; 1249-1252 (1981)

Kim C, Chen K, Hanson F V, Oblad A G, Tsai Y (1986) Manganese oxide as a promoter for C_2-C_4 olefin production in the hydrogenation of CO_2. *American Chemical Society,* *Division of Petroleum Chemistry, Preprints*; **31** (1); 198-207 (1986)

Kip B J, Hermans E G F, Van Wolput J H M C, Hermans N M A, Van Grondelle J, Prins R (1987) Hydrogenation of CO over rhodium/silica catalysts promoted with molybdenum oxide and thorium oxide. *Applied Catalysis*; **35**; 109-139 (1987)

Kip B J, Hermans, E G F, Prins R (1988) Particle size, promoter, and morphology effects in synthesis gas conversion over silica-supported rhodium catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 821-828 (1988)

Klier K (1982) Methanol synthesis. In: *Advances in Catalysis 31*. New York, NY, USA, Academic Press, pp 243-313 (1982)

Klier K, Herman R G, Young C W (1984) Direct synthesis of 2-methyl-1-propanol. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 273-280 (1984)

Klier K, Herman R G, Simmons G W, Lyman C E (1985) Direct synthesis of alcohol fuels over molybdenum-based catalysts. In: *Indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 70-80 (1985)

Klier K, Herman R G, Simmons G W, Bogdan C E, Nunan S G, Smith K J (1987) Direct synthesis of 2-methyl-1-propanol/methanol fuels and feedstocks. In: *indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, Vol I, pp 258-379 (1987)

Klinger R J, Bloom I, Rathke J W (1986) Exploring catalytic methanol synthesis using soluble metal oxide complexes. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 26-31 (1986)

Knifton J F (1987) The selective generation of acetic acid directly from synthesis gas. In: *Industrial chemicals via C_1 processes*. Washington, DC, USA. *ACS Symposium Series*; **328**; 98-107 (1987)

Knifton J F (1986) The selective generations of acetic acid directly from synthesis gas. *American Chemical Society, Division of Petroleum Chemistry Preprints*; **31** (1); 26-31 (1986)

Koelbel H, Ralek M (1980) The Fischer-Tropsch synthesis in liquid phase. *Catalysis Reviews - Science and Engineering*; **21** (2); 225-274 (1980)

Koelbel H, Ralek M (1984) The Koelbel-Engelhardt synthesis. In: *Fischer- Tropsch synthesis*. New York, NY, USA, Academic Press, Ch. 7 (1984)

Kondoh S, Muraki H, Fujitani Y (1986) Hydrogenation of CO on $Co/MgAl_2O_4$ and $Ce-Co/MgAl_2O_4$ catalysts. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 153-162 (1986)

Kotera Y, Oba K, Osawa K, Shimomura K, Uchida H (1976) The preparation of catalysts for methanol synthesis and their characteristics. In: *Preparation of Catalysts I*. Amsterdam, The Netherlands, Elsevier, Vol 1, pp 589-599 (1976)

Kuo J C W, Smith J, Kupte K M, Lieb T M (1985) Two-stage indirect coal liquefaction. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 113-144 (1985)

Kuwahara Y, Hamada H, Kinaichi V, Ito T, Wakabayashi K (1985) Hydrogenation of CO over silica supported Mo-Ir catalysts. *Chemistry Letters Japan*; 205-206 (1985)

Lambert R M, Nix R N, Jennings J R, Owen G (1988) Activation and deactivation of novel alloy-derived catalysts for methanol synthesis. In: *Catalysis 1987*. Amsterdam, The Netherlands, Elsevier, pp 131-140 (1988)

Langley K F (1987) *A ranking of synthetic fuel options for road transport application in the UK*. Harwell, United Kingdom, Department of Energy, ETSU-R-33, 91 pp (1987)

Lapidus A L, Savelev N M (1984) Transition metal complexes as catalysts of the synthesis of hydrocarbons from carbon oxides and hydrogen. *Russian Chemical Reviews*: **53** (6); 535-546. Translated from *Uspekhi Khimi*; **53**; 925- 947 (1984)

Larkins T H (1986) Chemicals from coal - the Eastman experience. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 74-78 (1986)

Lee G van der, Ponec V (1987) On some problems of selectivity in syngas reactions on group VIII metals. *Catalysis Reviews - Science and Engineering*; **29** (2/3); 183-218 (1987)

Lee G van der, Schuller B, Post H, Favre T L F, Ponec V (1986) On the selectivity of Rh catalysts in the formation of oxygenates. *Journal of Catalysis*; **98**; 522-529 (1986)

Lewnard J J, Stepanoff P R, Rao P (1986) Recent laboratory activities toward developing the liquid phase methanol process. In: *Indirect Liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 43-57 (1986)

Lin Z-Z, Okuhara T, Misono M, Tohji K, Udagawa Y (1985) Pronounced effect of particle size on selectivity observed for CO hydrogenation on Ru- alumina catalysts. *Journal of the Chemical Society Chemical Communications*; 1673-1675 (1986)

Lin Z, Okuhara T, Misono M (1986) Morphology of Ru particles on Al_2O_3 and its effect on selectivity in catalytic hydrogenation of CO. *Chemistry Letters Japan*; 913-914 (1986)

Liu D, Zhu Q, Li J (1988) Mechanistic studies on methanol synthesis over Cu-based catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry*. Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 577- 584 (1988)

Liu J, Wang H, Fu J, Li Y, Tsai K (1988) Insitu trapping of ketene intermediate in syngas conversion to ethanol over promoted rhodium catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry. Ottawa*, Ontario, Canada, Chemical Institute of Canada, pp 735-742 (1988)

Makihara H, Niwa K, Nagai H, Morita K, Horizoe H, Kobayashi K, Kuwada C (1987) Characteristics of a new methanol synthesis reactor. *Energy Progress*; 7 (1); 51-58 (1987)

Marschner F, Moller F W, Schulze-Bentrop R (1982) Methanol from synthesis gas. In: *Chemical feedstocks from coal*. New York, USA, Wiley and Sons, pp 433-466 (1982)

Marten J A, Camps J A (1986) Process for the production of ethanol by acetate esters. In: *State-of-art symposium -*

methanol as a raw material for fuel and chemicals. American Chemical Society, Division of Industrial and Engineering Chemistry, Marco Island, USA (1986)

Matsumoto D K, Satterfield C N (1987) Effects of poisoning a fused magnetite Fischer-Tropsch catalyst with dibenzothiophene. *Energy and Fuels*; **1**; 203-210 (1987)

Mauchausse C, Mozzanega H, Turlier P, Dalmon J-A (1988) Influence of the support on the catalytic properties of sulfide catalysts in CO hydrogenation. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 775-782 (1988)

McArdle J C, Humbach M J, Schoonover M W, Padrta F G (1986) Fischer-Tropsch wax characterization and upgrading. In: *Indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 1-33 (1986)

McCarty J, Wilson R B (1986) Improved FT synthesis catalyst for indirect coal liquefaction. In: *Indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 105-124 (1986)

McDonald M A (1986) Effects of H_2O and CO_2 on the activity and composition of iron FT catalysts. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (3); 17-22 (1986)

Meisel S L, McCullough J P, Lechthaler C H, Weisz P B (1976) Gasoline from coal in one step. *ChemTech*; **6**: 86-89 (1976)

Melsom G A, Zuckerman E B (1988) Bifunctional Ru/zeolite catalysts for CO hydrogenation. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada pp 807-812 (1988)

Meriandeau P, Dufaux M, Naccache C (1984) The role of support for Pt- based catalysts in selective formation of methanol from synthesis gas. In: *Proceedings 8th international congress on catalysis.* Berlin, FR Germany, Verlag Chemie, II, pp 185-194 (1984)

Miller J G, Yang C L, Rabo J A (1986) Bifunctional FT catalyst development. In: *Indirect liquefaction contractors meeting*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 1-15 (1986)

Miller J G, Yang C L, Rabo J A (1987) Bifunctional FT catalyst development. In: *Indirect liquefaction contractors meeting*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 1-17 (1987)

Mills G A (1977) Alternative fuels from coal. *ChemTech*; 7 (7); 418-423 (1977)

Mills G A, Ecklund E E (1987) Alcohols as components of transportation fuels. *Annual Review of Energy*; **12**; 47-80 (1987)

Mills G A, Knudsen C W (1979) Comparative economics of synthetic hydrocarbon sources. *Proceedings 10th world petroleum congress*, Bucharest, vol 3, pp 329-336 (1979)

Mills G A, Steffgen F W (1973) Catalytic methanation. *Catalysis Reviews*; **8** (2): 159-210 (1973)

Misono M, Okuhara T, Take J (1987) Production of hydrocarbons from CO and H_2 over ruthenium catalysts dispersed on solid acid supports having layered structures. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 169-174 (1987)

Mori T, Miyamoto A, Takahashi N, Fukagaya M, Hattori T, Murakami Y (1986) Promotion effects of V, Mo, W, and Re oxides on surface reactions in the CO hydrogenation over Ru/Al_2O_3 catalyst. *Journal of Physical Chemistry*; **90**; 5197-5201 (1986)

Mori Y, Mori T, Takashi N, Miyamoto A, Hattori T, Murakami Y (1986) Unique reaction characteristics of Rh catalysts for the CO hydrogenation by means of PSRA. *Chemistry Letters Japan*; 205-208 (1986)

Moser W R, Lo R, DeMattia E G, Willard J A (1984) Crystal and catalytic chemistry of methanol synthesis. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **29** (5); 240-242 (1984)

Murakami Y (1981) *Shokubai Sekkei* (Catalyst Design) Tokyo, Japan, Maki-Shoten, pp1- (1981)

Murakami Y (1987) Design of metal-metal oxide composite catalyst for FT synthesis. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 217-222 (1987)

Murchison C B, Conway M M, Stevens R R (1987) Mixed alcohols from syngas over molybdenum catalysts. In: *10th North American meeting of the Catalysis Society.* San Diego, USA, Paper A46 (1987)

Naito S, Yoshioka H, Orita H, Tamaru K (1984) The nature of active sites for oxygenated compound formation from $CO-H_2$ under mild conditions. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, III, pp 207-229 (1984)

Nakajo T, Sano K, Matsuhira S, Arakawa H (1986) Direct synthesis of acetic acid from synthesis gas over $Rh-Mn-Zr-Li/SiO_2$ catalyst. *Chemistry Letters Japan*; 1556-1560 (1986)

Nakajo T, Arakawa H, Sano H, Matsuhira S (1987) A striking effect of H_2S treatment of catalyst on the improvement of acetic acid selectivity in high pressure CO hydrogenation over $Rh-Ir-Mn-Li/SiO_2$. *Chemistry Letters Japan*; 593-596 (1987)

Nakamura R, Takahashi I, Yong C S, Niiyama H (1988) CO/H_2/alkene reactions over Co/oxide and cobalt carbonyl/oxide catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 759-766 (1988)

Natta G, Columbo U, Pasquon I (1957) Direct synthesis of higher alcohols from CO and H_2. In: *Catalysis V*, New York, NY, USA, Reinhold, pp 131- 174 (1957)

Natta G (1955) Synthesis of methanol. In: *Catalysis III*, New York, NY, USA, Reinhold, pp 349-411 (1955)

Niemantsverdriet J W, Louwers S P A, Grondelle J van, Kraan A M van der, Kampers F W H, Koningsberger D C (1988) High pressure CO hydrogenation over bimetallic catalysts: FeRu, FeRh, FeIr, FePt, CoIr, CoPt, NiIr, and NiPt on silica. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 674-681 (1988)

Niiyama H, Nakamura R (1987) Improvements in selectivities for FT reaction: CO/H_2 and CO/H_2/alkene reactions over Co/oxide and cobalt carbonyl/oxide catalysts. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 229-234 (1987)

Niwa M, Murakami Y (1987) Chemical vapor deposition zeolite: preparation, characterization, and molecular shape selectivity. *Materials Chemistry and Physics*; **17**; 73-85 (1987)

O'Dowd W, Smith D N, Reuther J A (1985) Slurry FT reactor hydrodynamics and scale-up. In: *Proceedings indirect liquefaction contractors meeting*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 451-478 (1985)

O'Hare T E, Sapienza R S, Mahajan D, Skaperdas G T (1986) Low temperature methanol process. In: *21 State-of-Art Symposium. American Chemical Society, Division of Industrial and Engineering Chemistry*, Marco Island, USA (1986)

Okada O, Ipponmatsu M, Kawai M, Aika K, Onishi Y (1984) The effect of strong interaction between Ru and Al_2O_3 on the activity for CO hydrogenation over Ru/Al_2O_3. *Chemistry Letters Japan*; 1041-1044 (1984)

Okamoto Y, Fukino K, Imanaka T, Teranishi S (1983) Surface characterization of CuO-ZuO methanol synthesis catalysts by X-ray photoelectron spectroscopy. I. Precursor and calcined catalysts. *Journal of Physical Chemistry*; **83**; 3740-3747 (1983)

Okamoto Y, Fukino K, Imanaka T, Teranishi S (1984) Synergy between Cu and ZnO for methanol conversion over Cu-ZnO catalysts. *Chemistry Letters Japan*; 71-74 (1984)

Olive H G, Olive S (1984) *Catalyzed hydrogenation of CO.* Berlin, FR Germany, Springer Verlag (1984)

Ono Y (1983) On the mechanism of methanol conversion over zeolite. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **28** (2); 142-145 (1983)

Ono Y (1987) Conversion of methanol to hydrocarbons over solid-acid catalysts. In: *Studies on utilization of coal through conversion.* Ministry of Education, Science, and Culture, Japan, SPEY-16, pp 181-186 (1987)

Oukaci R, Wu J C S, Goodwin J G (1986) CO hydrogenation on zeolite- supported Ru: Effect of neutralizing cations. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3) 66-70 (1986)

Oukaci R, Wu J C S, Goodwin J G (1987) Derivation and effect of bifunctionality on the FT synthesis on zeolite-supported metal catalysts. In: *10th North American Meeting of the Catalysis Society*, San Diego, USA, Paper A42 (1987)

Parris G E, Klier K (1984) Chemisorption of CO, CO_2, O_2, and H_2 on the Cu/ZnO methanol synthesis catalyst. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 218-225 (1984)

Pedersen K, Hjaelm I G, Jens J, Rostrup-Nielsen R. Process and Catalyst for the preparation of a gas mixture having a high content of C_2-hydrocarbons. *British Patent Application GB 2065491 A* (16 Dec 1980)

Petrini G, Montino F, Bossi A, Garbassi F (1983) Preparation and characterization of active $Cu/ZnO/Al_2O_3$ LTS catalysts using a single phase Cu-Zn precursor compound. In: *Preparation of Catalysts III*, Amsterdam, The Netherlands, Elsevier, 16, 735-745 (1983)

Peuchert M, Linden G (1984) Zeolite supported cobalt catalyst for CO hydrogenation. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, II, pp 135-144 (1984)

Pichler H (1952) Twenty-five years of synthesis of gasoline by catalytic conversion of CO and H_2. In: *Advances in Catalysis 4*, New York, NY, USA, Academic Press, 272-341 (1952)

Poels E K, Ponec V (1983) *Formation of oxygenated products from synthesis gas. A specialists periodic report.* London, United Kingdom, The Royal Society of Chemistry, pp 196-234 (1983)

Poels E K, Mangnus P J, Welzen J, Ponec V (1984) Rhodium and palladium catalysis of the CH_3OH synthesis. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, II, pp 59-68 (1984)

Ponec V (1982) *Fischer-Tropsch and related reactions. A Specialists Periodic Report 6.* London, United Kingdom, The Royal Society of Chemistry, 5, pp 49- 79 (1982)

Ponec V (1978) Some aspects of the mechanism of methanation and Fischer-Tropsch synthesis. *Catalysis Reviews - Science and Engineering*; **18**; 151-171 (1978)

Ponec V (1988) Personal communication (1988)

Poutsma M L, Clek L F, Ibarabia D A, Risceh A P, Rabo A J (1978) Selective formation of methanol from synthesis gas over palladium catalysts. *Journal of Catalysis*; **52**; 157-168 (1978)

Poutsma M L (1980) *Assessment of advanced process concepts for liquefaction of low H_2:CO ratio synthesis gas based on the Koelbel slurry reactor and the Mobil-gasoline process.* ORNL-5635, Oak Ridge National Laboratory, Chemistry Division, 47 pp (Feb 1980)

Pruett R L (1977) Industrial organic chemicals through utilization of synthesis. *Annals of the National Academy of Science*; (295); 239-248 (1977)

Rao S N, DeRosa J L (1987) *A technical and economic evaluation of the two-stage, low temperature methanol process.* US DoE Contract DE- AC22- 84PC72571 (Jan 1987)

Rao V U S, Gormley R J, Schehl R R, Chi R D H, Obermyer R T (1986) Methane suppression from metal-zeolite catalysts in synthesis gas conversion. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 169-176 (1986)

Rheinbraun Research and Development (1986) Cologne, FR Germany, Rheinische Braunkohlenwerks (1986)

Rogerson P L (1984) The ICI low-pressure methanol process. In: *Handbook of synfuels technology.* New York, NY, USA, McGraw Hill, Ch 2-2, pp 2-47 to 2-73 (1980)

Rossin J A, Davis M E (1986) Synthesis and CO hydrogenation activity of Ru zeolite A. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 71-74 (1986)

Rostrup-Nielson J R, Alstrup P (1988) Ensemble control by sulfur poisoning of nickel catalysts for steam reforming. In: *Catalysis 1987.* Amsterdam, The Netherlands, Elsevier, pp 725-732 (1988)

Rozovskii A Ya, Lin G I, Liberov L G, Slivinskii E V, Loketev S M, Kagan Yu B, Bashkirov A N (1977) Mechanism of LG methanol synthesis from carbon dioxide and hydrogen. III. Determination of rates of individual stages using ^{14}CO. *Kinetics and Catalysis (English Translation)*; **18** (3); 578-585 (1977)

Ryndin Y A, Hicks R F, Bell A T, Yermakov Y I (1981) Effect of metal support interaction on the synthesis of methanol over palladium. *Journal of Catalysis*; **70**; 287-297 (1981)

Sachtler W M H (1984) Elementary steps in the catalytic conversion of syngas. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, I, pp 151-173 (1984)

Sachtler W M H, Ichikawa M J (1986) Catalytic site requirements for elementary steps in syngas conversion to oxygenates over promoted. *Journal of Physical Chemistry*; 90; 4752-4758 (1986)

Saima H, Fujimoto K, Tominaga H (1984) Selective synthesis of aromatic hydrocarbons from synthesis gas. *Chemistry Letters Japan*; 1777-1780 (1984)

Salmon R (1986) *Economics of methanol production from coal and natural gas.* ORNL-6091 Springfield, VA, USA, National Technical Information Service, 82 pp (1986)

Santiesteban J G, Bogdan C E, Herman R G, Klier K (1988) Mechanism of C_1-C_4 alcohol synthesis over alkali/MoS_2 and alkali/Co/MoS_2 catalysts. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis, Vol 2. C_1 Chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 561- 568 (1988)

Satterfield C (1985) Fischer-Tropsch slurry phase process variation to understand wax formation. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 15-28 (1985)

Satterfield C (1986) Fischer-Tropsch slurry phase process variation to understand wax formation. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 37-46 (1986)

Saxena S, Shrivastava S (1986) Heat transfer investigations in a slurry bubble column. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 177-187 (1986)

Schulz R, Feller H G, Ralek M (1988) Surface analytical and synthesis studies of nitrided iron catalysts for the Fischer-Tropsch synthesis. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 800-806 (1988)

Shah P P, Humbach M J, Steigleder K Z, Padrta F G (1987) Fischer-Tropsch wax characterization and upgrading. In: *Indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, Vol I, pp 125-170 (1987)

Shah Y T, Perotta A J (1976) Catalysts for FT and Isosynthesis. *Industrial and Engineering Chemistry Product Research and Development*; **15** (2); 123-131 (1976)

Sheldon R A (1983) *Chemicals from synthesis gas. Catalytic reaction of CO and H_2.* Dordrecht, The Netherlands, Reidel Publishing Co, 216 pp (1983)

Shimogaki Y, Komiyama H, Inoue H, Masumoto T, Kimura H (1985) Porous and amorphous $Ni_{67}Zr_{33}$ catalyst prepared by hydrogenation of CO. *Chemistry Letters Japan*; 661-664 (1985)

Short G D (1987) Lecture, Catalysis Club of Philadelphia (1987)

Shui Y G, Sugiura T, Tatsumi T, Tominaga H (1986) Durability of zeolite supported Ru-Pt bimetallic catalysts for isoalkane synthesis from syngas. *Applied Catalysis*; **24**; 131-143 (1986)

Sie S T, Eilers J, Minderhout J (1988) Consequences of Fischer-Tropsch chain growth kinetics for process mode selection and product selectivity. In: *Catalysis: Theory to Practices. Proceedings: 9th international congress on catalysis. Vol 2. C_1 Chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 743-750 (1988)

Silver R G, Tseng S C, Ekerdt (1986) Isosynthesis mechanism over ZrO_2. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 11-16 (1986)

Slegier W, Sapienzo R, O'Hare T, Mahajan D, Foran M, Skaperdas G (1984) Methanol synthesis at low temperature. In: *9th EPRI Contractors Meeting*, Palo Alto, CA, USA, 15 pp (May 1984)

Slyvinsky E V, Voytsehovsky Yu P, Lokter S M (1988) Initiated hydrocondensation of carbon monoxide--new route of the syntheses of oxygenated compounds on the base CO and H_2. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol 2. C_1 chemistry.* Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 729-734 (1988)

Smith K J, Anderson R B (1984) The synthesis of higher alcohols on Cu/ZnO catalysts. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **29** (5); 269-272 (1984)

Snel R (1987) Olefins from syngas. *Catalysis Reviews - Science and Engineering*; **29** (4); 361-445 (1987)

Socha R F, Chang C D, Gould R M, Kane S S, Avidan A A (1986) Fluid-bed studies of olefin production from methanol. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 16-21 (1986)

Soto J L, Avidan A (1985) Status of 100 BPD fluid bed methanol-to- olefins demonstration plant. In: *Proceedings indirect liquefaction contractors meeting.* Pittsburgh, PA, USA. US DoE Pittsburgh Energy Technology Center, pp 353-369 (1985)

Stenger H G, Satterfield C N (1985) Effects of sulfur poisoning of a reduced fused magnetite catalyst in the Fischer-Tropsch synthesis. *Industrial and Engineering Chemistry Process Design and Development*; **24**; 415-420 (1985)

Stern D, Bell A T, Heinemann H (1985) A theoretical model for the performance of bubble-column reactors used for Fischer-Tropsch synthesis. *Chemical Engineering Science*; **40** (9); 1665-1677 (1985)

Stiles A (1977) Methanol, past, present, and speculation on the future. *AIChE Journal*; **23** (3); 362-375 (1977)

Stiles A (1983) Methanol: Bright past - brilliant future? In: *Heterogeneous catalysis*, Washington, USA, *ACS Symposium Series*; **222**; pp 349-374 (1983)

Storch H H, Columbic N, Anderson R B (1951) *The Fischer-Tropsch and related syntheses.* New York, NY, USA, Wiley, 610 pp (1951)

Studer D W, Holley E P, Hsiung T H, Mednick R L (1987) An update of the LaPorte liquid phase methanol program. In: *Indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, Vol I, pp 215-240 (1987)

Sudhakar C, Bhore N A, Bischoff K B, Manogue W H, Mills G A (1988) Molybdena enhanced Rh/Al_2O_3 catalysts. In: *Catalysis 1987.* Amsterdam, The Netherlands, Elsevier, pp 115-124 (1988)

Sugi Y, Takeuchi K, Matsuzaki T, Arakawa H (1985) The enhanced formation of C_2-oxygenates in hydrogenation of CO over modified cobalt catalyst. *Chemistry Letters*

Japan; 1315-1318 (1985)

Supp E (1985) Improved methanol production and conversion technologies. *Energy Progress*; 5 (3); 127-130 (1985)

Supp E, Quinkler R F (1984) The Lurgi low pressure methanol process. In: *Handbook of synfuels technology*, New York, NY, USA, McGraw-Hill, pp 2-9, 113-131 (1984)

Swedish Motor Fuel Technology Co. (1986) *Alcohol and alcohol blends as motor fuels, Executive Summary I*, 27 pp. State-of-Art IIA Ch 1-7, IIB Ch 8-14. Paris, France, International Energy Agency (1986)

Szmanski R, Charcosset H, Perrichon V (1984) Co, H_2 reactions on supported Pt and Pt-Zr catalysts. In: *Proceedings 8th international congress on catalysis*, Berlin, FR Germany, Verlag Chemie, II, pp 151-161 (1984)

Takahashi N, Mori T, Miyamoto A, Hattori T, Murakami Y (1986) Design of Fischer-Tropsch catalysts by PSRA. *Applied Catalysis*; **22**; 137-146 (1986)

Talbot A (1983) *Assessment of ether and alcohol fuels from coal.* Washington, DC, USA, Department of Energy, DOE/CE/54045 Vol 1, Summary 62 pp, Vol 2 Technical Report 310 pp and Appendices (1983)

Tamaru K (1978) *Dynamic heterogeneous catalysis*, New York, NY, USA, Academic Press, pp 115-129 (1978)

Tatsumi T, Muramatsu A, Tominaga H (1985) Alcohol synthesis from CO_2/H_2 over silica supported molybdenum catalysts. *Chemistry Letters Japan*; 593-594 (1985)

Tatsumi T, Muramatsu A, Fukunaga T, Tominaga H (1986) Nickel promoted Mo catalysts for alcohol synthesis from CO-H_2. *Chemistry Letters Japan*; 919-920 (1986)

Tatsumi T, Muramatsu A, Fukunaga T, Tominaga H (1988) Nickel-promoted molybdenum catalysts for synthesis of mixed alcohols. In: *Catalysis: theory to practice. Proceedings: 9th international congress on catalysis. Vol. 2. C_1 chemistry*. Ottawa, Ontario, Canada, Chemical Institute of Canada, pp 618-625 (1988)

Tatsumi T, Muramatsu A, Tominaga H (1987) Supported molybdenum catalysts for alcohol synthesis from CO-H_2. *Applied Catalysis*; **34**; 77-78 (1987)

Tatsumi T, Shul Y G, Sugiura T, Tominaga H (1986) Selective synthesis of isoalkanes from synthesis gas over zeolite-supported Ru-Pt bimetallic catalysts. *Applied Catalysis*; **21**; 119-131 (1986)

Teper M, Hemming D F, Holmes J M (1984) *The cost of liquid fuels from coal. Part 1. Executive summary* London, United Kingdom, IEA Coal Research, ICEAS/E3/1, 72 pp (1984)

Tominaga H, Tatsumi (1987) Isoparaffin synthesis from syngas catalyzed by Zeolite supported bimetallic clusters. In: *Studies on utilization of coal through conversion*. Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 163-169 (1987)

Tomlinson G, Gray D, El Sawy A (1985) The impact of water-gas shift requirements on the economics of indirect coal liquefaction. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 304-328 (1985)

Tong G T, McCarty J G (1987) Fischer-Tropsch synthesis with sulfur-treated iron catalysts. In: *10th North American Meeting of the Catalysis Society*, San Diego, USA, Paper C42 (1987)

Topp-Jorgensen J, Dibbern H C (1986) Topsoe integrated gasoline synthesis. In: *21st State-of-Art Symposium, American Chemical Society, Division of Industrial and Engineering Chemistry*, Marco Island, USA (1986)

Tsao T R, Heydorn E C (1985) Liquid phase methanol PDU results. In: *Proceedings indirect liquefaction contractors meeting*, Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 372-403 (1985)

Tsao T R, Rao P (1986) The development of the liquid phase methanol process: an update. In: *11th EPRI Contractors Conference*, CA (May 1986)

Tseng S C, Ekerdt J G (1987) Isosynthesis mechanisms over zirconium dioxide. In: *10th North American Meeting of the Catalysis Society*, San Diego, USA, Paper A48 (1987)

Uchijima T, Kunimori K (1987) Strong metal-support interaction in oxide- supported and oxide-modified metal catalysts and its effect on hydrogenation. In: *Studies on utilization of coal through conversion*. Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 223-228 (1987)

Uchiyama S, Obayashi Y, Shibata M, Uchiyama T, Kawata N, Konishi T (1985) Production of higher alcohols from synthesis gas on nickel oxide-based catalysts. *Journal of the Chemical Society Chemical Communications*; 1071-1072 (1985)

Underwood R P, Bell A T (1986) CO Hydrogenation over Rhodium Supported on SiO_2, La_2O_3, and Sm_2O_3. *Applied Catalysis*; **21** 7-168 (1986)

Vannice M A (1976) The catalytic synthesis of hydrocarbons from CO and H_2. *Catalysis Reviews - Science and Engineering*; **14**; 153-191 (1976)

Vannice M A (1987) Metal-support effects on the hydrogenation of CO and carbonyl bonds. In: *10th North American Meeting of the Catalysis Society*, San Diego, USA, Plenary Lecture (1987)

Vedage G A, Himelfarb P, Simmons G W, Klier K (1983) Alkali promoted Cu/ZnO catalysts for low alcohol synthesis. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **28** (5); 1261-1271 (1983)

Vedage G A, Pitchai R, Herman R G, Klier K (1984) Mechanism and intermediates of methanol synthesis over Cu/ZnO catalyst in the presence of water and carbon dioxide. *American Chemical Society, Division of Fuel Chemistry. Preprints*; **29** (5); 196-201 (1984)

Venter J, Vannice M A, Kaminsky K, Geoffrey G L (1986) Olefin formation from CO and H_2 over carbon-supported Mn-Fe and K-Mn-Fe carbonyl clusters. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 219-226 (1986)

Venter J, Kanisky M, Geoffrey G L, Vannice M A (1987a) Carbon-supported Fe-Mn and K-Fe-Mn clusters for the synthesis of C_2-C_4 olefins from CO and H_2. I. Chemisorption and catalytic behaviour. *Journal of Catalysis*; **103**; 450-465 (1987)

Venter J, Kanisky M, Geoffrey G L, Vannice M A (1987b) Carbon-supported Fe-Mn and K-Fe-Mn clusters for the synthesis of C_2-C_4 olefins from CO and H_2. II. Activity maintenance and regenerability. *Journal of Catalysis*; **105**; 155-162 (1987)

Voltz S E, Wise J J (1976) *Development studies on conversion of methanol and related oxygenates to gasoline* Final report, contract E (49-18)-1773 US Energy Research and Development Administration (Nov 1976)

Wender I, Seshadri K S (1984) The indirect liquefaction of coal. In: *Coal liquefaction - investigation of reactor performance, role of catalyst and PCT properties.* Technical progress report US DoE grant PC/600054/74 (Oct 1984)

Williams J A, Blackmond D G, Wender I (1986) Chemical trapping of CO/H_2 surface species. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 5-10 (1986)

Wilson T, Kasai P M, Ellgen (1981) The state of manganese promotion in rhodium-silica gel catalysis. *Journal of Catalysis*; **69**; 193-201 (1981)

Westerterp K R, Kuczynski M (1986) Retrofit methanol plants with this converter system. *Hydrocarbon Processing*; 80-83 (Nov 1986)

Whyman R (1986) Selective synthesis of synthesis gas into C_2-oxygenated products using mixed-metal homogeneous catalysts. *American Chemical Society, Division of Petroleum Chemistry, Preprints*; **31** (1); 32-37 (1986)

Wolf E E (1986) FTIR studies of hydrocarbon synthesis on PD/ZSM 5 catalysts. In: *University coal research projects*. Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 69-71 (1986)

Woodward H F (1967) Methanol. In: *Encyclopedia of Chemical Technology*. New York, NY, USA, John Wiley, pp 370-398 (1967)

Yoon H, Stouffer M R, Dudt P J, Burke F P, and Curran G P (1985) Methanol dissociation for fuel use. *Energy Progress*; **5** (2); 78-83 (1985)

Yashima T (1987) The development of reforming catalysts of hydrocarbons produced from synthesis gas. In: *Studies on the utilization of coal through conversion*. Ministry of Education, Science, and Culture, Japan. SPEY-16, pp 187-192 (1987)

Zhang X, Biloen P (1985) Suppression of methane formation in FT synthesis. In: Pittsburgh, USA, US DoE Pittsburgh Energy Technology Center, pp 405- 419 (1985)

Zuckerman E A, Melson G A (1986) ZSM 5 supported Fe and Ru from $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$: structure/activity correlations for synthesis gas conversion. *American Chemical Society, Division of Fuel Chemistry, Preprints*; **31** (3); 59-65 (1986)

Related publications

Further IEA Coal Research publications on coal science are listed below:

Catalysis in coal liquefaction: *new directions for research*
Frank J Derbyshire, IEACR/08, ISBN 92-9029-158-3, Jun 1988, £60

Understanding pulverised coal combustion
G F Morrison, ICTIS/TR34, ISBN 92-9029-138-9, 46 pp, Dec 1986, £20

Nuclear magnetic resonance studies of coal
R M Davidson, ICTIS/TR32, ISBN 92-9029-126-5, 108 pp, Jan 1986, £20

Catalytic coal gasification
J R Pullen, ICTIS/TR26, ISBN 92-9029-105-2, 57 pp, Jun 1984, £20

Mineral effects in coal conversion
R M Davidson, ICTIS/TR22, ISBN 92-9029-086-2, 100 pp, Jan 1983, £20

Solvent extraction of coal
J R Pullen, ICTIS/TR16, ISBN 92-9029-078-1, 124 pp, Nov 1981, £20

Methanation catalysts
G H Watson, ICTIS/TR09, ISBN 92-9029-053-6, 56 pp, Feb 1980, £20

Molecular structure of coal
R M Davidson, ICTIS/TR08, ISBN 92-9029-049-X, 86 pp, Jan 1980, £20

Other IEA Coal Research publications
Reviews, assessments and analyses of:
- supply, mining and geosciences
- transport and markets
- coal utilisation
- environment
- by-products and waste utilisation

Coal abstracts
Coal calendar
Coal research projects
Coal data base user aids
Reference works on coal resources

Details of all IEA Coal Research publications
are available from:
IEA Coal Research
Publications Department
14-15 Lower Grosvenor Place
London SW1W 0EX
United Kingdom

Tel: 01-828 4661
Telex: 917624 NICEBA G
Fax: 01-828 9508

END

DATE FILMED

7 / 2 / 93