THE INDIRECT LIQUEFACTION OF COAL

by

Irving Wender
and
Kalkunte S. Seshadri

Chemical and Petroleum Engineering Department
University of Pittsburgh
Pittsburgh, PA 15261

Page Intentionally Left Blank

CONTENTS

Section Page

II THE INDIRECT LIQUEFACTION OF COAL

LIST OF TABLES

LIST OF FIGURES

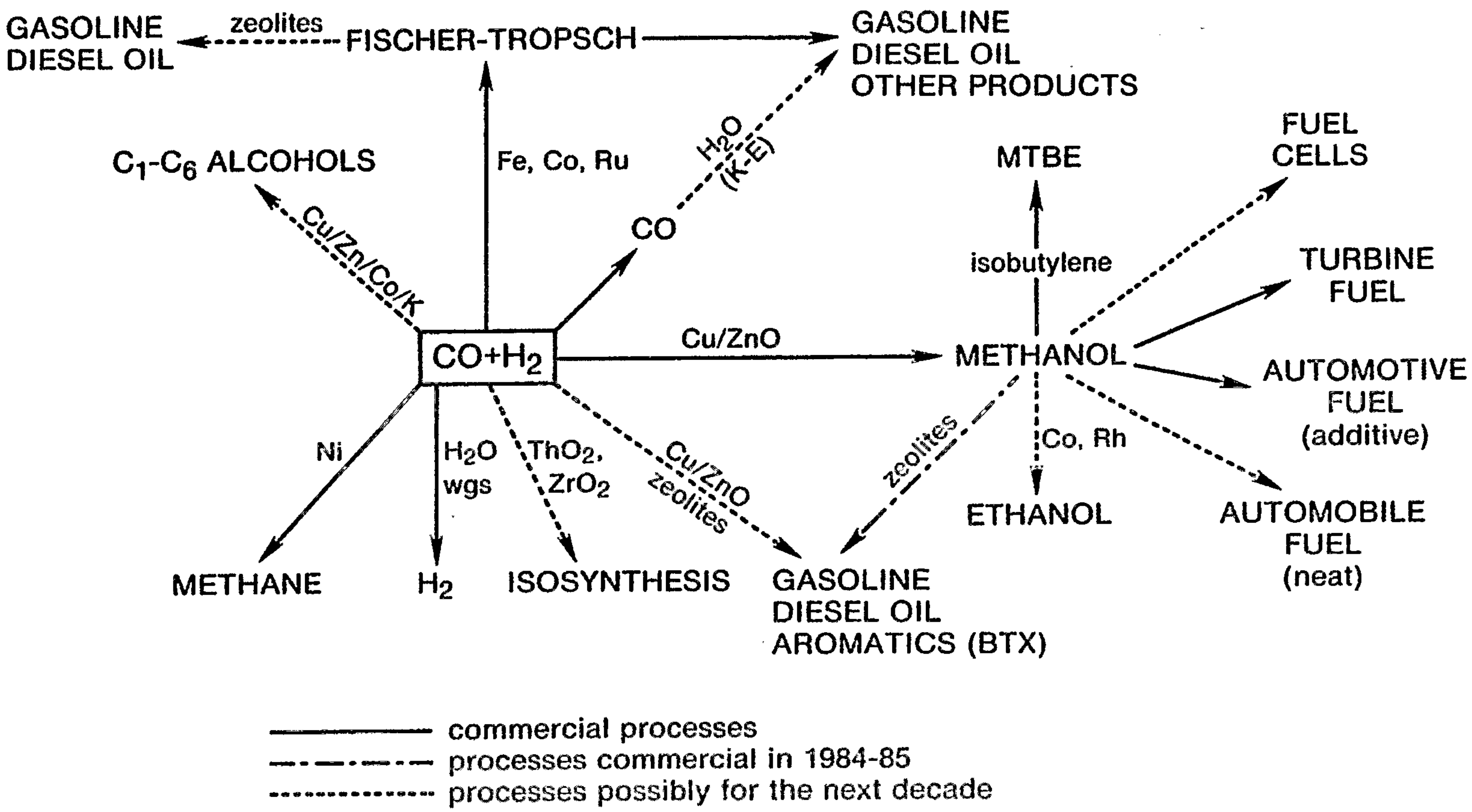
SUMMARY

The objective of this report is to furnish an overview of various routes for converting synthesis gas (syngas, a mixture of hydrogen and carbon monoxide) to liquid fuels and to chemicals. The designation, indirect liquefaction, derives from the fact that the coal or other fossil fuel is first gasified to syngas which, in other usually catalytic steps, is then converted to the desired products. The primary aim is to produce liquid fuels from syngas, but this report will also, to a lesser extent, cover the synthesis of chemicals from syngas.

The field designated as indirect liquefaction is an enormous subject and this report can only hope to outline the main reactions of syngas involved. The commerical, near-commercial and promising fuels that are and that can be produced by this route are diagrammed in Figure II-1. The coresponding routes from syngas to chemicals are summarized in Figure II-2.

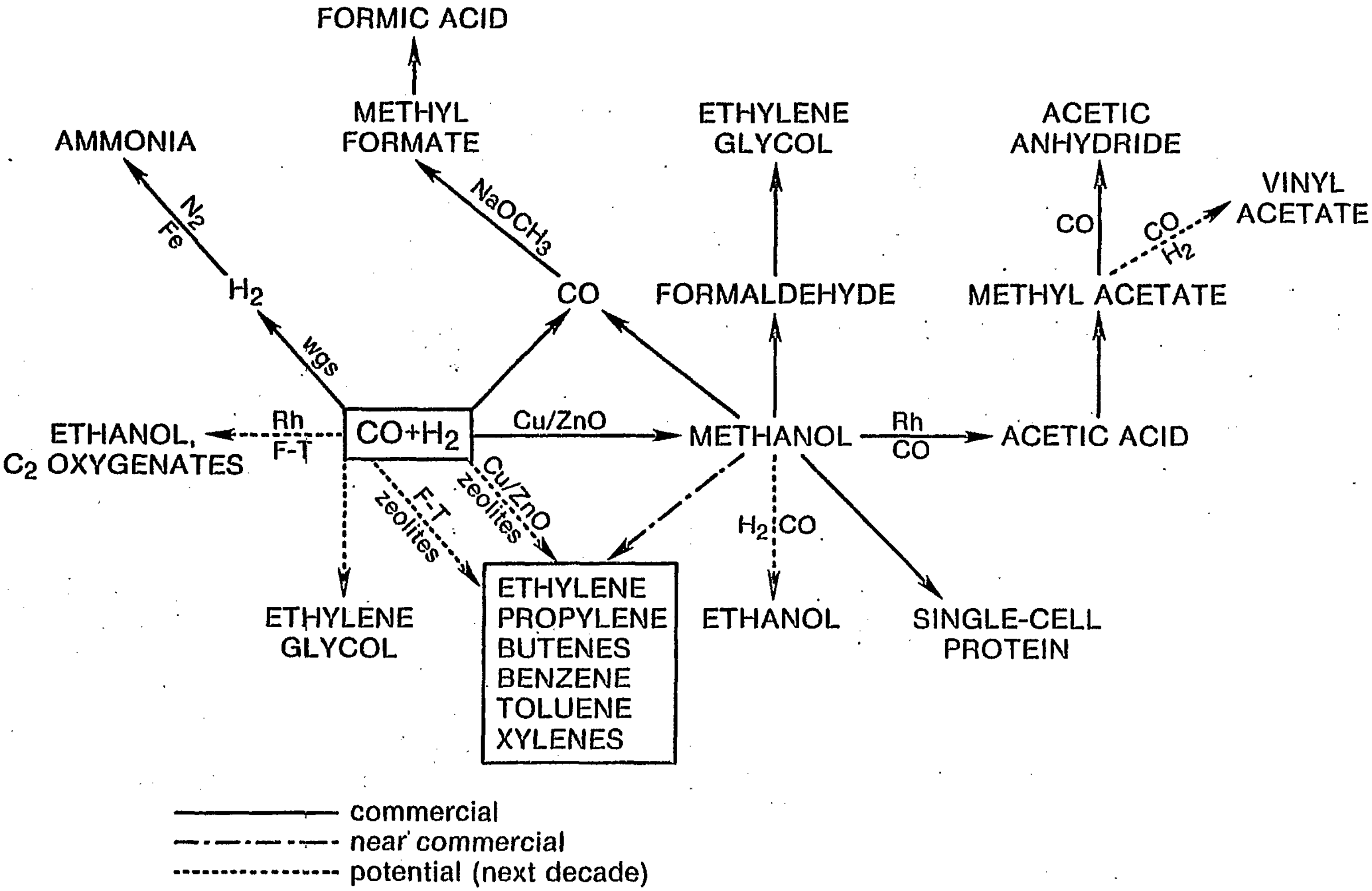
The two chief routes to liquid fuels from coal, as practiced in Germany during World War II, and termed direct liquefaction (originally the Bergius Process) and indirect liquefaction (the hydrogenation of carbon monoxide or the Fischer-Tropsch and related reactions). Because of difficulties encountered in gasifying and especially in removing sulfur impurities from the syngas, about 85% of the synthetic fuels used by Germany in WW II were made using the direct liquefaction process. Excellent gas purification systems are now available and, while there are now no commerical direct liquefaction plants in operation, there is a growing number of commercial processes that produce synthetic liquid fuels and chemicals using the indirect liquefaction route. The potential for further growth using this route is very large.

Figure II-1: **Commercial or Near Commercial Processes For The Production of Liquid Fuels From Synthesis Gas**



MTBE is an octane enhancer, $(CH_3OC(CH_3)_3)$

Figure II-2: **Commercial, Near Commercial, and Potential Chemicals From Synthesis Gas**



THE FISCHER-TROPSCH AND RELATED REACTIONS

Introduction

The two chief routes to liquid fuels from coal, as practiced in Germany during World War II are termed direct liquefaction (originally the Bergius Process) and indirect liquefaction (the Fischer-Tropsch and related processes).

In direct liquefaction, coal is treated with hydrogen at about 723K and high pressures (13.6 MPa - 34.0 MPa, although pressures as high as 68 MPa were used in Germany during World War II). The hydrogen added in this way raises the H/C ratio of the products so that liquid products are obtained. The H_2 is obtained by gasification of part of the heavy hydrogenation products or of coal itself to yield synthesis gas (syngas), a mixture of carbon monoxide and hydrogen ($CO + H_2$). The CO in the syngas can yield an equivalent molecule of H_2 by the water-gas shift (wgs) reaction: $CO + H_2O \rightarrow H_2 + CO_2$.

This report is concerned with the other major route to liquid fuels; indirect liquefaction. Here, all of the coal is treated in a gasification reactor to yield syngas; unlike the direct coal liquefaction process, essentially every bond in the original coal is broken during gasification of the coal. The clean syngas is then catalytically converted to liquid fuels. The Fischer-Tropsch (F-T) process and the synthesis of methanol are the two processes now in commercial use for the synthesis of liquid fuels from syngas. The F-T process produces a complex mixture of hydrocarbons and oxygenated products; it will be discussed first. In contrast, the processes for the synthesis of methanol from syngas are highly selective, yielding over 99% of this alcohol, which is both a fuel, a chemical and a fuel and chemical precursor.

It is important to point out that gasification to syngas is part of both the direct and the indirect liquefaction routes to coal liquids. In direct liquefaction processes, gasification to obtain H_2 comprises about 40% of the capital cost of the plant. In indirect liquefaction processes, gasification of coal to produce clean syngas comprises some 60-80% of the capital cost with the remainder of the capital cost of the plant devoted to the conversion of the syngas to liquids, along with some gaseous products.

Coal gasification, involving the use of steam and oxygen to form syngas, is discussed only very shortly in this report. Indirect liquefaction, the conversion of the syngas to hydrocarbons and oxygenates, constitutes its main subject. However, it will be important to know the composition of the typical gases obtained from the principal coal gasification processes. These are given in Table II-1.

Table II-1: Typical Gas Composition From Principal Gasification Processes

	GAS COMPOSITION				
PROCESS	FEED	% H_2	% CO	% CO_2	% CH_4
Lurgi	Sized Coal	16/20	39	30	10
Koppers-Totzek	Pulverized Coal	53/57	27/32	10/14	0.1
Winkler	Granular Coal	46	36	14	2
Shell-Koppers	Pulverized Coal	60/65	25/30	2/3	0.1
Texaco	Coal-Water Slurry	40/50	30/40	15/20	0.1

There are many routes for converting syngas to liquid fuels. Two, the F-T process and the synthesis of methanol, have been practiced commercially for several decades, others will be coming on stream in the next two years and some are processes that show promise in the coming decade. These are shown in Figure II-1. A similar breakdown of commercial, near-commercial and promising routes to chemicals from syngas are shown in Figure II-2.

THE FISCHER-TROPSCH SYNTHESIS

The Fischer-Tropsch process was the first one to be used to convert syngas to liquid fuels on a large scale. The following is a short history of events leading to the establishment of the F-T process as practiced on a large scale in South Africa. Sabatier and Senderens (1902) hydrogenated CO over a nickel catalyst to produce methane. In 1913, BASF obtained patents on the preparation of hydrocarbons and related oxygenated compounds by hydrogenation of CO at high pressure, mostly on oxide catalysts. In 1923, Fischer and Tropsch obtained mostly oxygenated products from syngas using alkalized Fe and other catalysts; they called the process the Synthol process. Fischer and Tropsch, in 1923, synthesized higher hydrocarbons using Ni and Co at one atm (BASF had patents covering higher pressures). Several countries, including the U.S., England and Japan initiated studies on the F-T process starting about 1926. Smith, Hawk and Golden (1930) found that ethylene was incorporated into the F-T synthesis using cobalt catalysts; they reported, however, that ethylene was not incorporated when iron catalysts were used. Fischer and his co-workers at the Kaiser Wilhelm Institute for Coal Research (KWIK-now the Max Planck Institute for Coal Research) at Mulheim developed Ni-ThO_2-kieselguhr and Co-ThO_2-kieselguhr catalysts for the F-T synthesis. Nickel catalysts gave too high yields of methane and the work with this catalyst was dropped.

In the decade following 1935, the F-T process was operated commercially in Germany using cobalt catalysts usually in the 0.5-2.0 MPa range (so-called medium pressure). Cobalt was expensive and in short supply; after World War I cobalt catalysts were replaced with alkalized iron catalysts. During this period, Pichler produced high molecular weight waxes using ruthenium catalysts at high pressures. Fischer and Pichler (Pichler,1952) while investigating new catalysts and studying the mechanism of the F-T synthesis, developed a process called the Isosynthesis (Cohn, 1956). Roelen (1943), in the course of studies on the mechanism of the F-T reaction, discovered the homogeneously catalyzed hydroformylation (oxo) reaction, now used extensively around the world to produce aldehydes and alcohols from olefins and syngas.

The production of F-T products in Germany during WW II reached a maximum of about 650,000 tons per year in 1944. The standard catalyst used in all their plants had the composition in relative mass units of Co:ThO_2:MgO:kieselguhr of 100:5:8:200. Bomb attacks reduced the output of these plants to about 10,000 tons per year by early 1945. All these F-T plants ceased operation by the end of the war and no large scale plant has been started up again in Germany.

After the war, Ruhrchemie and Lurgi jointly developed the ARGE process based on the use of iron catalysts in fixed bed units operated at medium pressure. In 1948, Kolbel and Engelhardt developed a hydrocarbon synthesis from CO and steam to utilize the then available CO-rich blast furnace gas (Kolbel and Engelhardt, 1951, 1952; Kolbel, 1957) In 1935, the British Fuel Research Station initiated work on the F-T process using both cobalt and iron catalysts in fixed-bed reactors (Hall and Gall, 1952). At about the same time, work on the F-T synthesis was started at the Bureau of Mines in the U.S.

In 1950, U.S. firms built a commercial (365,000 tons per year) F-T plant, developed by Hydrocarbon Research, in Texas (Keith, 1946). Syngas was obtained by reforming natural gas. The process used a fluidized bed reactor and, after severe operating troubles requiring the design of a new reactor, finally operated properly in 1953. Iron impregnated with about 1 wt % of K_2CO_3 was used as the catalyst. Since the price of natural gas rose during this period and it was more profitable to sell the gas than to convert it to gasoline and chemicals (among other products), the plant (using what was called the Hydrocol Process) was shut down very soon after operation was deemed satisfactory.

At about the same time, in the Republic of South Africa, the SASOL 1 Fischer-Tropsch plant was built and commercial operation started in 1955. This country has an abundance of coal, much of it of poor quality (high ash), a dearth of petroleum resources, and large centers of population far from the sea, together with a political and economic need for resource autonomy. The SASOL acronym was derived from the South African Coal, Oil and Gas Corporation, Ltd. a quasi-government corporation formed and capitalized to convert coal to liquid fuels and chemicals via the F-T process. SASOL 1 produced about 8000 BBL/day of products, supplying about 5% of South Africa's motor fuel needs plus other fuels and chemicals. SASOL 2, with an output of 50,000 BBL/day started operation in 1980. SASOL 3, the same size as SASOL 2, went on stream in 1983. South Africa now has the capability of providing about 40% of their liquid fuel and petrochemical needs from coal using the F-T process.

SASOL 1 uses two types of reactors. The fixed bed tubular reactor (Kuo, 1984; Dry, 1981) termed the ARGE reactor, uses a precipitated iron catalyst promoted with copper and a potassium salt such as K_2CO_3. The other type of reactor is an entrained fluidized-bed reactor, the Synthol reactor, which uses a fused iron catalyst with alkali and other proprietary promoters. SASOL 2 and 3, however, use only the Synthol reactor. SASOL 2 and 3 each consume about 40,000 tons of coal per day. SASOL 2 (about the same size as SASOL 3) is the largest grass roots, single-purpose processing complex in the world, occupying an area of one mile by one and one-half miles and valued at several billion U.S. dollars.

Since the SASOL plants are the only operating F-T plants in the world, we shall use the SASOL experience as the nucleus of the discussion of the F-T process. It is important to note that the SASOL plants are very specific applications of the F-T synthesis. Coal is gasified in Lurgi gasifiers which yield significant amounts of CH_4 and large amounts of CO_2 in the gaseous products and H_2/CO ratios that hover around two (see Table II-1). Lurgi gasifiers are generally best used with lower rank, non-caking coals. Two types of iron catalysts are used at SASOL; no other transition element is used as a catalyst. Although other catalysts such as ruthenium and perhaps cobalt are more active F-T catalysts, iron is a cheap and, importantly, a versatile catalyst.

However, in the F-T process as practiced at SASOL, the overall methane yield can exceed 50% since the Lurgi gasifier and the F-T synthesis itself both yield large amounts of methane. Since no pipelines for the distribution of the CH_4 exist in South Africa and the amount of CH_4 made exceeds the country's demand, the SASOL plants are forced to reform the excess methane to make more syngas, which is then recycled. As a result, the thermal efficiency at SASOL, defined as the lower heating value (LHV) of the products divided by the LHV of all the coal used, is only about 40% for the production of motor fuels (gasoline, diesel oil and LPG) (Eisenlohr and Gaensslen, 1981). The efficiency would rise to nearly 60% if the methane could be utilized as such.

The SASOL process for the synthesis of fuels can be outlined as shown in Figure II-3.

Other mostly second generation gasifiers (Table II-1) yield low H_2:CO ratios and very little methane. Use of these gasifiers for the synthesis of fuels and chemicals is currently under active development. These gasifiers (Koppers-Totzek, Texaco, Shell) might well require different types of F-T

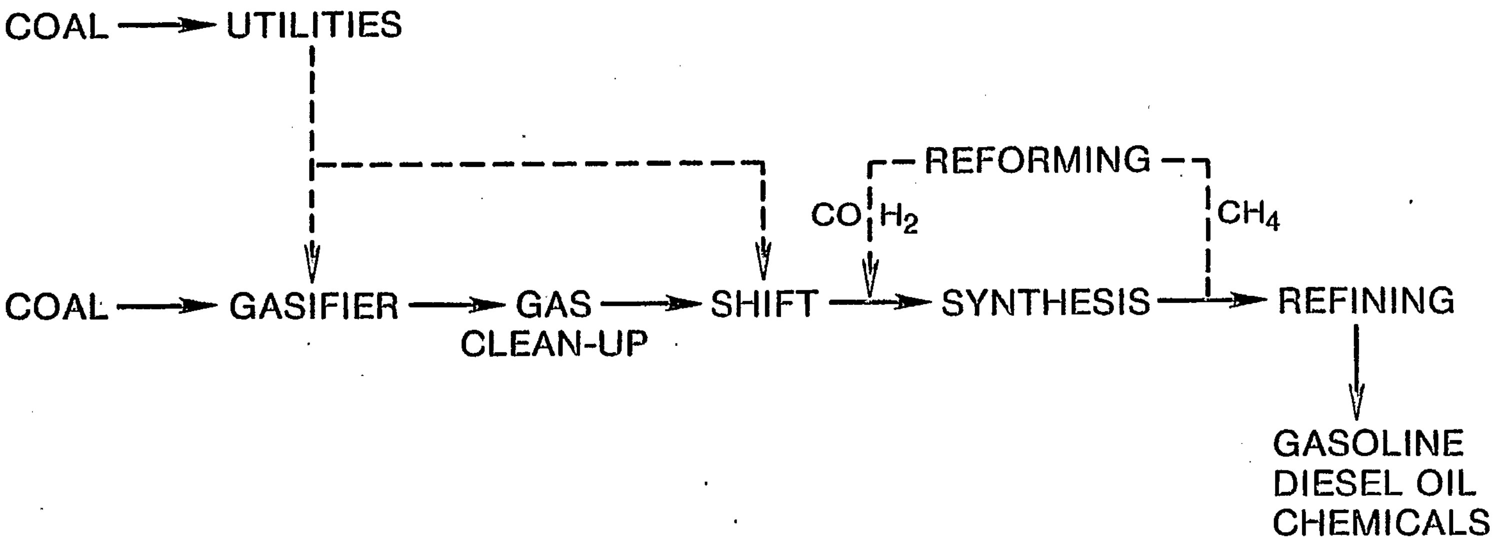


Figure II-3: SASOL PROCESS FOR THE SYNTHESIS OF FUELS AND CHEMICALS reactors or, if used for the synthesis of methanol or ammonia, may require a water-gas shift to obtain a higher H_2:CO ratio.

It should be noted at this point that there has been a remarkable surge in interest and funding for F-T research since about 1970. Research on the synthesis had decreased abruptly in the 1950s; only SASOL had a modest program devoted mostly to practical problems that arose from operation of SASOL 1, while a small group continued research at the U.S. Bureau of Mines.

The new researchers, with excellent new instrumentation and analytical tools, nevertheless required some 2-3 years to come to grips with the huge amount of information already in existence. Since 1978, thousands of publications on the F-T and related reactions have been published. It is a herculean job to keep up with all the work in this field but certain excellent and surprising findings have been made; the main reactions that occur during the F-T synthesis are now better undertood although there are still many unanswered questions as to the mechanism(s) of the F-T synthesis, especially when different catalysts are used and conditions varied.

The Arab oil embargo of 1973, of course, furnished great impetus for new research on the F-T reaction with emphasis on improving gasoline and diesel oil yields. The SASOL people had greatly improved the Lurgi gasifier operation, learned how to clean the gases that emerged from the gasifier, removing CO_2 and almost all the sulfur compounds, and developed clever and very workable methods for the separation of the multitude of products obtained. They are now able to maximize gasoline and diesel production while separating out many "petroleum" feedstocks (ethylene, propylene, etc.) and oxygenated chemicals (ethanol, acetic acid, acetone, etc.). They have built, in a way, a "petroleum-less" refinery. The projected distribution of products from SASOL 2, in millions of tons per year, is: motor fuels, 1,500,000;

ethylene 185,000; chemicals 85,000; tar products, 185,000; ammonia (as N), 100,000; and sulphur, 90,000. Some 2,140,000 million tons per year of saleable products are envisioned. But the new SASOL plants are flexible enough to make possible wide adjustments in output of transportation fuels, petrochemicals and fuel gas. Possible production slates are shown in Figure II-4.

Under certain conditions, synthetic fuels from coal are viable and improvements, some quite striking and valuable, will continue to be made in the F-T and related processes. Much was learned from the building of SASOL 2 so that the cost of SASOL 3 was much less than that of SASOL 2 (P du P Kruger, 1983).

Chemistry of the Fischer-Tropsch Synthesis

The F-T reaction yields a wide spectrum of hydrocarbons and oxygenated compounds. The major constituents of the hydrocarbons are paraffins and olefins while primary alcohols are usually the chief oxygenated products. Straight-chain paraffins along with some 2-methyl-branched paraffins predominate among the saturated hydrocarbons; the major olefin components are terminal olefins.

A large number of reactions occur during the F-T reaction; the chief ones are given below;

Paraffins	$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$	(1)
Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$	(2)
Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$	(3)
Water-Gas Shift	$CO + H_2O \rightarrow CO_2 + H_2$	(4)
Boudouard Reaction	$2CO \rightarrow C + CO_2$	(5)
Coke Deposition	$H_2 + CO \rightarrow C + H_2O$	(6)

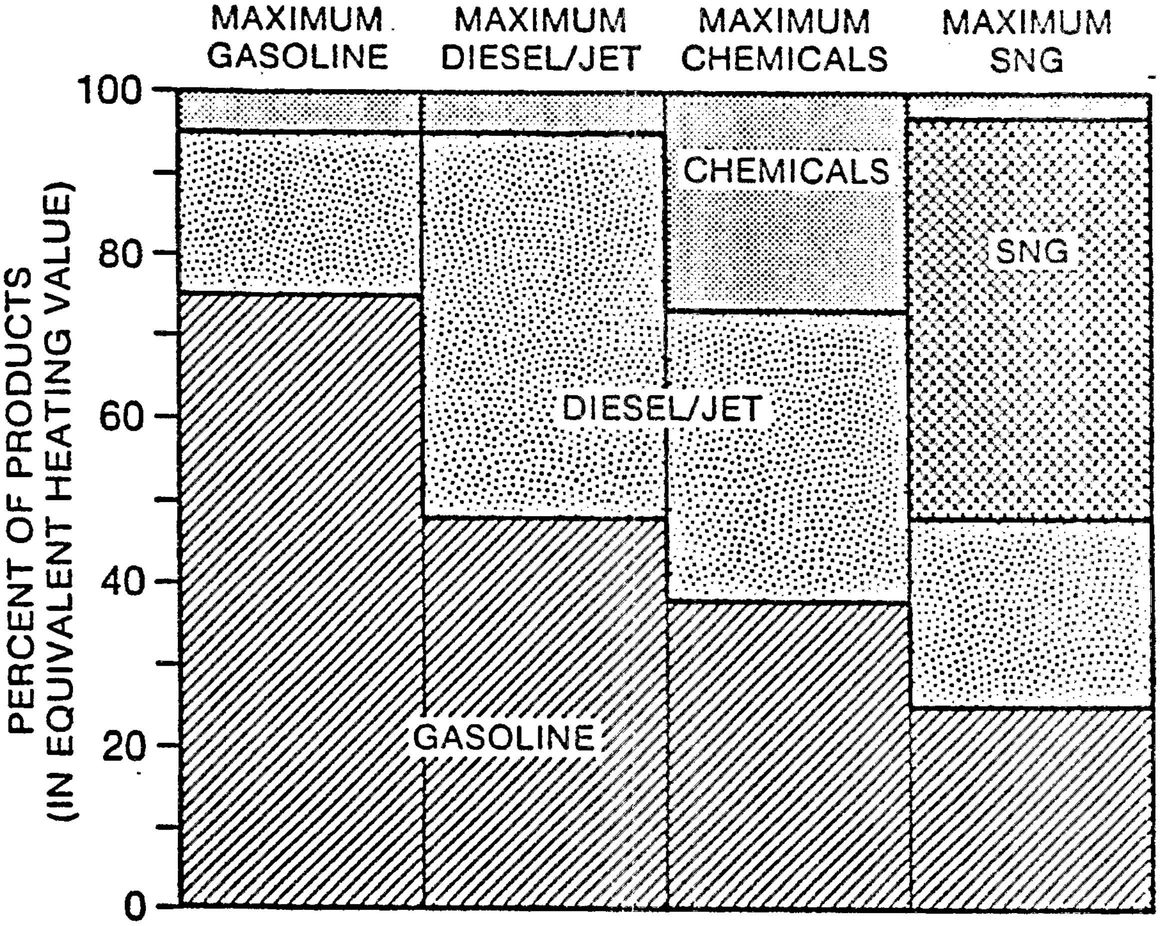


Figure II-4: TYPICAL MAXIMUM YIELDS OF PRODUCTS FROM SASOL 2 AND SASOL 3

For catalysts such as cobalt, which is not a good water-gas shift catalyst (Eq. 4), water is the main reaction product. For catalysts that are good water-gas shift catalysts, such as alkalized iron, the water formed in Eqs. 1-3 reacts with CO to form H_2, so that the apparent H_2/CO usage becomes smaller. The carbon number distribution of organic compounds is extremely wide and much effort has been expended in finding ways to improve the selectivity of the F-T synthesis to desirable products; gasoline, diesel fuel, C_2-C_4 olefins, ethanol, etc. Glycols are not produced in the F-T reaction. Aromatic products become significant only at high reaction temperatures.

Thermodynamics of the Fischer-Trospch Reaction

When several reactions involving the same reactants are thermodynamically possible the yields of various products depend upon their relative reaction rates as well as the rates of the following reactions. At the temperatures usually employed in the F-T synthesis, the actual selectivity found differs very much from that expected from thermodynamic calculations. An excellent summary of the thermodynamics of the F-T synthesis has been given by Anderson (1956).

Anderson (1984) and Frohning et al. (1982) have pointed out that data on the heats of reaction are important, since the F-T synthesis is strongly exothermic. Indeed, removal of the heat of reaction, about 25% of the calorific value of the syngas, is probably the chief problem in practical application of the synthesis. Excessive catalyst temperatures can lead to undesirable products, carbon deposition, catalyst deactivation or catalyst disintegration.

The heats of reaction per carbon atom of the products vary only slightly with temperature, increasing (becoming less negative) with increasing carbon number for paraffins and decreasing with increase in the carbon number of the olefins formed. Enthalpy changes for reactions yielding hydrocarbons and CO_2 (Eqs. 7, 8) exceed those for the corresponding reactions yielding H_2O. The

$$(n+1)H_2+2nCO \rightarrow CnH_{2n+2} + nCO_2 \quad (7)$$

$$nH_2 + 2CO \rightarrow C_nH_{2n} + nCO_2 \quad (8)$$

enthalpy difference, about 9 kcal, is due to the water-gas shift reaction (Eq. 4), which is relatively independent of temperature.

The heats of reaction for the formation of alcohols, also somewhat independent of temperature, in kcal/mole/carbon atom are: -23.9 for methanol, and -29.5 for ethanol (Wagmann et al. 1982).

The F-T reaction is normally carried out at pressures of from 0.1 to 4 MPa with about 700K as the upper temperature limit. Since F-T synthesis reactions involve a decrease in the number of moles, conversions at a given temperature increase rapidly with increase in pressure. The pressure and temperature limits of the reaction are determined by changes in selectivity and rate of catalyst deterioration.

Anderson (1956) has presented equilibrium data for the hydrogenation of CO to hydrocarbons and water, plotting $\Delta G^o/n$ (ΔG^o per mole per carbon atom) versus temperature. The $\Delta G^o/n$ curves for paraffins are about parallel but become more positive with increasing carbon number (Figure II-5). Below 573K, $\Delta G^o/n$ becomes more negative with increasing carbon number for olefins. In the F-T temperature range, $\Delta G^o/n$ values for aromatic and saturated cyclic hydrocarbons, which are not significant F-T products, are essentially the same as those for olefins of the same carbon number (Anderson, 1956).

Large equilibrium yields are possible for all primary, straight-chain alcohols except for methanol. Methanol is formed in very small amounts in the

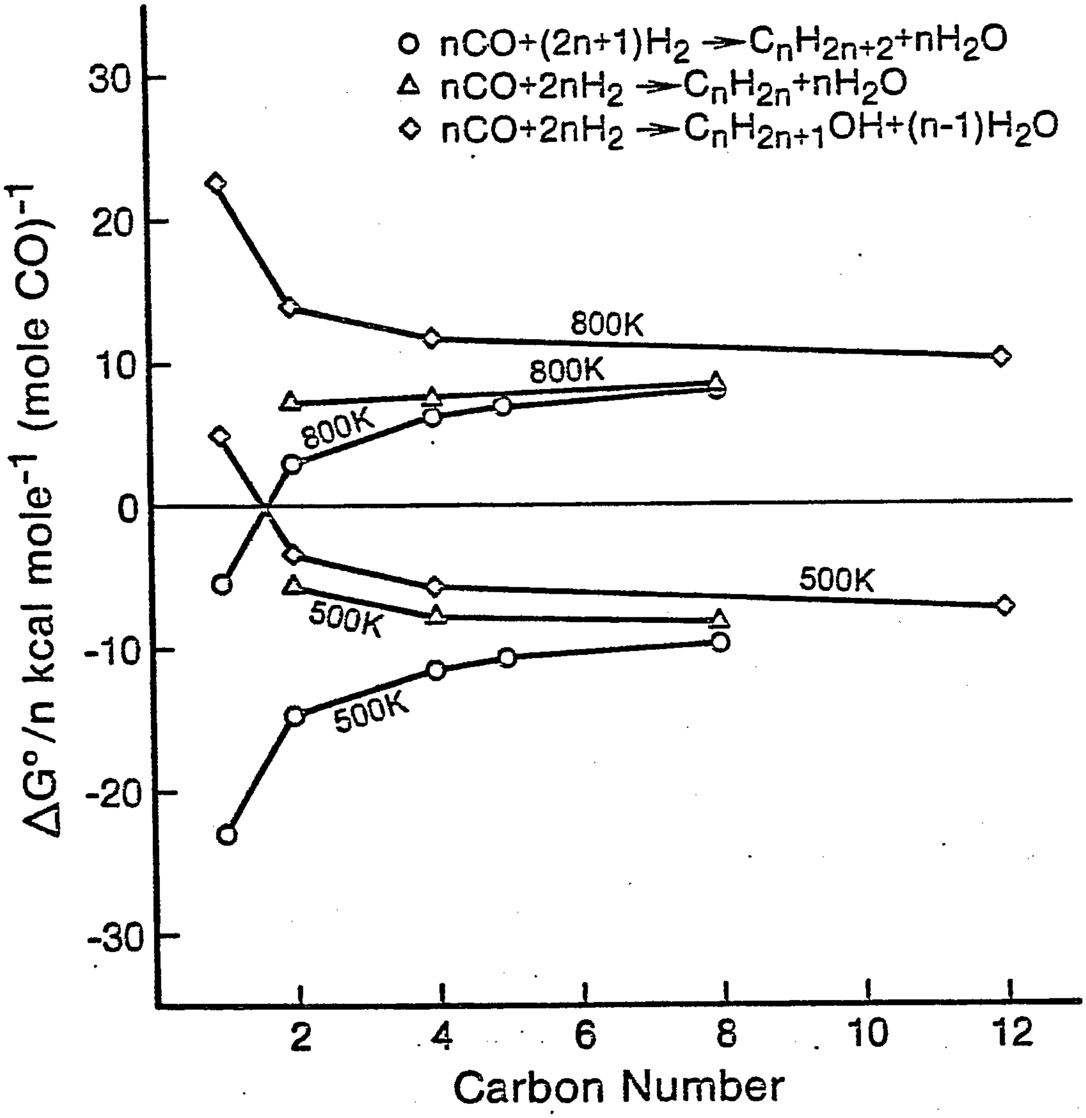


Figure II-5: PLOT OF $\Delta G^{o}/n$ VERSUS CARBON NUMBER AND TEMPERATURE (ADAPTED FROM STULL, 1969; JANAF TABLES, 1971)

F-T reaction, (The synthesis of methanol will be discussed in the following section).

Since kinetic rather than equilibrium considerations are controlling in the F-T reaction, only limited amounts of useful information is furnished by thermodynamics. The products obtained depend on the selectivity of the catalyst. But certain conclusions derived from thermodynamics help us understand these syngas reactions:

- methane is the preferred product at all F-T conditions.

- the relative stability of various compounds varies with the temperature of the F-T synthesis (300-700 K). The order is: paraffins > olefins > alcohols

- Although methane is the preferred paraffin, for olefins the favored products are compounds with the highest carbon number. Above about 600K at 0.1 MPa this reverses and light olefins are favored. Aromatics and naphthenic hydrocarbons, formed in only small amounts in the F-T synthesis, behave in a similar manner to olefins of the same carbon number.

- The favored alcohol is the one with the highest carbon number.

- the free energy change for reactions producing CO_2 are more favorable than reactions which produce water.

- the equilibrium conversion of the syngas increases with pressure. But, because of the effect of pressure (and temperature) on the activity and selectivity of the catalyst, the upper limits of usefulness for iron catalysts are 3-4 MPa and about 673K.

- the water gas shift reaction (Eq. 4) is favored under F-T conditions; iron is a particularly good catalyst for this reaction. The rate of the water-gas shift reaction must be slow when water is obtained in large amounts.

- The Kolbel-Engelhardt reaction (Kolbel and Engelhardt, 1951, 1952), the reaction of CO plus H_2O to produce hydrocarbons, is thermodynamically more favored than the usual F-T synthesis from syngas. This reaction will be discussed later.

- The concentrations of n-paraffins and terminal olefins greatly exceed equilibrium values in the F-T synthesis. Subsequent isomerization reactions are not important.

- The reaction of any amounts of ethylene and of ethanol with syngas is thermodynamically possible at F-T temperatures. The incorporation of higher olefins or of higher alcohols is less favored. Thermodynamically, methanol incorporation is favored over that of ethanol. The term "incorporation" denotes the building-in of an organic molecule together with CO and H_2 in the F-T synthesis.

- As with higher hydrocarbons and olefins, the amounts of oxygenated compounds (alcohols, aldehydes, acids, ketones) are also formed in much higher concentrations than predicted from thermodynamic calculations. But it seems that these oxygenated compounds readily interact with each other (Weitkamp and Frye, 1963) under F-T conditions.

$$CH_3CH_2OH \rightleftharpoons CH_3CHO + H_2 \tag{9}$$

$$CH_3CHO + H_2O \rightleftharpoons CH_3COOH + H_2 \tag{10}$$

$$CH_3COCH_3 + H_2 \rightleftharpoons CH_3CHOHCH_3 \tag{11}$$

- Olefin hydrogenation and alcohol dehydration are thermodynamically favored under F-T conditions. Olefins and paraffins may be formed by dehydration of alcohols and hydrogenation of the olefins, respectively, as well as by primary reactions.

- the Boudouard reaction, in which CO can form free carbon and CO_2 (Eq. 5) is favored under all synthesis conditions. It is, however, possible to suppress this reaction in many F-T reactions.

Kinetics of the Fischer-Tropsch Synthesis

It is difficult to arrange experiments amenable to analysis on a group of reactions of the high degree of complexity of the F-T reaction. This is true despite the fact that powerful new analytical methods of great accuracy now permit the use of differential reactors, in which conversion is low enough so that the composition of the feed gas remains essentially unchanged. And in integral reactors, there are great difficulties in interpreting data involving considerable changes in conversion often involving large changes in composition of the reacting gases.

Anderson (1956) has discussed the kinetics of the F-T synthesis whose goal is to find a fundamental rate equation relating the differential rate to the partial pressures or concentration of reactants and of products. Unfortunately, the kinetics of the this complex series of reactions are not well understood. There are too many catalyst variables affecting the kinetics, including the method of preparation, composition and aging, as well as operating conditions and the transport phenomena involving the catalyst and the reactants, intermediates and products. Storch et al. (1951), Anderson (1956), Kuo (1984), and Dry (1981) have summarized kinetic expressions derived for nickel, cobalt, iron and ruthenium catalysts.

Vannice (1975) using Al_2O_3 as the support, reported that the activites of Group VIII metals declined in the order Ru, Fe, Ni, Co, Rh, Pd, Pt and Ir. With SiO_2 as the support, the activity declined in the order: Co, Fe, Ru, Ni, Rh, Ir and Pd (Vannice, 1977).

The particle size of the iron catalyst affects the activity of the F-T catalyst in the SASOL plants (Dry, 1981). Activity increases linearly with the amount of external surface area of the catalysts. It seems likely that outside film diffusion resistance is the principal factor involved.

The SASOL Plants

The F-T reactions are highly exothermic and it is most important in maintaining catalyst stability and selectivity to have proper heat removal. The ARGE reactor in use today in SASOL 1 (Figure II-6) is a vertical tube heat exchanger reactor with catalyst inside the tube and steam generation in the shell. The inside diameter of the reactor is 2.9 meters. The 12 meter high catalyst bed contains 2052 tubes of 4.6 cm inside diameter (Kuo, 1984). The capacity of each reactor is 18 million kilograms per year of hydrocarbons and oxygenated products. The catalyst is an alkali promoted iron on a support.

The entrained fluidized bed reactor (Synthol reactor) is the largest F-T reactor now in commercial use. Many modifications of the original Synthol reactor used in SASOL 1 were incorporated into SASOL 2 and SASOL 3, which, as noted earlier, use only Synthol reactors. A schematic diagram of the Synthol reactor is shown in Figure II-7.

In the Synthol reactors, feed gas enters at the bottom, meeting the down flowing hot catalyst from the standpipe which heats gas to its ignition temperature (Dry, 1982 a). The turbulent flow of gas and catalyst passes through heat exchangers to the wide settling hopper above the standpipe; here catalyst and gas disengage. Hydrocarbon vapors and gas leave the reactor via cyclones to remove entrained catalyst, returning them to the settling hopper. About a third of the generated heat is removed by internal heat exchangers; the rest leaves with the recycle gas. Temperatures of the exit gas are about 590-630K.

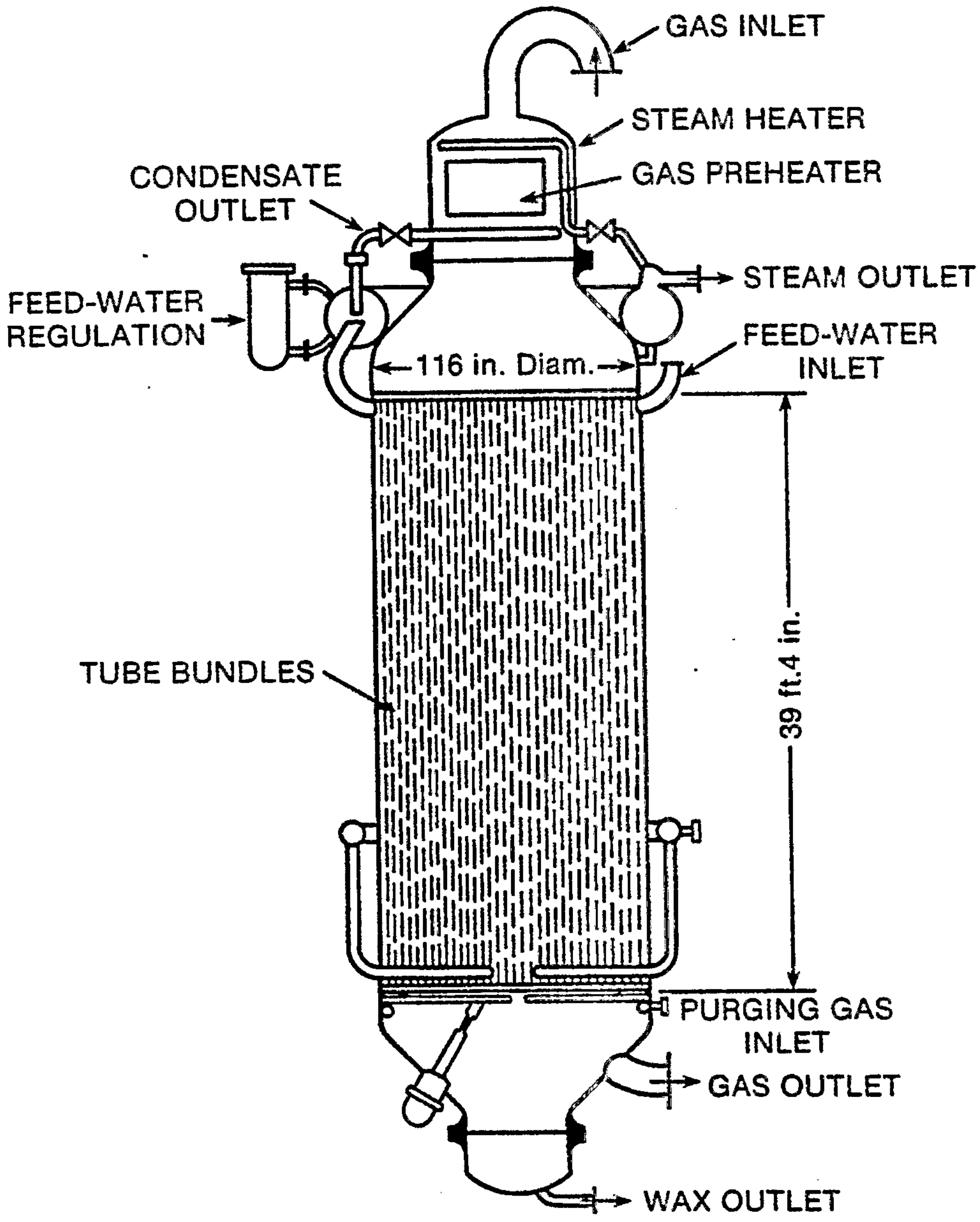


Figure II-6: FIXED-BED REACTOR, ARGE PROCESS

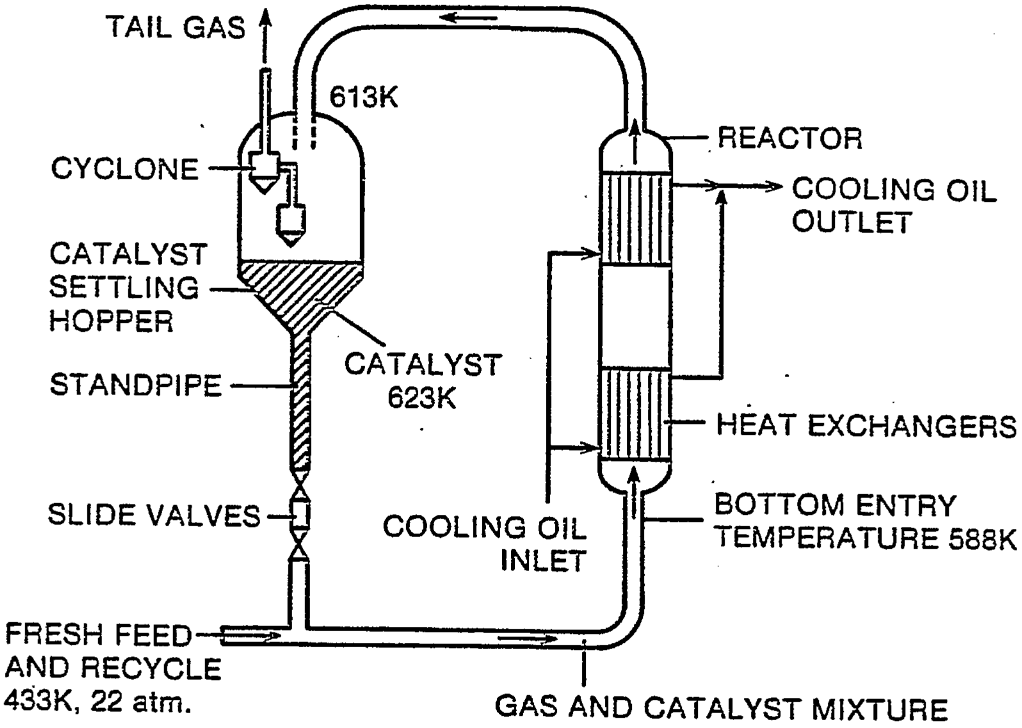


Figure II-7: SYNTHOL REACTOR

Typical performance data and products from the SASOL 1 and SASOL 2 reactors are compared with the Arge (SASOL 1) reactor in Table II-2. The SASOL 2 reactor has a capacity about 2.5 times that of SASOL 1. The Synthol reactor, in comparison with the Arge reactor, produces more light hydrocarbons, more oxygenated compounds, more gasoline, much more olefins and less paraffins. Other reactor designs are described by Kuo (1984) and by Dry (1981). Slurry bed reactors are not as yet commercial but are under active development. SASOL also operates pilot plants using fixed fluidized beds as well as slurry phase reactors. The product spectrum has been found to be independent of the type of reactor but rather varies with the catalyst and operating conditions. (Dry, 1981).

At present, most of the SASOL products are thus produced using Synthol reactors. At SASOL 2 and 3, the light olefins are oligomerized to yield mostly diesel fuel (Dry, 1983).

The Arge catalyst uses fine metallic iron filings as the raw material; it is a precipitated catalyst with alkali promoters. It has been estimated (Poutsma, 1979) that the catalyst composition is $Fe:Cu:K_2O:SiO_2$ = 100:5:5:25. Catalyst changes are made after 70-100 days.

The Synthol catalyst is made from mill scale obtained from a nearby steelworks (Hoogendoorn, 1973). The ground catalyst with added promoters is then fused in an open arc furnace. The catalyst leaves the furnace at about 1773 K, solidifying as it cools. The ground catalyst (~ 200 mesh) is reduced with hydrogen and stored in the absence of oxygen.

Table II-2

Typical Performance Data and Products From the SASOL 1 and SASOL 2 Reactors
(Hoogendoorn, 1976; Pay, 1980)

		SASOL 1		SASOL 2
		ARGE	SYNTHOL	SYNTHOL
Operating Parameters				
Temperature (K)		493-523	593	593
Pressure (MPa)		2.5	2.0	2.2
H_2:CO Mole Ratio		1.8	2.5	2.0
Catalyst: Alkali-promoted Fe		Precipitated	Fused	Fused
Conversion per pass (mole %)		70	85	85
Product Distribution (wt %)				
CH_4		5.0	10.0	11.0
C_2H_4		0.2	4.0	7.5
C_2H_6		2.4	6.0	
C_3H_6		2.0	12.0	13.0
C_3H_8		2.8	2.0	
C_4H_8		3.0	8.0	11.0
C_4H_{10}		2.2	1.0	
C_5-C_{12}	(Gasoline)	22.5	39.0	37.0
$C_{13}-C_{18}$	(Diesel)	15.0	5.0	11.0
$C_{19}-C_{21}$	Heavy Oil and Wax	6.0	1.0	3.0
$C_{22}-C_{30}$		17.0	3.0	
C_{31}		18.0	2.0	0.5
Non-Acid Chemicals		3.5	6.0	6.0
Acids		0.4	1.0	NA

On the Mechanism of the Fischer-Tropsch Synthesis

The F-T reaction may be defined as the catalytic polymerization and hydrogenation of CO to give hydrocarbons and oxygenated products with various chain lengths; H_2O and CO_2 are also formed. There are many reactions that occur on an F-T catalyst. Those listed in Eq. 1-6 are probably the most important ones but the list of possible intermediates, reactions and products, varying with the catalyst and with reaction conditions, is large. It is likely that these reactions occur in a series of linked steps termed elementary reactions. In such a complex reaction as the F-T synthesis, it is difficult to separate these simpler steps; this task is frustrating in itself but the realization that any one or set of elementary reaction occurs exclusive of other possible reactions makes it clear that there is presently no clear mechanistic picture of the F-T synthesis although we have learned much in the last decade. Up to 1954, some 4000 publications and over 4000 patents dealing with the synthesis had appeared (Anderson et al. 1954). Since then many more thousands of publications on the F-T reaction have appeared and interest is still very high. In a way, the complexity and versatility of the F-T reaction constitute driving forces for continued work on this reaction. There is much to learn from a fundamental point of view about catalysis of syngas reactions and about catalysis in a general way; in addition, there is the promise of new pathways to commercial syntheses of fuels and chemicals.

Rofer-DePoorter (1981) has given an account of the chemisorption of CO and H_2 that occurs during the F-T synthesis. In addition, she has tackled the mechanism of the F-T reaction from the point of view of the elementary reactions involved. After a short summary of this approach, the mechanism(s) of the F-T synthesis will be taken up from the usual point of view - that is, based on the importance of product distribution in the practical application of the F-T synthesis. A better understanding of the process should lead to greater flexibility of usage of the synthesis.

We begin with the realization that no understanding of the F-T mechanism exists that allows prediction of products under various conditions or unification of the numerous observations in a detailed way. This is not discouraging; rather it furnishes challenges and opportunities.

There exists an enormous number of possible combinations of catalysts, pressures and temperatures in the F-T synthesis. Most of the reaction mechanisms proposed have been based on inferential deductions or spectral identifications of supposedly critical intermediates or reaction paths, although a series of multiple paths has also been proposed. Nevertheless, contradictory or insufficient data exist for all the mechanisms proposed.

As Rofer-DePoorter (1981) has pointed out, the question in proposing a F-T mechanistic scheme is probably less which intermediate is the critical intermediate than to what degree each intermediate contributes. The first approach has predominated in most mechanistic studies.

It is important to realize that some intermediates are produced by more than one route and a particular intermediate may lead to more than one product. With this multiplicity of reaction paths, the picture has been of parallel paths or of forking late in the reaction path to produce a number of products from some intermediates. But it is much harder to obtain meaningful interpretations for the result of a network of reactions than for parallel paths or forks. Because of this complexity, few systematics have been derived from F-T studies. For instance, the idea of a rate determining step may not be too meaningful in such a complex series of reactions.

It should be realized that, under certain reaction conditions, the rates of some reactions may even approach zero relative to other reaction rates.

During the F-T synthesis, the nature of the catalyst surface usually changes, the concentration of intermediates may change and the rates may change with some reactions disappearing from the surface. But the disappearance of a product (zero reaction rate) does not mean that the step has necessarily been removed from the F-T mechanistic pathway.

At a certain set of reaction conditions, a given reaction path may approach or reach an overall effective rate of zero and the experiment may appear to disprove participation of a particular intermediate. But this is not a proof that the intermediate is not important for other catalysts and/or reaction conditions. For instance, data in the literature on the production of hydrocarbons have been explained using a network in which the relative rates for paths leading to oxygenated products are effectively zero. One must remember that Fischer's (Fischer and Tropsch, 1923) first experiments gave high yields of oxygenated products. There is a tendency for investigators, for the sake of simplicity, to study only mechanisms for the synthesis of hydrocarbons, implying, in a way, that the F-T synthesis of hydrocarbons is the main reaction while the synthesis of oxygenated compounds is either a side reaction or perhaps not even to be classified as an F-T reaction. This has served to confuse an already complex picture, for, under higher pressures, almost the entire F-T product can consist of oxygenated compounds. Rather, as a large number of investigators have done, comparisons of systems producing hydrocarbons with those producing oxygenates may lead to a more informative understanding of the types of intermediates and rate changes that lead to the different product distribution.

Those interested in Fischer-Tropsch studies should be acquainted with certain excellent publications on the subject. Among these are the works of Anderson and co-workers (Storch et al. 1951), Anderson (1956; 1984), Dry

(1981), Pichler (1952), Vannice (1976), Schulz (1982), Ponec (1978, 1984), Bell and co-workers (1984), and Somorjai (1981).

Most of the mechanisms that will be discussed will be chiefly the outcome of studies on product distribution. As noted earlier, F-T products are generally not in thermodynamic equilibrium with respect to the reactants or with respect to other products. Selectivity data probably contain the most valuable mechanistic information. We can reasonably account for the water, CO and CO_2 product pathways. Water is the principal primary product with most catalysts; the CO_2 product is formed in a subsequent water-gas shift reaction. It has also been said that terminal olefins or primary alcohols are primary products but considerable hedging exists on this point. It is often difficult to distinguish between primary and secondary products. Primary products are produced directly by the reactions of the proposed mechanism(s) while secondary products may be produced by readsorption and further reaction of primary products. But the readsorption of stable product molecules (olefins, aldehydes, etc) can furnish intermediates indistinguishable from so-called primary products. The formation of some products early in the synthesis may result from the kinetics of formation of the various products.

In general, methane is formed in large amounts, C_2 products may pass through a minimum and, after a maximum at C_3 or C_4, the carbon number distribution then decreases monotonically.

In spite of much attention being paid to the straight-chain nature of hydrocarbons formed in the F-T reaction, monomethyl-substituted hydrocarbons are present in significant amounts. Methyl groups are found in about equal amounts all along the carbon chain. Dimethyl-substituted hydrocarbons are present in smaller amounts; ethyl groups are found in about the same amounts as the dimethyls. Quaternary carbons are not found in the F-T products.

The carbon skeletons of the alcohols formed in the F-T reaction are similar to those found in hydrocarbons. Yields of alcohols, on a molar basis, are highest at C_2 and decrease monotonically with molecular weight. Thermodynamics probably limits the yields of methanol, which are very low.

The literature contains a plethora of product selectivities obtained from various catalysts (mostly Fe, Co, Ru, and Ni) under a variety of reaction conditions. At SASOL, copious information on a commercial scale has been generated on product selectivities obtained with iron catalysts operating under various reaction conditions. All sorts of reactors, fixed, fluidized bed and slurry reactors have been employed. In addition, a number of catalysts, promoted, sintered, and fused, with different particle sizes have been tested. Synthesis temperatures have varied from about 450 to 700K and pressures have ranged from atmospheric to 7.5 MPa. Also varied over wide ranges have been the relative amounts of H_2, CO and CO_2 in the fresh feed gases; the fresh feed to recycle gas ratio has also been varied. SASOL selectivities to methane have ranged from about five to about 80%; hard wax from zero to up to 50%. A study of all the data obtained at SASOL and other F-T units showed that there was a definite interrelationship among the various products (Weitkamp and Frye, 1953; Dry, 1981). This is in line with earlier work that demonstrated that if the selectivity of any one particular carbon number species is changed, then the selectivities of all the other carbon number species will also change by a predictable amount. This holds no matter how the shift is brought about - whether by a change in the catalyst used or by a change in the F-T process conditions.

Herington (1946), first introduced into F-T studies the probabilities of chain growth and chain termination, terms common to polymer chemistry. He considered the paraffins and olefins formed on a cobalt catalyst and postulated that they were formed by stepwise addition of a methylene ($-CH_2-$) entity to the growing chain on the surface of the catalyst. Anderson and his co-workers (Storch, et al. 1951; Anderson, 1956; Friedel and Anderson, 1950) analyzed the product distribution of a large number of F-T runs using different fixed bed catalysts. They found that plots of log W_n/n against the carbon number, n, yielded straight lines over a fairly large range of products (W_n is the mass fraction of a particular product). This showed that the probability of chain growth, α, was essentially constant. Most F-T mechanisms assume that the monomer unit is the same weight wherever it is found in the chain. From Herington (1946) and Anderson's work, (1956) an equation for mass fraction can be written as

$$W_n = n(1-\alpha)^2 \alpha^{n-1} \tag{12}$$

This expression is equivalent to the Schulz-Flory equation (Flory, 1950; 1967, Schulz 1935) which treats the F-T product distribution as a polymerization process. Equation (12), to give proper credit to Anderson, might well be termed the Anderson-Schulz-Flory (A-S-F) equation. It is usually used in the logarithmic form:

$$\log \frac{W_n}{n} = n\log\alpha + \log \frac{(1-\alpha)^2}{\alpha} \tag{13}$$

It is evident that, if this equation for the F-T product distribution holds, the calculated value of α from the slope ($\log \alpha$) should be consistent with that calculated from the intercept, $\log (1-\alpha)^2/\alpha$. The probability of chain growth, α, is the ratio of the chain propagation rate constant to the chain propagation plus the termination rate constants.

The SASOL experience as well as numerous other F-T studies leave no doubt that the A-S-F equation usually predicts the proportion of methane to gasoline to diesel oil to waxes that will be produced in most F-T reactions. The highest selectivities attainable by F-T synthesis are, in weight %, methane, 100; ethylene, 30; C_2-C_4 olefins 56; gasoline, 48. The large array of products from the SASOL operation, including a wide range of hydrocarbons mixed with some oxygenated compounds, necessitates a considerable number of separation steps.

A great deal of work has been and is being done on circumventing the A-S-F "constraints". Usually the efforts have been unsuccessful but this is not always true. Madon (1979) has presented evidence that the A-S-F model does not apply to data for a Ru/Al_2O_3 catalyst. It is true that data plotted in semi-logarithmic form using this equation tends to mask information so that subtle changes in growth patterns may not be differentiated easily on such plots. Madon has suggested that attempts to address the problem of product selectivity be made by carrying the extensive past work of Anderson and other workers a step further, and questioning how akin the synthesis reaction on different catalytic surfaces, giving products usually less than C_{40}, and traditional polymerization processes, with products usually greater than C_{1000}, really are.

Deviations from the A-S-F relationship would be most likely for products of low carbon number where the assumption that α is independent of chain length would be least likely to hold. The CH_4 fraction is often reported to be higher than expected and other low carbon number fractions are reported to be lower than expected (Satterfield and Huff, Jr., 1982).

Two-carbon compounds are postulated to have a greater reactivity due to chain growth at both ends and CH_4 can be formed by cracking or other means.

Deviations from the expected A-S-F product distribution may also be due to cracking of higher molecular products, to incomplete or poor analytic techniques or to changes in the catalysts due to oxidation, sintering or pore plugging.

It is more than probable that the mechanisms of the F-T reaction actually consists of a number of pathways. The same intermediate can yield different products and different intermediates can lead to the same product. Owing to the wide diversity of F-T synthesis products, it is not surprising that so many mechanistic postulations for the synthesis have been put forth (Anderson, 1956; Dry, 1981). The evidence to support these postulated pathways is usually indirect and can often be interpreted in more than one way.

The proposed mechanisms may be placed in about four categories, although similar steps may be found in each of these proposed schemes. In general, the catalysts are reduced in hydrogen before use and it is understood that CO can be adsorbed both dissociatively and associately on these transition metal catalysts. It seems quite likely that, on certain catalysts under certain conditions, dissociative adsorption of CO is the main route; on Pd, Pt and Cu, associative adsorption is most likely and on most catalysts (Rh is probably the best example), CO is adsorbed in both ways. A better understanding of these observations can be gained from an examination of Figure II-8 (Broden et al., 1976).

The dotted line at the left separates those metals (Cr, Mo, etc) that dissociatively chemisorb CO at room temperature. As the temperature is increased the line is shifted to the right. At 473-573K the borderline is between nickel and copper, rhodium and palladium, and osmium and iridium. It is fairly well established (Kellner and Bell, 1981; Katzer et al., 1981; Biloen and Sachtler, 1982) that metals to the left of the line catalyze the

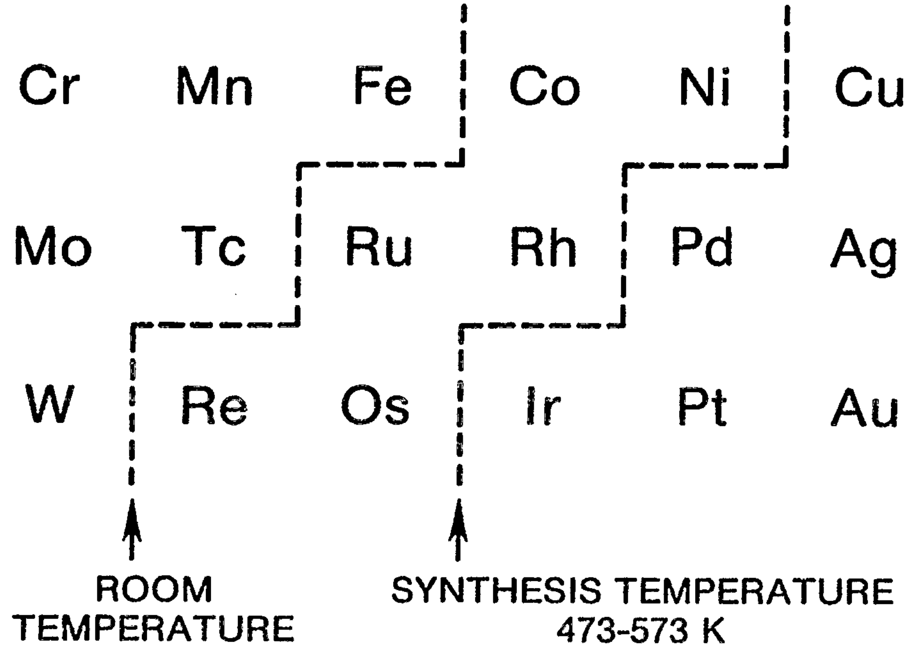


Figure II-8: METALS THAT ADSORB CO DISSOCIATIVELY AND NON-DISSOCIATIVELY AT AMBIENT TEMPERATURE AND FISCHER-TROPSCH REACTION TEMPERATURES

F-T synthesis whereas those to the right are methanol synthesis catalysts. In fact, at still higher tmeperatures, the line is shifted further to the right and at these temperatures CO is dissociatively chemisorbed on even copper and palladium. Poutsma and co-workers (1978) showed that Pd, Ir and Pt catalyzed the synthesis of methanol with 100% selectivity at higher synthesis gas pressures.

The "Carbide" Mechanism

Fischer and his coworkers (1926, 1932) based in part on what must be considered brillant intuition, postulated that the catalyst surface was carbided by CO and that the carbide was then hydrogenated to methylene ($-CH_2-$) groups. These polymerized to a series of longer chain hydrocarbons. This mechanistic approach was later refined by Craxford and Rideal (1939). Several workers evaluated Fischer's carbide mechansism and concluded that it was not satisfactory (Anderson, 1956; Browning and Emmett, 1952). The postulation of CH_2 polymerization did not seem too reasonable originally since F-T hydrocarbons are mostly linear and not branched as would be expected by a block polymerization in two or three dimensions. But in the last few years, there has been a strong resurgence of research which essentially furnishes support for his theory (Joyner, 1977, Ponec, 1978; Araki and Ponec, 1976; Biloen et al. 1979; Ekerdt and Bell, 1979, Biloen and Sachtler, 1982).

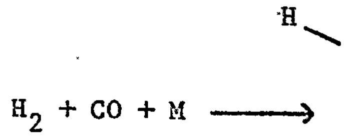
It must be borne in mind that very high selectivities to oxygenated compounds can be obtained with the usual F-T catalysts (Fe, Co, Ru, Ni) by changing reaction conditions; recall again that Fischer and Tropsch (1923) obtained mostly oxygenates using alkalized Fe and other catalysts. While use of the standard $Co-ThO_2-MgO-SiO_2$ catalyst at about 460K yields only about 1% of oxygenates (Dry, 1981), at lower temperatures (430-445K) the alcohol content of the liquid organic products rose to some 40% (Gall et al. 1952).

Kagan et al. (1966) obtained a product boiling below 433K that had an alcohol content of 86% using promoted iron catalysts at high pressures. More recently, Knifton (1981) obtained very high yields of oxygenated products using a Ru catalyst at high pressures (43 MPa).

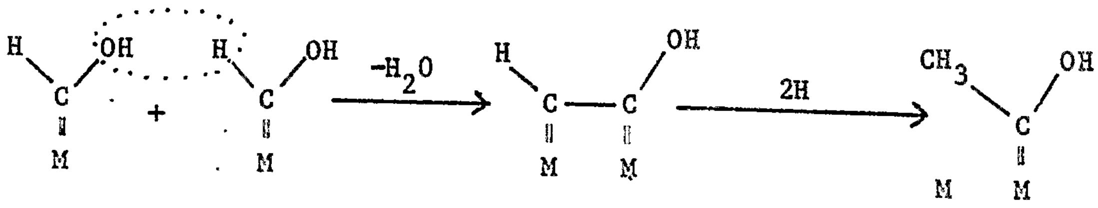
It is easy to understand, in the light of these findings, how Elvins and Nash (1926) were led to postulate that oxygenated species existed on the catalyst surface. Storch and Anderson (1951), and Anderson (1956) wrote a mechanistic picture in which hydroxycarbene intermediates were the basic building blocks in the F-T synthesis. This scheme was supported by the work of Emmett and his co-workers by studying the incorporation of alcohols labelled with ^{14}C in the F-T synthesis (1951, 1953).

The Hydroxycarbene Mechanism

The Anderson-Emmett hydroxycarbene mechanism may be written:

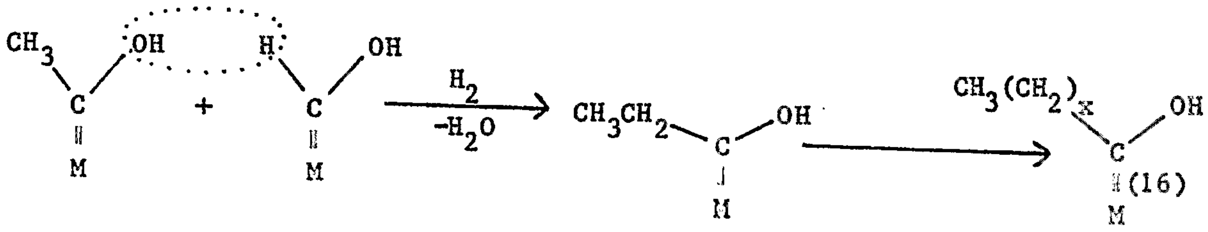


(14)



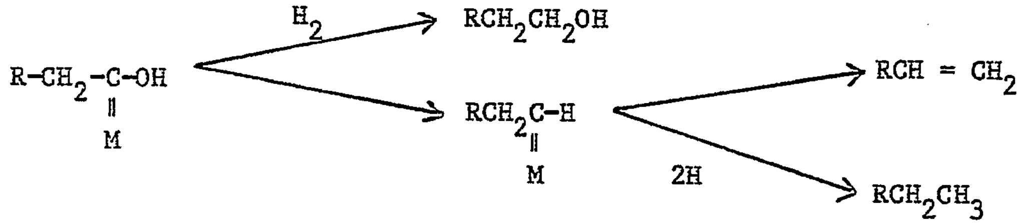
(15)

Propagation is proposed to take place by alternating hydrogenation and condensation steps.



(16)

Termination to give paraffins, olefins or alcohols occurs as shown:



(17)

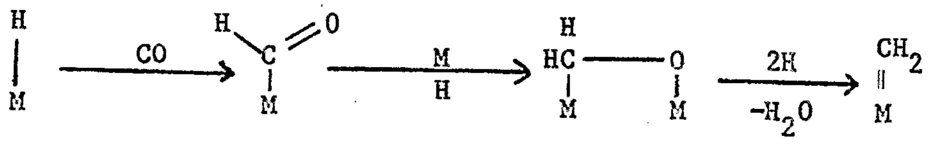
In this mechanism, the CO does not dissociate but is hydrogenated to hydroxycarbenes which eliminate water to form carbon-carbon bonds on the surface. This type of "lasso" chemistry (Eq. 15), formerly used to explain organic reactions, rarely occurs in homogeneous systems and it is unlikely to occur here.

The evidence to support this enolic mechanism has not been substantial. Nevertheless, the suggestions that such oxygenated surface intermediates are involved in the F-T reaction has much merit. Kolbel and co-workers (1970), obtained IR spectra under F-T conditions which indicated the presence of carbonyl, carbonate and carboxyl species on the catalyst surface. Blyholder (1966) has postulated that alkoxide (M-OR) structures are active F-T surface intermediates.

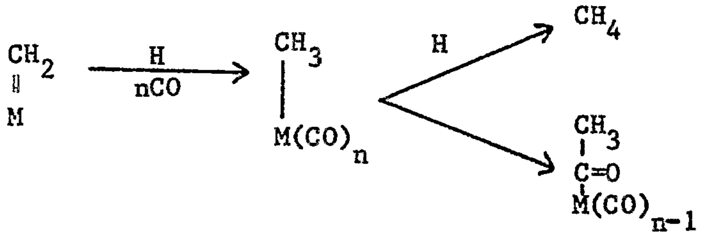
The Carbon Monoxide Insertion Mechanism

Pichler, as early as 1940, noted that the rate of the F-T reaction increased with increasing (CO) pressure until conditions were reached under which metal carbonyls were formed (Pichler, 1952). He postulated that the F-T reaction took place at conditions just below those favorable for metal carbonyl formation. Later, Wender and coworkers (1957, 1958, 1959) proposed a sequence of reactions for the F-T synthesis based on their work on homogeneous catalysis of syngas reactions catalyzed by metal carbonyls. They postulated the migratory insertion of surface CO groups into an alkyl-metal bond to form an acyl-metal entity (RCO-M). This could be hydrogenated to primary alcohols, which could be dehydrated to olefins or hydrogenated to paraffins.

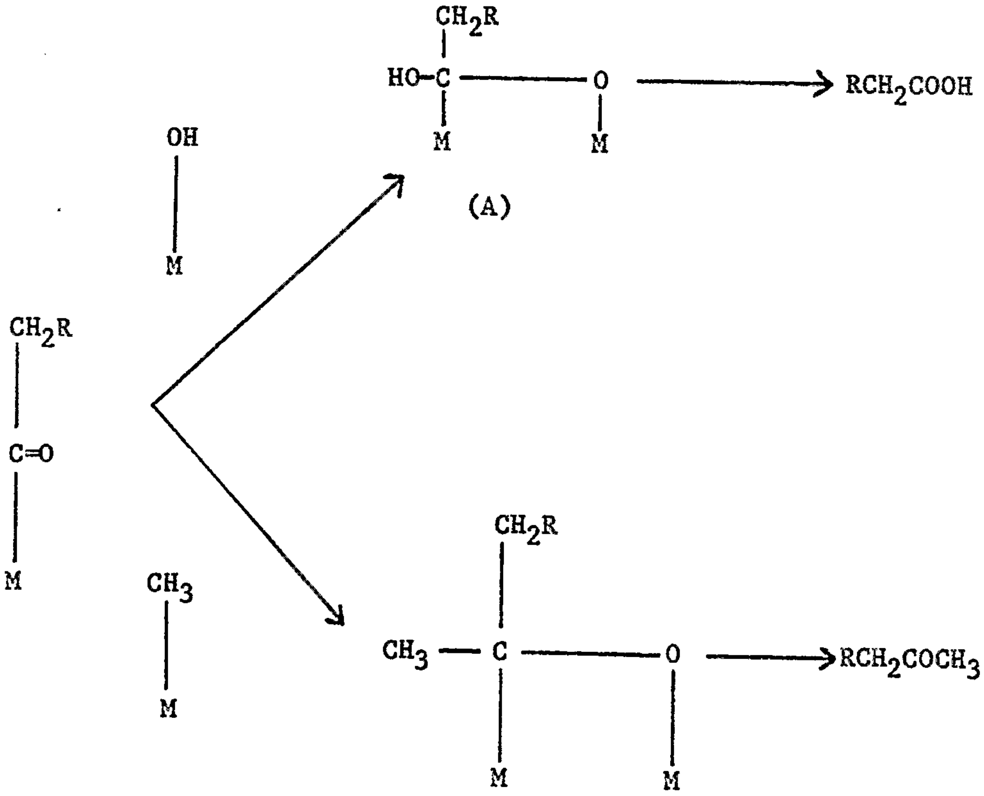
Pichler and Schulz (1970) and Schulz and El Deen (1977) have proposed a more complete version of this CO insertion mechanism, based also on reactions occurring in homogeneous organometallic chemistry (Dry, 1981),



(18)

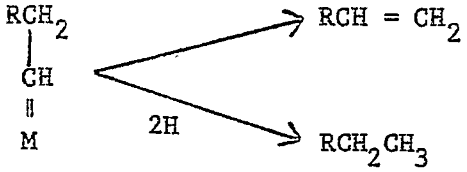


(19)



(20)

$$A \xrightarrow{2H} RCH_2CH_2OH \qquad (21)$$



$$\begin{array}{c} RCH_2 \\ | \\ CH \\ \| \\ M \end{array} \begin{array}{l} \nearrow RCH = CH_2 \\ \\ \underset{2H}{\searrow} RCH_2CH_3 \end{array} \qquad (22)$$

Here, rather stable surface carbonyl compounds form and a migratory insertion of alkyl group to adsorbed CO occurs.

Deluzarche et al. (1977) have proposed that CO inserts into an M-OH surface group to form M-OCOH which then hydrogenates to $M\text{-}OCH_3$. Insertion of CO into $M\text{-}OCH_3$ yields $M\text{-}OCOCH_3$ and the reactions are then repeated.

All the steps in the Pichler-Schulz mechanism appear plausible and almost all known F-T products are explained. There is still some question concerning the formation of the formyl intermediates in the first step although thermodynamic calculations indicate that a small amount of formaldehyde (~ 0.3%) is formed in a corresponding homogeneous reaction:

$\overset{H}{\overset{|}{M}} - CO \rightleftharpoons M\text{-}\overset{H}{\overset{|}{C}} = O$ (Fahey, 1981; Dombeck, 1980; Costa, 1983). Most workers feel that the migratory insertion of CO to form alcohols is a termination step in the F-T synthesis. There is little doubt, however, that several of the reactions in this mechanism contribute, sometimes greatly, sometimes only in a small way, to the overall F-T mechanism.

The CH_x-Stepwise Polymerization Mechanism

As pointed out earlier, there has been a strong resurgence of support for a somewhat modified version of Fischer's original carbide theory of the F-T mechanism (Joyner, 1977; Ponec, 1978, Araki and Ponec, 1976; Biloen et al., 1979; Ekerdt and Bell, 1979). Studies has indicated that CO adsorption on F-T metals at normal F-T temperatures is largely dissociative although significant amounts of undissociated CO are present on the catalyst surface under F-T conditions (Ekerdt and Bell, 1979; Rabo et al., 1978; Sexton and Somorjai, 1977; Bell, 1981).

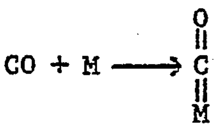
Wentricek et al. (1978), in a seminal paper, showed that hydrogenation of carbon deposited by the disproportionation of CO readily yielded methane. Later studies (Araki and Ponec, 1976) showed that C_{2+} hydrocarbons could also be formed.

Bonzel et al. (1980, 1982) examined catalyst surfaces by Auger and x-ray photoelectron spectroscopy; these studies revealed that at least three types of carbon probably exist on an F-T catalyst surface: a CH_x moiety, carbidic carbon and graphitic carbon. Only the graphitic carbon fails to react to give methane and higher hydrocarbons at F-T temperatures. Biloen et al. (1979) and Biloen and Sachtler (1981) obtained further evidence for the role of carbidic carbon in hydrocarbon chain growth. Ni, Co, and Ru catalysts were precovered with ^{13}C atoms and then exposed to a mixture of ^{12}CO and H_2. A good yield of $^{13}CH_4$ and hydrocarbons with a number of ^{13}C atoms were obtained in the product. The times to convert ^{13}C atoms and adsorbed ^{12}CO molecules to methane were essentially the same. Biloen and his co-workers concluded that CO dissociation is very rapid and that CH_x species are the most reactive C_1 species on the catalyst surface. Methane and hydrocarbons are products of the same building blocks, namely CH_x ($x = 0{-}3$). Since deposited surface carbon will gradually convert to the less reactive graphitic carbon in an inert environment (McCarty and Wise, 1979; Wentrcek, et al., 1978; Rabo et al, 1978) we conclude that chain growth proceeds by polymerization of CH_x species. The migratory insertion of CH_x (usually methylene) into the M-C bond on a catalyst surface led Biloen (1980), and Biloen and Sachtler (1981) to postulate a plausible mechanism for the chain growth of hydrocarbons.

These views were reinforced by the elegant work of Brady and Pettit (1980). These workers, taking advantage of the dissociative chemisorption of diazomethane (CH_2N_2) to obtain methylene groups, were able to put methylene groups on the surface of F-T catalysts. Diazomethane in an inert gas passed over supported Fe, Co, Ru, Ni, Pd and Cu at 298-473K and 0.1 MPa yielded mostly ethylene and N_2. But the addition of H_2 to the CH_2N_2 gave entirely different products. The amounts and types of compounds obtained very much resembled F-T products using Fe, Co, and Ru. Mostly CH_4 along with some higher hydrocarbons were obtained with Ni and Pd; Cu gave only ethylene. The data are in concordance with the idea that methylene plus H_2 react as do the intermediates postulated in a CH_x stepwise polymerization scheme.

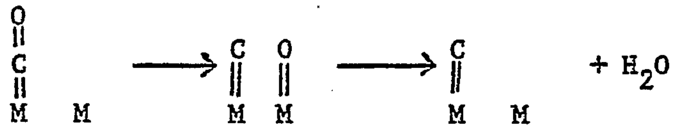
In a second paper, Brady and Pettit (1981), conducted experiments with a cobalt catalyst in which the $^{13}CO/^{12}CH_2N_2$ ratio was varied; the results were consistent with calculated product predictions of the surface carbide mechanisms. Deviations were large for the hydroxycarbene hypothesis and moderate for the CO insertion mechanism. While it is true that strongly adsorbed intermediates added to a system may dominate the catalytic route and give a distorted idea of the reaction path, the work of Brady and Pettit furnishes strong support for the CH_x stepwise polymerization mechanism.

Based on this and on much other evidence we can write the following mechanism for the F-T synthesis: (Kellner and Bell, 1981; Katzer et al., 1981; Biloen and Sachtler, 1982).



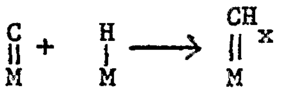
$$\mathrm{CO} + \mathrm{M} \longrightarrow \begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{C} \\ \| \\ \mathrm{M} \end{array}$$

Adsorption (23)



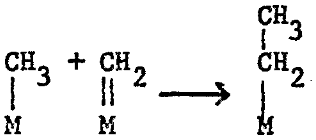
$$\begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{C} \\ \| \\ \mathrm{M} \end{array}\ \mathrm{M} \longrightarrow \begin{array}{c} \mathrm{C} \\ \| \\ \mathrm{M} \end{array}\ \begin{array}{c} \mathrm{O} \\ \| \\ \mathrm{M} \end{array} \longrightarrow \begin{array}{c} \mathrm{C} \\ \| \\ \mathrm{M} \end{array}\ \mathrm{M} + H_2O$$

Dissociation of CO (24)



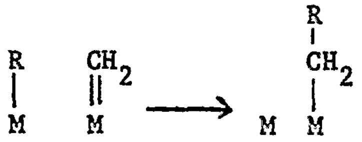
$$\begin{array}{c}C\\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow \begin{array}{c}CH_x\\\|\\M\end{array}$$

Synthesis of CH_3 initiator or CH_x monomer (25)



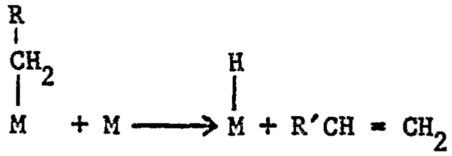
$$\begin{array}{c}CH_3\\|\\M\end{array} + \begin{array}{c}CH_2\\\|\\M\end{array} \longrightarrow \begin{array}{c}CH_3\\|\\CH_2\\|\\M\end{array}$$

Chain growth, initial step, migratory insertion of $:CH_2$ into an R–M bond (26)



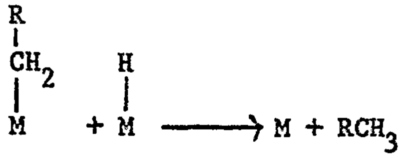
$$\begin{array}{c}R\\|\\M\end{array} \quad \begin{array}{c}CH_2\\\|\\M\end{array} \longrightarrow M \quad \begin{array}{c}R\\|\\CH_2\\|\\M\end{array}$$

Propagation, further $:CH_2$ insertion (27)



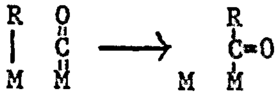
$$\begin{array}{c}R\\|\\CH_2\\|\\M\end{array} + M \longrightarrow \begin{array}{c}H\\|\\M\end{array} + R'CH = CH_2$$

Termination: Olefin formation (28)



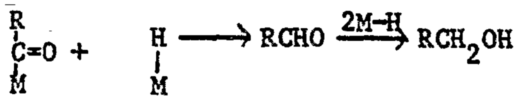
$$\begin{array}{c}R\\|\\CH_2\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow M + RCH_3$$

Termination: Paraffin formation (29)



$$\begin{array}{c}R\\|\\M\end{array} \quad \begin{array}{c}O\\\|\\C\\\|\\M\end{array} \longrightarrow M \quad \begin{array}{l}R\\|\\C{=}O\\|\\M\end{array}$$

Migratory insertion of CO, acyl formation (30)



$$\begin{array}{l}R\\|\\C{=}O\\|\\M\end{array} + \begin{array}{c}H\\|\\M\end{array} \longrightarrow RCHO \xrightarrow{2M-H} RCH_2OH$$

Termination: aldehyde and alcohol formation (31)

As stated earlier, it is difficult to prove or disprove any of these F-T mechanisms. It does seem that any mechanistic scheme that excludes CO dissociation on the catalysts seems unlikely. But the CH_x stepwise or carbide mechanism does not adequately explain the production of oxygenated products, among other facets of the F-T synthesis.

Oxygenated products, particularly alcohols, are postulated to be formed in a termination step whereby a surface alkyl group supposedly migrates to an undissociated CO molecule on the catalyst surface. The pertinence of the carbide mechanism has been questioned by Henrice-Olive′ and Olive′ (1983), who claim that the findings of the researchers who advocate this pathway for the F-T reaction are just as compatible with a mechanism based primarily on the migratory insertion of CO. There is obviously much work yet to be done on clarifying the nature of the mechanistic pathways involved in the F-T synthesis. A major objective of F-T research is to develop new catalyst systems that improve selectivity.

The Effect of Temperature

The effect of temperature on selectivity is consistent for all F-T catalysts. As the temperature of the synthesis is increased, the CH_4 selectivity increases, the amount of olefins in the product rises and the selectivities toward oxygenated compounds decreases. The temperatures used at SASOL bear out these effects and take them into account in actual operation.

Promoters

Promoters have been divided into two types according to their mode of action. Oxides that are difficult to reduce such as SiO_2, Al_2O_3, MgO, ThO_2, La_2O_3 and ZnO are called structural promoters. They furnish a large surface area and prevent recrystallization and sintering of the active catalyst. Recent work has indicated that these so-called textural promoters often interact chemically with various oxidation states of the catalyst and even exchange oxygen atoms (Orita et al., 1984). Chemical promoters exert their influence by mechanisms not yet clearly understood. They may transfer electrons to the catalysts or even block pores. Alkalis and their salts are the chemical promoters most often used - they are basic salts and catalyst basicity, especially for the iron catalysts used at SASOL, is a key parameter. The effect of these promoters are dependent not only on the type and amount of the alkali salt added but also on the interaction of the alkali with the support, with other promoters, and with impurities. Potassium oxide, K_2O, is the chemical promoter used most often. If the alkali reacts with the support, the basicity will be decreased and more alkali must be added. For instance, supports such as Al_2O_3 or TiO_2 are too acidic to be used as promoters at SASOL. Alkalis are considered to be electron donors.

The effects of alkali promotion on F-T catalysts such as iron (Dry et al. 1969; 1972), ruthenium (Gonzales and Miura, 1982), and nickel (Campbell and Goodman, 1982) may be summarized as follows: (a) suppression of hydrogenation capability, (b) increase in CO dissociation, (c) increase in formation of long chain hydrocarbons, and (d) decrease in the conversion activity of CO.

Gas Composition and Reaction Pressure

The simple ratio P_{H_2}/P_{CO} adequately represents the selectivity for the SASOL fixed bed reactor operating at a low temperature with an extruded iron catalyst (Dry, 1982). The partial pressure of CO_2 as well as the total pressure (Dry, 1981) influence the selectivity for the SASOL Synthol catalysts which operate at a higher temperature. This is an ongoing area of research at SASOL.

Deactivation of Catalysts

F-T catalysts can lose activity for a number of reasons: (a) sintering (loss of active surface area due to growth of crystals), (b) conversion of the active parts of the catalyst to inert phases (i.e. metal to a metal oxide), (c) deposition of carbonaceous substances on the active surface area (carbon deposition) or, (d) chemical processing or poisoning of the surface (sulfur is the chief culprit here). Coke deposition is likely the most important mode of catalyst deactivation at SASOL.

Most sulfur compounds are dissociatively adsorbed on F-T metals with the surface sulfur held much more strongly than the sulfur in bulk sulfides (Anderson, 1984). Poisoning by sulfur compounds apparently occurs chiefly by adsorption of sulfur atoms on active metal sites, destroying their catalytic activity. The amount of allowable sulfur in the F-T reaction is on the order of a few parts per billion.

Tungsten and molybdenum catalysts that are more sulfur resistant than the usual F-T catalysts have been found. In general, they have low activity and poor selectivity. An alkalized molybdenum catalyst that is selective to low molecular weight products has been developed (Murchison and Murdick, 1980).

The SASOL technology has been a remarkable success in South Africa. But conditions in other countries are different: cheap coal may not be available, labor is not as cheap and the oil supply perhaps more assured. In general, SASOL technology is limited to non-caking or poorly caking coal (really only a limitation of the gasifier used at SASOL). Other disadvantages in SASOL technology are the broad product distribution and the straight-chain nature of the products (resulting in a low octane number for use as gasoline, but the cetane number for the diesel fraction is good). The maintenance cost for the SASOL plant tends to be fairly high and the thermal efficiency (to transportation fuels) is low.

THE KOLBEL-ENGELHARDT (K-E) SYNTHESIS

Two excellent reviews summarizing work on the Kolbel-Engelhardt (K-E) synthesis, which may be considered an offshoot or variant of the F-T synthesis, have been published by Kolbel and Ralek (1982; 1984). The K-E synthesis occurs on iron (Kolbel and Engelhardt, 1951;1952) cobalt, (Kolbel and Vorwek, 1957), nickel, (Kolbel and Gaube, 1961), and ruthenium (Kolbel and Bhattacharyya, 1958) catalysts.

The K-E synthesis was originally conceived as a way of using CO-containing gas streams which had little or no hydrogen. The synthesis consists of two well-studied reactions, the F-T synthesis and the water-gas shift reaction. The products obtained are essentially the same as those obtained with the F-T reaction. Equations for the K-E synthesis of paraffins (Anderson, 1984) may be written:

$$\text{F-T reaction} \qquad (2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O \tag{32}$$

$$\underline{\text{Water-gas shift} \quad (2n+1)H_2O + (2n+1)CO \longrightarrow (2n+1)H_2 + (2n+1)CO_2} \tag{33}$$

$$\text{K-E reaction} \qquad (n+1)H_2O + (3n+1)CO \longrightarrow C_nH_{2n+2} + (2n+1)CO_2 \tag{34}$$

The reaction enthalpies of the F-T and K-E reactions differ only by the single or multiple values of the enthalpy of the water-gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H = -9.5\ \text{kcal/mole} \tag{35}$$

Essentially all active F-T catalysts that are resistant to oxidation under K-E conditions are also K-E synthesis catalysts, with iron catalysts particularly suitable (Kolbel and Engelhardt, 1951; 1952).

Kolbel and Engelhardt used both fixed bed and slurry reactors; the slurry bed synthesis was found preferable. In 1953, a slurry phase demonstration plant began operation in Germany and was operated successfully for two years, producing about 11.5 tons of product per day (Kolbel et al., 1956; Kolbel and Ralek 1980). The availability of cheap oil prevented construction of other, larger K-E plants.

The successful construction and operation of the K-E demonstration plant, using CO and water, however, may have made its greatest contribution to the enhancement of the recent growing interest in slurry phase F-T reactors. Second generation coal gasifiers yield CO-rich syngas ($H_2/CO \sim 0.6$). The SASOL reactors deactivate rapidly with syngas with a high CO/H_2 ratio due to carbon deposition. The U.S. Department of Energy and several industrial companies are supporting research on the use of slurry phase reactors in the F-T synthesis and in the methanol synthesis (Lee et al., 1983; Sherwin and Blum, 1978).

Fischer and co-workers were the first to use slurry reactors in the F-T synthesis (Fischer et al., 1932). In general, this type of reactor uses finely divided iron catalysts suspended in a high-boiling oil (which may be a high-boiling F-T fraction). Kolbel's pioneering work in Germany has aleady been referred to. Hall et al. (1952), in England, Schlesinger et al. at the U.S. Bureau of Mines (1951), and Sakai and Kunugi (1974) in Japan have all carrried out work on slurry phase F-T reactions.

As opposed to fixed bed or entrained bed reactors, slurry reactors using high CO/H_2 synthesis gas offer advantages for use in the F-T synthesis. These include (a) avoidance of a separate water-gas shift reaction, (b) excellent temperature control of the reactor, (c) high single pass synthesis gas conversion which maximizes heat recovery and minimizes utility requirements and (d) comparatively simple reactor design.

THE ISOSYNTHESIS

Isoparaffins, especially isobutane and isobutylene, are excellent raw materials for conversion to high octane gasoline. Pichler and Ziesecke (1949), working with Fischer, began work on the synthesis of these types of compounds in 1941. Cohn (1956) reviewed this synthesis, termed the Isosynthesis, in which syngas is catalytically converted to products consisting predominantly of branched, mostly saturated hydrocarbons, using certain difficulty reducible oxides as catalysts. Development of the process was rapid (Cohn 1956; Pichler and Ziesecke, 1950) but its commercial use was cut off by the successful development of new catalysts for the production of high octane gasoline from readily available petroleum.

One method for the synthesis of isoparaffins from syngas consists in the preparation of isobutyl alcohol, produced when alkali is added to a zinc oxide methanol synthesis catalyst (Pichler and Ziesecke, 1950). The branched alcohols thus produced, largely isobutyl alcohol, can be dehydrated to isobutylene which can then be converted to high octane gasoline. But methanol is the main product over these catalysts.

The Isosynthesis differs from the Fischer-Tropsch reaction in several ways, although both use syngas as the feed. The Isosynthesis gives high yields of isoparaffins rather than normal paraffins, the catalysts are difficulty reducible oxides such as thorium oxide (ThO_2) rather than reduced transition metals. Isosynthesis temperatures and pressures are considerably higher than those used in the F-T synthesis.

Thorium oxide is a good catalyst for the Isosynthesis reaction. This catalyst is prepared by precipitation with Na_2CO_3 and then pretreated by sintering in air at 573K. The catalyst could be regenerated with air after several weeks so that it had considerable activity for a lengthy period of time. Carbon monoxide and hydrogen are consumed in $1.2CO/1H_2$ ratio in a single pass. The thorium oxide catalyst is not affected by sulfur compounds but the synthesis should be carried out in vessels (chrome alloy steel or copper-lined reactors) which exclude F-T catalysts (U.S. Bureau of Mines Bull. 488). In addition to ThO_2, ZrO_2 and to a lesser extent, CeO_2 are active Isosynthesis catalysts at 723K and 150 atm (15 MPa).

The type of products formed over ThO_2 in the Isosynthesis do not follow the A-S-F equation. At temperatures below 673K, especially below 648K, alcohols are the main products; above 773K, low molecular weight hydrocarbons predominate. At 723K, 25% of iso-C_4 compounds, chiefly isobutane, are formed, together with about 16% of methane and 46% of liquid products containing mostly branched aliphatics plus some aromatics and naphthenes. Optimum pressures for the production of liquid hydrocarbons in the Isosynthesis are between 30 and 60 MPa. At the higher pressures, methane and dimethyl ether predominate.

The activity of ThO_2 is greatly increased by the addition of Al_2O_3; best results were obtained when 20% Al_2O_3 was added to the ThO_2 catalyst. The addition of 3% of K_2CO_3 (based on Al_2O_3) gave a further increase of iso-C_4 compounds. While Al_2O_3 added to ThO_2 increased the formation of isobutane, the addition of ZnO increased the formation of liquid products (Shah and Perrotta, 1976).

The nature of the products in the Isosynthesis process is determined chiefly by the type of catalyst and the reaction temperature and pressure. It is important to note, however, that alcohols are the main products at lower temperatures and pressures; there is little doubt that alcohols are the primary products in this synthesis. ThO_2 is an active catalyst for the hydrogenation of CO to alcohols; it is also an excellent dehydration catalyst. Al_2O_3 addition to thoria may aid in the dehydration of the alcohols.

Details of the mechanism of the Isosynthesis have not been worked out. Anderson and co-workers postulate that formaldehyde is the initial product; this is reduced to methanol (Storch et al. 1951). Successive additions of CO to methanol give the higher alcohols. Dimethyl ether, formed from methanol by dehydration, may be an intermediate in the Isosynthesis.

As will be shown in the a later section, interest in the F-T and in the Isosynthesis reactions, (Chang et al., 1979) is reviving owing to the combination of synthesis gas conversion catalysts with shape selective (zeolite) catalysts. The product slates are dramatically altered in this way.

Anderson, H.C., Wiley, J.L., and Newell, A., "Bibliography of The Fischer-Tropsch Synthesis and Related Processes" U.S. Bureau of Mines Bull. 544, U.S. Government Printing Office, Washington, D.C., 1954.

Anderson, R.B., "The Thermodynamics of the Hydrogenation of Carbon Monoxide and Related Reactions" (Chapt. 1) and "Kinetics and Reaction Mechanism of the Fischer-Tropsch Synthesis" (Chapt. 3), in Catalysis Vol. IV (Emmett, P.H. Ed.), Reinhold Publishing Corporation, New York, New York, 1956.

Anderson, R.B., "The Fischer-Tropsch Synthesis", Academic Press, New York, New York, 1984.

Araki, M. and Ponec, V., "Methanation of Carbon Monoxide on Nickel and Nickel-Copper Alloys", J. Catal. 44, 439-448 (1976).

Bell, A.T., Imelik, B., Martin, G., Ronouprez, A., "Fundamentals and Industrial Aspects of Catalysis by Metals", Editions du Center National de la Recherche Scientifique, Paris, 1984.

Bell, A.T., "Catalytic Synthesis of Hydrocarbons Over Group VIII Metals. A Discussion of the Reaction Mechanism", Catal. Rev. - Sci. Eng., 23, 203-232 (1981).

Biloen, P. and Sachtler, W.M.H., "Mechanism of Hydrocarbon Synthesis Over Fischer-Tropsch Catalysts", Adv. Catal., 30, 165-216 (1981).

Biloen, P., Helle, J.N., and Sachtler, W.M.H., "Incorporation of Surface Carbon into Hydrocarbons During Fischer-Tropsch Synthesis - Mechanistic Implications", J. Catal., 58, 95-107 (1979).

Biloen, P., "On the Mechanism of the Fischer-Tropsch Synthesis" J. Royal Neth. Chem. Soc., 99, 33 (1980).

Blyholder, G. and Neff, L.D., "Structures of Some C_xH_yO Compounds Adsorbed on Iron", J. Phys. Chem. 70, 893-900 (1966).

Bonzel, H.P., and Krebs, H.J., "On the Chemical Nature of the Carbonaceous Deposits on Iron After CO Hydrogenation", Surface Sci., 91, 499-513 (1980).

Broden, G., Rhodin, T.N., Bruckner, C., Benbow, R., and Hurych, Z., "Synchrotron Radiation Study of Chemisorptive Bonding of CO on Transition Metals - Polarization Effect on Ir(100)", Surface Sci., 59, 593-611 (1976).

Brady, R.C., III, and Pettit, R., "Reactions of Diazomethane on Transition Metal Surfaces and Their Relationship to the Mechanism of the Fischer-Tropsch Reaction", J. Am. Chem. Soc., 102, 6181-6182 (1980).

Brady, R.C., III and Pettit, R., "On the Mechanism of the Fischer-Tropsch Reaction. The Chain Propagation Step", IBID, 103, 1287-1289 (1981).

Browning, L.C., and Emmett, P.H., "Equilibrium Measurements in the Ni_3C-Ni-CH_4-H_2 and Co_2C-CO-CH_4-H_2 Systems" J. Am. Chem. Soc., 74, 1680-1682 (1952).

Campbell, C.T., and Goodman, D.W., "A Surface Science Investigation of the Role of Potassium Promoters in Nickel Catalysts for CO Hydrogenation", Surface Sci., 123, 413-426 (1982).

Chang, C.D., Lang, W.H., and Silvestri, A.J., "Synthesis Gas Conversion to Hydrocarbons", J. Catal. 56, 268-273 (1979).

Cohn, E.M., "The Isosynthesis" in Catalysis, Vol. IV (Emmett, P.H. Ed.) Reinhold Publishing Corporation, New York, New York, 1956, pp. 443-472.

Costa, L.C., "Factors Which Determine Product Selectivity in the Homogeneous Hydrogenation of Carbon Monoxide to Oxygenates", Catal. Rev. - Sci. Eng., 25, 325-363 (1983).

Craxford, S.R. and Rideal, E.K., "The Mechanism of the Synthesis of Hydrocarbons from Water Gas", J. Chem. Soc., 1604-1614 (1939).

Deluzarche, A., Hinderman, J.P., Kieffer, R., Muth, A., Papdopoulos, M., and Tanielian, C., "Synthesis De Fischer-Tropsch (CO, H_2) II. Mecanisme De Reaction Et Application De La Chromatographic En Phase Gazeuse A Son Etude E Catalyse Heterogene", Tetrahedron Lett., 9, 797-800 (1977).

Dombek, B.D., "Hydrogenation of Carbon Monoxide to Methanol and Ethylene Glycol by Homogeneous Ruthenium Catalysts", J. Am. Chem. Soc., 102, 6855-6857 (1980).

Dry, M.E., Shingles, T., Boshoff, L.J., "Rate of the Fischer-Tropsch Reaction Over Iron Catalysts", J. Catal. 25, 99-104 (1972).

Dry, M.E., Shingles, T., Boshoff, L.J., and Oosthuizen, G.J., "Heats of Chemisorption on Promoted Iron Surfaces and the Role of Alkali in Fischer-Tropsch Synthesis", J. Catal., 15, 190-199 (1969).

Dry, M.E., "The Fischer-Tropsch Synthesis" in Catalysis Science and Technology Vol. I., Chap. 4, (Anderson, J.R., and Boudart, M., Eds) Springer-Verlag, New York, New York, 1981.

Dry, M.E., "Sasol's Fischer-Tropsch Experience" Hydrocarbon Processing, pp. 121-124, August (1982a).

Dry, M.E., "Catalytic Aspects of Industrial Fischer-Tropsch Synthesis", J. Mol. Catal., 17, 133-144 (1982b)

Dry, M.E., "SASOL Routes to Diesel Fuel Production", Proceedings, Tenth Annual International Conference on COGLAC, University of Pittsburgh, August 9-11, 1983 pp. 235-247.

Eisenlohr, K.H., and Gaensslen, H., "Motor Fuels from Coal-Technology and Economics", Fuel Process Techn., 4, 43-61 (1981).

Ekerdt, J.G., and Bell. A.T., "Synthesis of Hydrocarbons from CO and H_2 over Silica-Supported Ru: Reaction Rate Measurements and Infrared Spectra of Adsorbed Species", J. Catal. 58, 170-187 (1979).

Elvins, O.C., and Nash, A.W., "The Reduction of Carbon Monoxide", Nature, 118, 154 (1926).

Fahey, F.R., "Rational Mechanism for Homogeneous Hydrogenation of Carbon Monoxide to Alcohols, Polyols and Esters", J. Am. Chem. Soc., 103, 136-141 (1981).

Fischer, F., and Koch, H., "Uber den Chemismus der Benzinsynthese und uber die Motorischen und Sonstigen Eigenschaften der dabei Auftretenden Produkte (Gasol, Benzin, Dieselol, Hartparaffin)," Brennst-Chemie 13, 428-434 (1932).

Fischer, F., and Tropsch, H., "Die Erdolsynthese bei Gewohnlichem Druck aus den Vergasungsprodukten der Kohlen," Brennst-chemie 7, 97-104 (1926).

Fischer, F., and Tropsch, H., "The Preparation of Synthetic Oil Mixture (Synthol) from Carbon Monoxide and Hydrogen", Brennst-Chem., 4, 276-285 (1923).

Fischer, F., Roelen, O. and Feisst, W., "Uber den Nunmehr Erreichten Technischen Stand der Benzinsynthese", Brennst-Chem., 13, 461-480 (1932).

Flory, P.J., "Molecular Size Distribution in Linear Condensation Polymers", J. Am. Chem. Soc., 58, 1877-1885 (1950).

Flory, P.J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1967.

Friedel, R.A., and Anderson, R.B., "Composition of Synthetic Fuels I. Product Distribution and Analysis of C_5-C_8 Paraffine Isomers from Cobalt Catalysts", J. Am. Chem. Soc., 72, 1212-1215, 2307 (1950).

Frohning, C.D., Kolbel, H., Ralek, M., Rottig, F., Schmur, F., and Schulz, H., "Fischer-Tropsch Process" in Chemical Feedstocks from Coal (Falbe, J. Ed., Translated by Mullen, A. Jr.), John Wiley & Sons, New York, New York, 1982 Chap. 8, p. 309.

Gall, D. Gibson, E.J., and Hall, C.C., "The Distribution of Alcohols in the Product of the Fischer-Tropsch Synthesis", J. Appl. Chem. (London), 2, 371-380 (1952).

Gonzales, R.D. and Miura, H., "Methanation and Fischer-Tropsch Studies on Potassium-Promoted Silica-Supported Ru Catalysts", J. Catal. 77, 338-347 (1982).

Hall, C.C., Gall, D. and Smith, S.L., "A Comparison of the Fixed-Bed, Liquid-Phase (Slurry) and Fluidized Bed Techniques in the Fischer-Tropsch Synthesis", J. Inst. Petroleum Technologists, 38, 845-875 (1952).

Henrice-Olive, G., and Olive, S., "The Carbide Theory of the Fischer-Tropsch Synthesis in the Light of Homogeneous Coordination Chemistry", J. Mol. Catal. 18, 367-373 (1983).

Herington, E.F.G., "The F-T Synthesis Considered as a Polymerization Reaction", Chem. Ind., 346-347 (1946).

Hoogendoorn, J.C., "Experience with Fischer-Tropsch Synthesis at SASOL", Presented at the IGT Symposium on Clean Fuels from Coal, Chicago, IL, Sept. 10-14, 1973.

JANAF. Thermodynamic Tables, U.S. Department of Commerce, N.B.S., NSRDS-NBS-37, 1971.

Joyner, R.W., "Mechanism of Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen", J. Catal., 50, 176-180 (1977).

Kagan, Y.B., Bashkirov, A.N., Morozov, L.A., Kryulov, Y.B., and Orlova, N.A., "Influence of Promoters on the Selectivity of the Action of Sintered Fe Catalysts in the Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen", Neftekhimiya, 6 (2), 262-270 (1966).

Katzer, J.R., Sleight, A.W., Gajardo, P., Michel, J.B., Gleason, E.F., and McMillan, S., "The Role of Support in CO Hydrogenation Selectivity of Supported Rhodium", Royal Soc. of Chemistry, Faraday Disc., 72, (1981), paper 8.

Keith, P.C., "Gasoline from Natural Gas", Oil Gas J., 45 (No. 6), 102 (1946).

Kellner, C.S., and Bell. A.T., "Synthesis of Oxygenated Products From Carbon Monoxide and Hydrogen Over Silica- and Alumina-Supported Ruthenium Catalysts", J. Catal., 71, 288-295 (1981).

Knifton, J.F., "Ethylene Glycol from Synthesis Gas via Ruthenium Melt Catalysis", J. Am. Chem. Soc., 103, 3959-3961 (1981).

Kolbel, H., "Ver Wertungmoglichkeiten Kohlenoxydhaltiger Abgase Zur Synthese von Kohlenwasserstoffen" Chem. Ing. Technik, 29, 505-511 (1957).

Kolbel, H., Ackerman, P., and Engelhardt, F., "Neue Entwicklungen Zur Kohlenwasserstoff-Synthese. III die Synthese Von Kohlenwasserstoffen aus Co und H_2O-Dampf", Erdol und Kohle, Erdgas, Petrochemie, 9, 303-307 (1956).

Kolbel, H., and Engelhardt, F., "Synthese von Kohlenwasserstoffen und Sauerstoffhaltigen Verbindungen aus Kohlenoxyd und Wasserdampf", Brennst-Chem. 32, 150 (1951).

Kolbel, H., and Engelhardt, F., "Synthese von Kohlenwassertoff und Sauerstoffhaltigen Verbindungen aus Wasser and Kohlenoxyd", IBID, 33, 13-21 (1952).

Kolbel, H., and Englehardt, F., "Kohlenwasserstoffe aus Kohlenoxyd und Wasser", Angew. Chem., 64, 54-58 (1952).

Kolbel, H., and Gaube, J., "Synthese von Kohlenwasserstoffen aus Kohlenoxyd und Wasserdampf VIII Mitteilung: Synthese an Nickel Katalystoren", Brennst-Chem., 42, 149-153 (1961).

Kolbel, H., Ralek, M., and Jiru, P., "Infrarotspektren der Adsorptionskomplexe des Kohlenmonoxids und des Wasserstoffs auf einem Eisen-Magnesiumoxid-Mischkatalysator," Erdol und Kohle 23, 580-583 (1970).

Kolbel, H., and Vorhek, E., "Synthese von Kohlenwasserstoffen aus Kohlenoxyd und Wasserdampf III. Mitteilung: Synthese an Kobalt-Katalysatoren", Brennst-Chem., 38, 2-9 (1957).

Kolbel, H., and Bhattacharyya, K.K., Synthese Hochsehmelzender Paraffine An Ruthenium-Kontaklen, Ann. Chem., 618, 67-71 (1958).

Kolbel, H., and Ralek, M., "The Fischer-Tropsch Synthesis in the Liquid Phase", Cat. Rev. - Eng. Sci. 21, 225-274 (1980).

Kolbel, H., and Ralek, M., "Liquid Phase Synthesis" (Section 8.3 of chapter 8, titled "Fischer-Tropsch Process in "Chemical Feedstocks from Coal" (Falbe, J. Ed.), John Wiley & Sons, New York, New York, 1982.

Kolbel, H., and Ralek, H., "The Kolbel-Engelhardt Synthesis" in the Fischer-Tropsch Synthesis" By Anderson, R.B., Academic Press, New York, New York, 1984, Chapt. 7.

Krebs, H.G., and Bonzel, H.P., "Hydrogenation Kinetics of Carbonaceous Layer on Polycrystalline Iron" Surface Sci., 99 570-580 (1980).

Kruger, p du P., "Startup Experience at SASOLS Two and Three", Tenth Annual International Conference on COGLAC, University of Pittsburgh, August 9-11, 1983 pp 45-59.

Kummer, J.T., Podgurski, H.H., Spencer, W.B., and Emmett, P.H., "Mechanism Studies of the Fischer-Tropsch Synthesis. The Addition of Radioactive Alcohol", J. Am. Chem. Soc. 75 564-569 (1951).

Kummer, J.T. and Emmett, P.H., "Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas", J. Am. Chem. Soc., 75, 5177-5182 (1953).

Kuo, J.C.W., "Gasification and Indirect Liquefaction" in Science and Technology of Coal and Coal Utilization (Cooper, B.R., and Ellingson, W.A., Eds). Plenum Press, New York, New York, 1984.

Lee, W., Gould, R.M., Kuo, J.C.W., and Yurchak, S., "Transportation Fuels from Synthesis Gas via ZSM-5" Tenth Annual International Conference on COGLAC, University of Pittsburgh, August 9-11, 1983, pp. 258-267.

Madon, R.J., "On the Growth of Hydrocarbon Chains in the Fischer-Tropsch Synthesis", J. Catal., 57, 183-186 (1979).

McCarty, J.G., and Wise, H., "Hydrogenation of Surface Carbon on Alumina-Supported Nickel", J. Catal., 57, 406-416 (1979).

Murchison, C.B., and Murdick, D.A., "Syngas to LPG over Moly Catalysts" 88th National Meeting, A.I.Ch.E., June 8-12, 1980, Philadelphia, PA.

Orita, H., Naito, S., and Tamaru, K., "Mechanism of Acetaldehyde Formation from the Carbon Monoxide-Hydrogen Reaction Below Atmospheric Pressure Over Supported Rh Catalyst", J. Chem. Soc., Chem. Commun., 150-151 (1984).

Pay, T.D., "Foreign Coal Liquefaction Technology Survey and Assessment, SASOL-The Commercial Experience, Gilbert Associates, Inc., ORNL/Sub-79/13837/4, 1980.

Pichler, H., "Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen: Adv. Catal., 4, 272-341 (1952).

Pichler, H., and Schulz, H., "Neuere Erkenntnisse and dem Gebeit der Synthese Von Kohlenwasserstoffen aus CO and H_2", Chem.-Ing. Tech., 42, 1162-1174 (1970).

Pichler, H., and Ziesecke, K.H., "The Isosynthesis", U.S. Bureau of Mines Bulletin, 488, U.S. Government Printing Office, Washington, D.C., 1950.

Pichler, H., and Ziesecke, K.H., "Uber die Hochdruck-Hydrierung Von Kohlenoxyd Zu Vorzugsweise Isoparaffinischen Kohlenwasserstoffen ("Isosynthese") 1. Teil," Brennst-chemie 30, 13-22 (1949).

Pichler, H., and Ziesecke, K.H., "Uber die Hochdruck-Hydrierung Von Kohlenoxyd Zu Vorzugsweise Isoparaffinischen Kohlenwasserstuffen ("Isosynthese") II. Teil: Versuche an Mehstoffkatalysatoren und Umsetzungen Von Dimethylather," IBID 30, 60-68 (1949).

Pichler, H., and Ziesecke, K.H., "Uber die Hochdruck-Hydrierung Von Kohlenoxyd Zu Vorzugsweise Isoparaffinischen Kohlenwasserstoffen ("Isosynthese") II. Teil: Versuche an Mehrstoffkatalysatoren und Umsetzungen Von Dimethylather," IBID 30, 81-84 (1949).

Ponec, V., "Some Aspects of the Mechansim of Methanation and Fischer-Trospch Synthesis", Catal. Rev. - Sci. Eng., 18, 151-171 (1978).

Ponec, V., "Fischer-Tropsch Synthesis and Some Related Heterogeneous Reactions", in Coal Science, Vol. 3 (Gorbaty, M., Larsen, J., and Wender I., Eds.) Academic Press, New York, New York, 1984 (in press).

Poutsma, M.L., Clek, L.F., Ibarabia, P.A., Risch, A.P. and Rabo, J.A., "Selective Formation of Methanol from Synthesis Gas over Palladium Catalysts," J. Catal. 52, 157-168 (1978).

Poutsma, M.L., "Chemical Assesment of Advanced Process Concepts for Liquefaction of Low H_2:CO Ratio Synthesis Gas Based on the Kolbel Slurry Reactor and Mobil Gasoline Process, ONRL-5635, July, 1979.

Rabo, J.A. , Risch, A.P., and Poutsma, M.L., "Reactions of Carbon Monoxide and Hydrogen on Co, Ni, Ru, and Pd Metals," J. Catal. 53, 295-311 (1978).

Roelen, O., "Production of Oxygenated Carbon Compounds" U.S. Pat., 2,327,066 (1943).

Rofer-DePoorter, C.K., "A Comprehensive Mechanism for the Fischer-Tropsch Synthesis," Chem. Rev. 81, 447-474 (1981).

Sabatier, P., and Sendersen, J.B., "Nouvelles Syntheses du Methane" Compt. Rend. 134, 514-516 (1902).

Shah, Y.T. and Perrotta, A.J., "Catalysts for Fischer-Tropsch and Isosynthesis," Ind. Eng. Chem. Prod. Res. Dev. 15 (2), 123-131 (1976).

Sakai, T., and Kunugi, T., "Liquid Phase (Slurry) Method for Fischer-Tropsch Synthesis", Sekiyu Gokkai Shi, 17, 853-858 (1974).

Satterfield, C.N. and Huff, G.A., Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor," J. Catal. 73, 187-197 (1982).

Schlesinger, M.D., Crowell, J.H., Leva, M., and Storch, H.H., "Fischer-Tropsch Synthesis in Slurry Phase", Ind. and Eng. Chem., 43, 1474-1479 (1951)

Schulz, H., "Selectivity of the Fischer-Tropsch CO-Hydrogenation" in Coal: Phoenix of the 80's - Proceedings 64th CIC Coal Symposium (A.M. Al Tawell, Ed.), 1982, 486-493.

Schulz, G.V., "Uber die Beziehung Zwischen Reaktionsgeschwindigkert und Zusammensetzung des Reactionsproduktes bei Makropolymerisation Svovgangen" Z. Phy. Chem. 30, 379-398 (1935).

Schulz, H., and El Deen, A.Z., "New Concepts and Results Concerning the Mechanism of Carbon Monoxide Hydrogenation. I. Organic Oxygen Compounds Produced During Medium-Pressure Synthesis with Iron Catalysts," Fuel Process Technology 1, 31-44 (1977).

Schulz, H., and El Deen, A.Z., "New Concepts and Results Concerning the Mechanism of Carbon Monoxide Hydrogenation. II. Evolution of Reaction Steps on the Basis of Detailed Product Composition and Other Data," IBID 1, 45-56 (1977).

Sexton, B.A., and Somorjai, G.A., "The Hydrogenation of CO and CO_2 Over Polycrystalline Rhodium: Correlation of Surface Composition, Kinetics and Product Distribution", J. Catal., 46, 167-189 (1978).

Sherwin, M., and Blum, D., "Liquid-Phase Methanol, Chem Systems, Inc., EPRI AF-1291, Res. Project 317-2, Final Report, December, 1978.

Smith, D.F., Hawk, C.O., and Golden, P.L., "The Mechanism of the Formation of Higher Hydrocarbons from Water Gas", J. Am. Chem. Soc., 52, 3221-3232 (1930).

Somorjai, G.A., "Catalytic Hydrogenation of Carbon Monoxide," in Chemistry in Two Dimensional Surfaces, Cornell University Press, Ithaca, New York, 1981, pp. 514-543.

Sternberg, H.W., and Wender, I., "Metal Catalysts and Related Compounds as Catalytic Intermediates in Organic Synthesis", Spec. Publ. - Chem. Soc. (London) No. 13, 1959.

Storch, H.H., Golumbic, N., and Anderson, R.B., "The Fischer-Tropsch and Related Synthesis", John Wiley & Sons, New York, New York, 1951.

Stull, D.R., Westrum, E.F., Jr. and Sinke, G.C., "The Chemical Thermodynamics of Organic Compounds," Wiley & sons, New York, New York, 1969.

Vannice, M.A., "The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures Over Group VIII Metals - 1. The Specific Activities and Product Distribution of Supported Metals", J. Catal. 37, 449-461 (1975).

Vannice, M.A., "The Catalytic Synthesis of Hydrocarbons from CO and H_2", Catal. Rev. - Sci. Eng. 14, 153-191 (1976).

Vannice, M.A., "The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures Over Group VII Metals - V. The Catalytic Behavior of Silica-Supported Metals", J. Catal., 50, 228-236 (1977).

Wagmann, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., and Nuttall, R.L., "The NBS Tables of Chemical Thermodynamic Properties Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units", J. Of Physical and Chemical Reference Data, 11, 1982 (Supplement No. 2) pp. 84 and 95.

Weitkamp, A.W., and Frye, C.G., "Products of Hydrogenation of Carbon Monoxide-Relation of Product Composition to Reaction Mechanism" Ind. Eng. Chem., 45, 363-367 (1953).

Wender, I., and Sternberg, H.W., "Homogeneous Metal Carbonyl Reactions and their Relation to Heterogeneous Catalysis" Adv. Catal. 9, 594-608 (1957).

Wender, I., Friedman, S., Steiner, W.A., and Anderson, R.B., "Exchange of Carbonyl Groups in Anhydrides with CO. Mechanism of CO Transfer to Organic Molecules via Transition Metals", Chem. Ind. (London), 1964 (1958).

Wentrcek, P.R., Wood, W.J., and Wise, H., "The Role of Surface Carbon in Catalytic Methanation", J. Catal. 43, 363-366 (1976).