typically utilized cobalt-thoria-kieselguhr catalysts in packed bed reactors, operated at atmospheric or medium (ca. 10 atmospheres) pressure; staged, internally cooled reactors were required to control the heat of reaction (54).

The German plants closed at the end of World War II, but Fischer-Tropsch research continued in Germany, in Britain at the Fuel Research Station, and the United States at the U.S. Bureau of Mines. Emphasis was placed on the refinement of iron catalysts, and the development of reactors designed for improved heat removal (1,2,21, 28,54).

Interest in synthetic fuels decreased rapidly as inexpensive petroleum became available in the 1950's. An exception was the start up in 1955 of a commercial Fischer-Tropsch plant in South Africa, operated by South African Synthetic Oil, Ltd. (SASOL) (20). Two types of reactors were used at SASOL: fixed bed ARGE reactors, designed by Ruhrchemie in West Germany, for producing paraffinic waxes, and entrained bed Synthol reactors, designed by M. W. Kellogg in New Jersey, for producing gasoline boiling range products (2,19,20). The products were upgraded and blended as necessary to manufacture high grade gasoline and diesel fuels (20).

The most recent surge of Fischer-Tropsch research activity followed the 1973 Middle East oil crisis. Since then a great deal of work has been done with ruthenium catalysts, as well as catalysts based on other non-traditional Group VIII metals, manganese, molybdenum, and tungsten (2,13,40). Novel supports for Fischer-Tropsch catalysts, or for product upgrading, such as Mobil's ZSM-5 zeolite, have also been investigated (38,39,4). SASOL has built two additional Fischer-Tropsch plants, each employing only Synthol reactors. The second SASOL plant came on line in 1980, the third in 1984; the original plant is still in operation (19). In addition to liquid fuel production, there has also been a great deal of commercial interest in producing chemical feedstocks, primarily gaseous olefins, from coal-derived synthesis gas via Fischer-Tropsch (6,27,41,52).

2. Reactions and Thermodynamics.

The Fischer-Tropsch synthesis can be represented as a set of reactions which utilize a variety of reactants to form a spectrum of products. Carbon monoxide and hydrogen are the typical reactants, and over certain catalysts, ethylene can also be an important participant

(58). Carbon dioxide may also be a reactant, and it is thermodynamically feasible to incorporate methane into synthesis products. Usually, both carbon dioxide and methane are considered to be net products of the synthesis. Higher olefins may also participate as reactants to a limited degree (2,44).

The major hydrocarbon products of the Fischer-Tropsch synthesis are normal paraffins and alpha-olefins. Smaller quantities of branched hydrocarbons are usually observed, as are olefins with interior double bonds, and the production of aromatics is also possible (19). Ketones, aldehydes, and organic acids may also be formed, although water and alcohols are the primary oxygen-containing liquid products of the synthesis (2,19). The equations for paraffin and olefin production from carbon monoxide and hydrogen are:

$$(2 + 1/n)H_2 + CO = (1/n)C_nH_{2n+2} + H_2O \qquad [1]$$

$$2H_2 + CO = (1/n)C_nH_{2n} + H_2O \qquad [2]$$

By adding the water-gas shift reaction [3] to reactions [1] and [2], carbon dioxide can replace water as a product:

$$CO + H_2O = CO_2 + H_2 \qquad [3]$$

$$(1 + 1/n)H_2 + 2CO = (1/n)C_nH_{2n+2} + CO_2 \qquad [4]$$

$$H_2 + 2CO = (1/n)C_nH_{2n} + CO_2 \qquad [5]$$

In general, carbon dioxide has a more negative Gibbs free energy of formation than does water; consequently, any reaction with carbon dioxide as a product is favored thermodynamically over an analogous reaction which has water as a product. The free energies of reactions [1] and [4] at 227°C are compared in Figure 3. Similarly, reactions which produce paraffinic product have more negative free energy changes than do corresponding reactions which produce olefinic product, as shown in Figure 4. The effect is more pronounced for lower molecular weight products.

It is also possible to incorporate olefins into the synthesis product to produce higher olefins:

$$C_nH_{2n} + CO + 2H_2 = C_{n+1}H_{2n+2} + H_2O \qquad [6]$$

$$C_nH_{2n} + 2CO + H_2 = C_{n+1}H_{2n+2} + CO_2 \qquad [7]$$

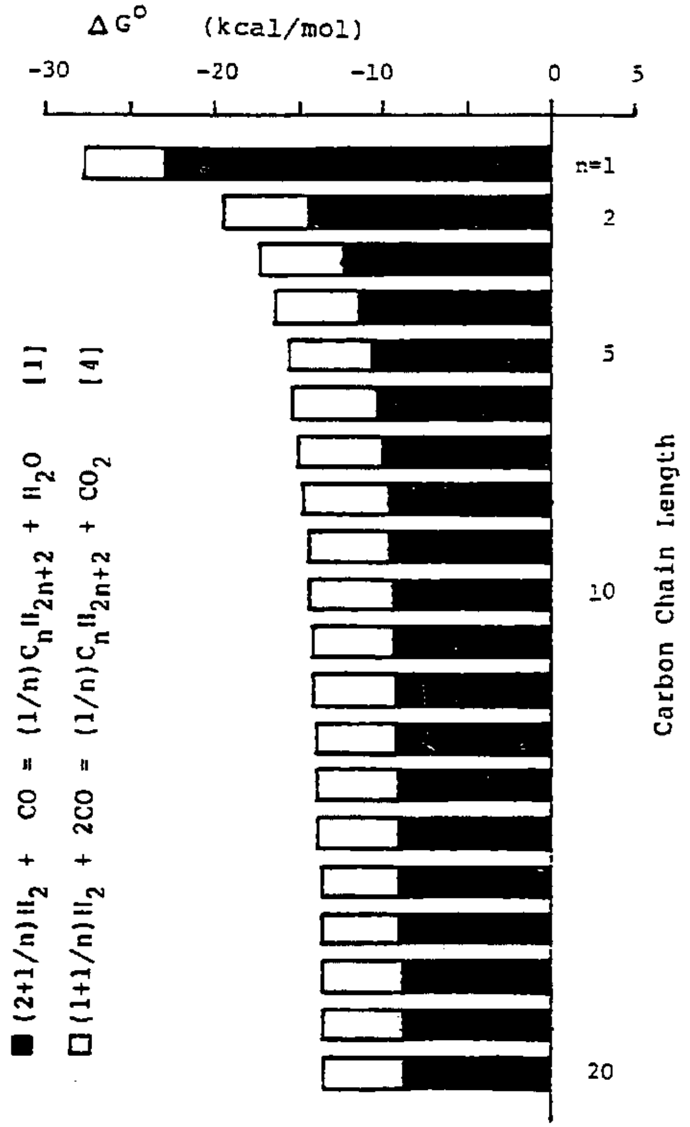

Figure 3. Comparison of Gibbs free energy of reaction with water (■) and carbon dioxide (☐) as products. T = 227°C (45,55).

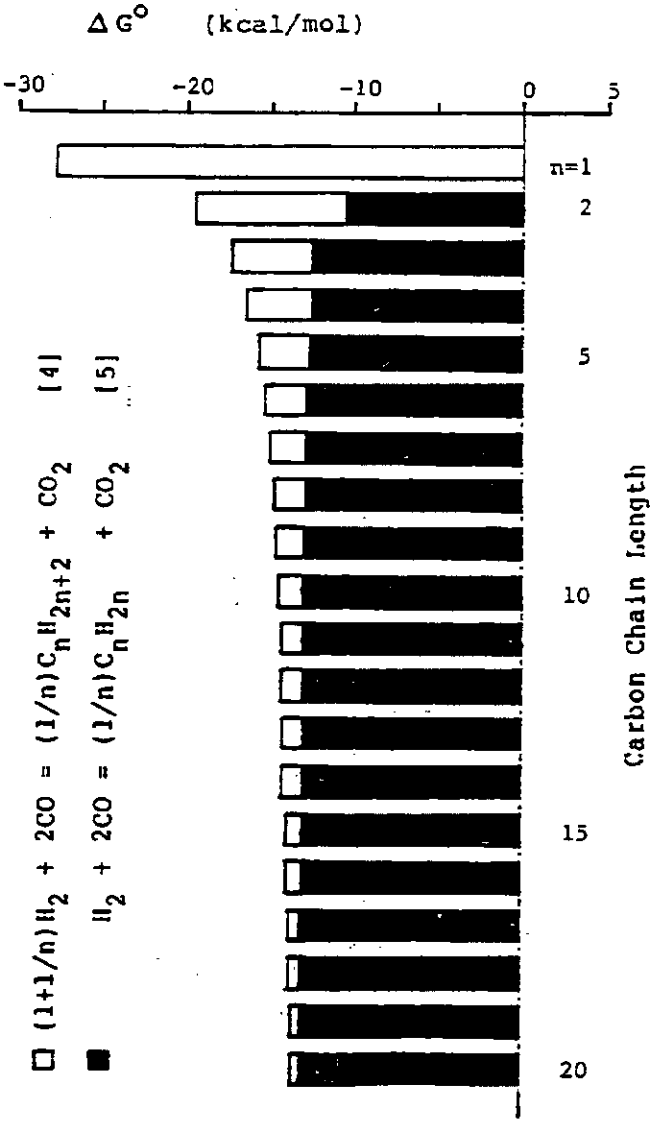

Figure 4. Comparison of Gibbs free energy of reaction for reactions with olefinic (■) and paraffinic (□) product. T = 227°C (45,55).

A similar pair of olefin incorporation reactions may be written with paraffins as the hydrocarbon product. A second method of utilizing olefins is through the hydropolymerization of ethylene:

$$(1/2)\ (n - 1)C_2H_4 + CO + 2H_2 = C_nH_{2n} + H_2O \qquad [8]$$

Reactions [6], [7], and [8] have been found to occur most readily over cobalt catalysts when the feed gas contains ethylene; over iron catalysts, the reactions proceed at insignificant rates (1,58).

Under typical synthesis conditions, the major liquid phase oxygen-containing products besides water are the primary alcohols:

$$CO + 2H_2 = (1/n)C_nH_{2n+2}O + (1 - 1/n)H_2O \qquad [9]$$

$$CO + (n + 1)/(2n - 1)H_2 = 1/(2n - 1)C_nH_{2n+2}O + (n - 1)/(2n - 1)CO_2 \qquad [10]$$

Pressures above 100 atmospheres and specialized catalysts are required to produce significant quantities of oxygenated hydrocarbons (2,54).

The reactions which utilize only hydrogen and carbon monoxide, the principal Fischer-Tropsch reactants, are highly exothermic, as shown in Table 3. Reactions incorporating olefins are less exothermic. All of the reactions remain exothermic over a wide range of temperatures, Figure 5, and they become more exothermic as the chain length of the product increases. Adequate heat removal is one of the most important considerations in Fischer-Tropsch reactor design (2,28,57).

Under most conditions, carbon formation is possible via the Boudouard reaction [11], or coking:

$$2CO = C(s) + CO_2 \qquad [11]$$

Carbon deposition, Figure 6, is enhance by low H_2/CO feed ratios, and high temperatures and pressures. Carbon formation within the catalyst may decrease activity by blocking pores and/or the disintegration of the catalyst pellet (48). In slurry reactors, finely divided filamentous carbon in the slurry leads to poor mass transfer between the gas and liquid phases (11,21).

Table 3. Heats of reaction and Gibbs free energy change for 8 carbon chain length Fischer-Tropsch products at 227°C (45,55).

		kcal/mol	
	REACTION	$-H^{\circ}_{500}$	$-G^{\circ}_{500}$
1*	$17H_2 + 8CO = C_8H_{18} + 8H_2O$	311.3	79.34
2*	$16H_2 + 8CO = C_8H_{16} + 8H_2O$	280.6	64.67
4*	$9H_2 + 16CO = C_8H_{18} + 8CO_2$	387.4	118.1
5*	$8H_2 + 16CO = C_8H_{16} + 8CO_2$	356.7	103.4
6*	$2H_2 + CO + C_7H_{14} = C_8H_{16} + H_2O$	37.49	8.29
7*	$H_2 + 2CO + C_7H_{14} = C_8H_{16} + CO_2$	47.00	13.13
8*	$2H_2 + CO + (7/2)C_2H_4 = C_8H_{16} + H_2O$	95.76	25.86
9*	$16H_2 + 8CO = C_8H_{18}O + 7H_2O$	288.7	56.52
10*	$9H_2 + 15CO = C_8H_{18}O + 7CO_2$	355.2	90.40

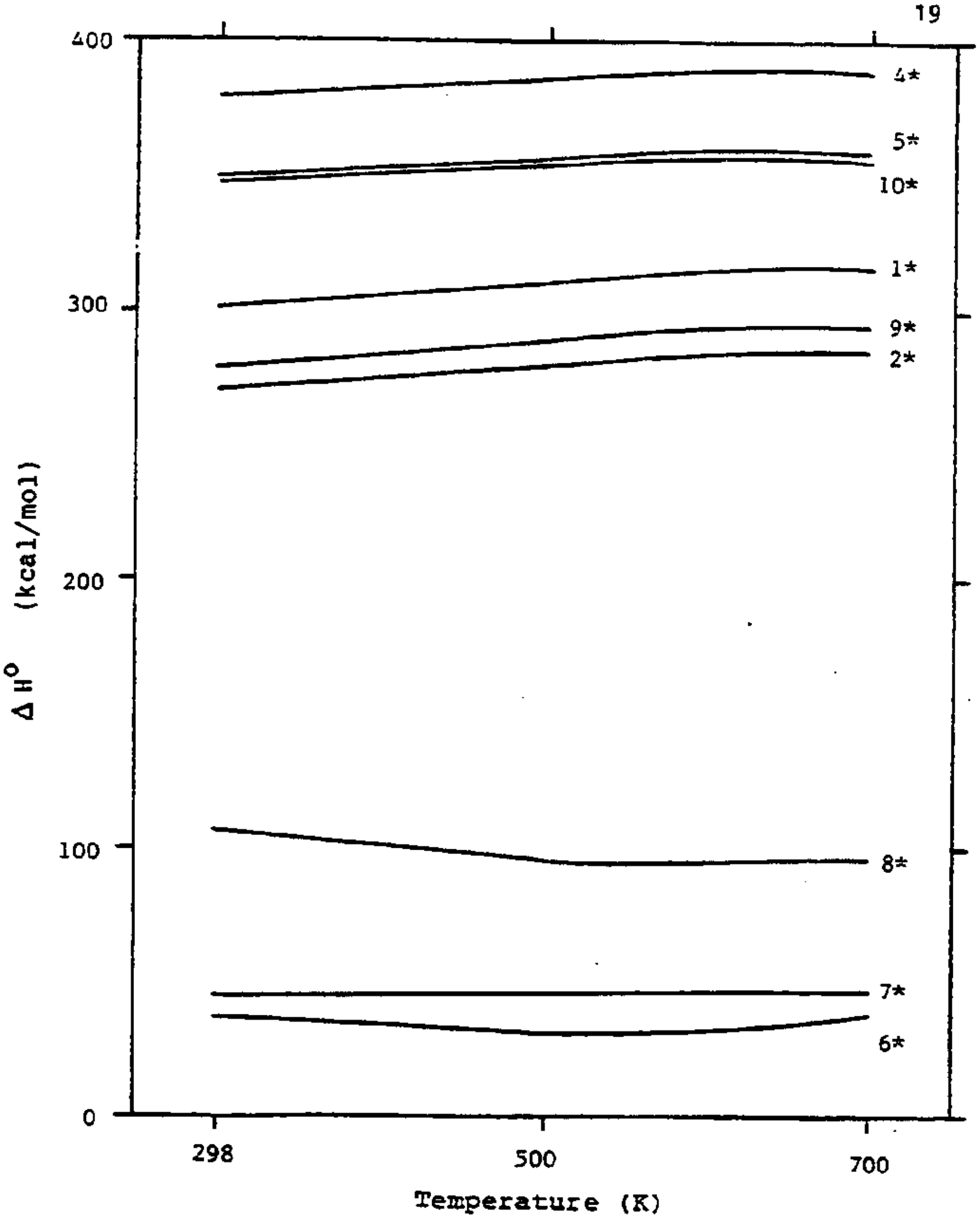

Figure 5. Heats of reaction as a function of temperature for 8 carbon chain length products (45,55).

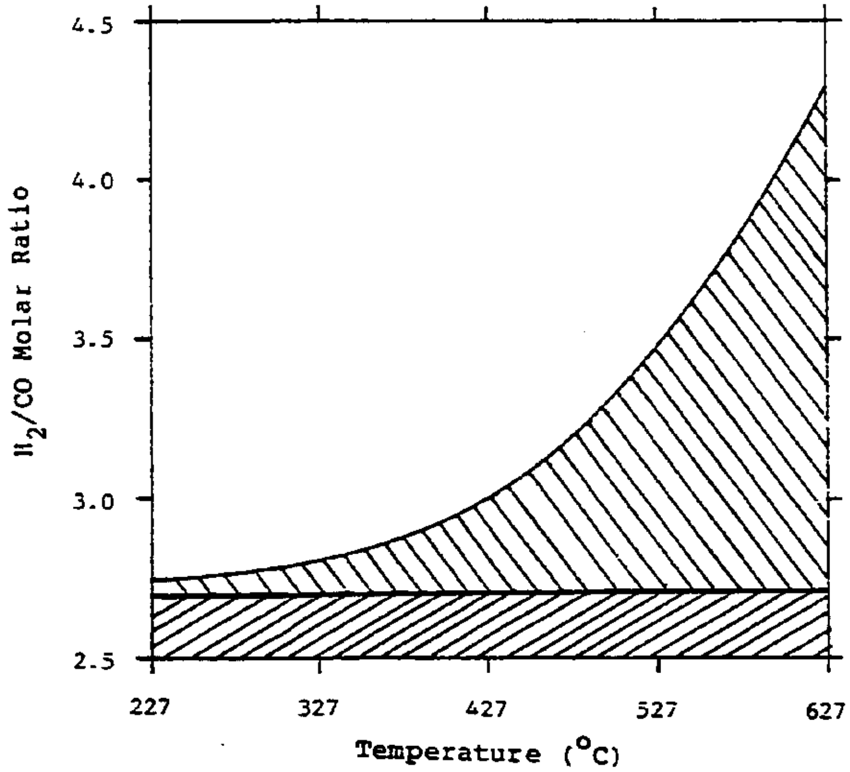

Figure 6. Carbon deposition boundaries for the H-C-O system. Upper curve: 25 atm. Lower curve: 1 atm (32).

3. Hydrocarbon Product Distributions.

The primary products of interest in the Fischer-Tropsch synthesis are paraffins and olefins in the range of C_1 through C_{20}. The product distribution in this range can often be represented by the Schulz-Flory equation (24).

$$m_p = (\ln^2\alpha)P\alpha^P \qquad [12]$$

or in linearized form:

$$\log(m_p/P) = \log(\ln^2\alpha) + P\log(\alpha) \qquad [13]$$

where m_p is the weight fraction of product containing P carbon atoms in the chain, and α is the probability of chain growth. The value of α depends on the catalyst and operating conditions.

Deviations from the Shulz-Flory equation for Fischer-Tropsch products usually occur for the lower molecular weight products. This is caused by the incorporation of lower olefins into the synthesis product, their reduction to methane, and to a lesser degree, the hydrocracking of higher hydrocarbons (25,26). Distributions using two chain growth probabilities instead of one have been proposed to characterize the full range of Fischer-Tropsch products (25).

A number of thermodynamic equilibrium studies have been reported in the literature. Anderson (2) studied equilibrium yields as a function of temperature, pressure, and the hydrogen/carbon monoxide feed ratio. In all cases, methane was the predominant product. Methane yields increased with temperature and the hydrogen/carbon monoxide ratio, and decreased with pressure. As the methane yield decreased, the yields of higher hydrocarbons increased.

Campbell (9) performed a similar study using a feed containing hydrogen, carbon monoxide, and ethylene, which is typical of biomass-derived pyrolysis gas. His conclusions agreed with Anderson: methane yields were enhanced by higher temperatures and subdued by higher pressures. Methane was again the predominant hydrocarbon product.

Since methane is usually considered a less desirable product than higher hydrocarbons, favorable product distributions must be obtained using selective catalysts. Also, the selectivity of conventional Fischer-Tropsch catalysts is more likely to be limited by the Schulz-Flory distribution, rather than by equilibrium. Highly selective metal cluster catalysts are also able to exceed the Schulz-Flory maximums for products in the gasoline and diesel fuel range (7).

4. Catalysts.

Iron and cobalt are the metals most often used as catalysts in the Fischer-Tropsch synthesis, although all of the Group-VIII metals display some Fischer-Tropsch activity. The specific activity (based on turnover number) of the Group-VIII metals is the highest for ruthenium and decreases in the order: Ru>Fe>Ni>Co> Rh>Pd>Pt>Ir (56). Only the first four members of this series have been seriously considered as candidates for Fischer-Tropsch catalysts; even nickel is believed to have too high a methanation activity for a successful Fischer-Tropsch catalyst.

Iron catalysts are usually made by fusing iron oxide, or by precipitating aqueous solutions of iron salts, with or without a support. The precipitation of ferric nitrate, mixtures of ferric and ferrous nitrates, or mixtures of ferric and ferrous chlorides lead to catalysts with high activities. Catalysts made with ferrous nitrate, ferrous chloride, or ferric chloride have low to moderate activities (1). On a weight basis, a properly prepared, precipitated catalyst is generally more active than a fused catalyst, while the fused catalyst is stronger physically than the precipitated catalyst. SASOL uses fused iron catalysts in the entrained bed Synthol reactors, where catalyst attrition is high (19).

Precipitated iron catalysts are often unsupported. When supported, kieselguhr and alumina are often used as carriers. Silica gel, carbon, magnesium oxide, calcium oxide, and dolomite have also been used, with varying success (33,54). Supported catalysts are made either by precipitating the iron from an aqueous salt solution/ support slurry, or by mixing the support with the iron precipitate prior to washing. The presence of a carrier is known to affect the performance of Fischer-Tropsch catalysts. Kieselguhr supported catalysts tend to produce lighter, less oxygenated products than do the wax producing, precipitated, unsupported catalysts (1,2,54). Kolbel also reported that calcium oxide increased the catalyst's activity, and that magnesium oxide seemed to inhibit the formation of carbon (54).

Alkali, primarily potassium, are the most common promoters for iron based Fischer-Tropsch catalysts. Alkali promotion both increases catalyst activity and alters their selectivity towards higher hydrocarbons. Promotion levels are typically less than 1% by weight of the iron present. Kieselguhr and other silica based supports tend to neutralize the alkali, requiring excessive promotion to achieve any activity or selectivity changes (54). The presence of alkali also promotes the formation of carbon, and the water-gas shift reaction (7).

Copper is another widely used iron catalyst promoter, although its purpose is to facilitate the reduction of the iron oxide to metal. Concentrations of up to 20% copper by weight have been used without altering the activity of the catalyst (1). Small amounts of magnesium oxide and calcium oxide have been added to packed bed reactor catalysts to improve catalyst strength and inhibit carbon formation.

Under synthesis conditions, iron catalysts are rapidly carbided. Cementite, Hagg carbide, and hexagonal carbide are formed, and all have Fischer-Tropsch activity, as does metallic iron. Pre-carbided iron catalysts have higher initial activities and longer lifetimes than do uncarbided catalysts (2). Raupp and Delgass (42), using in-situ Mossbauer spectroscopy, found that conversions, paraffin/olefin ratios, and the

C_2/C_1 ratios all increased directly with the extent of the carbiding on an alumina supported iron catalyst. Cobalt, rutheium, and nickel will not form carbides under normal Fischer-Tropsch synthesis conditions.

Cobalt based catalysts have been used extensively at ASU for pyrolysis gas liquefaction. Cobalt catalysts are usually prepared via impregnation of a support, or by precipitation. Since cobalt is fairly expensive, these catalysts are usually supported.

The carriers typically used for cobalt are kieselguhr or alumina. Kieselguhr was used exclusively in the German commercial plants, because the Germans felt that this support uniquely enhanced the activity and product selectivity of cobalt. The source and pretreatment (i.e., calcination, acid extractions) of the kieselguhrs have been found to have a profound influence on the performance of the catalyst; these factors are not important for iron/kieselguhr catalysts (1).

Since WWII, iron catalysts have been more popular than cobalt catalysts, because iron is widely available and less expensive than cobalt. Iron catalysts produce a wider spectrum of products than cobalt, which is useful if the selectivity can be altered to suit individual needs (19,20). Cobalt catalysts tend towards a lighter, less oxygenated product than does iron. Iron catalysts, particularly when alkali promoted, are better shift catalysts than cobalt catalysts, which is advantageous for carbon monoxide rich feeds (42).

A major advantage of cobalt over iron is its ability to incorporate olefins into synthesis product. High concentrations of ethylene in the feed gas leads to high liquid product yields, when a cobalt catalyst is used (58). ^{14}C tracer studies by Pichler and Schulz (2) compared olefin incorporation over iron and cobalt catalysts. Under similar conditions, cobalt incorporated about 30% of the available ethylene and propylene into the synthesis product, while iron incorporated only 10% of the ethylene and 1% of the propylene. Although ethylene was observed to polymerize to a small extent via Equation [8], the predominant pathway appeared to be the olefin incorporation reactions [6] and [7].

Cobalt is also a much better cracking catalyst than is iron, which is disadvantageous for their use in slurry reactors. In another ^{14}C tracer study by Kolbel (26), methane formation by the hydrocracking of slurry waxes under Fischer-Tropsch synthesis conditions was studied. Even at temperatures above 300°C, less than 3% of the methane formed over iron catalysts was due to hydrocracking. This percentage was largely independent of temperature. Hydrocracking over cobalt catalysts was found to be temperature dependent. At 214°C, cracking accounted for 6% of the methane formed; above 214°C, methane formation via hydrocracking became too extensive to be measured by the methods used by Kolbel.

5. Reactors.

Entrained bed and packed bed reactors have both been used in commercial Fischer-Tropsch processes. Conventional packed bed reactors are no longer considered practical for large scale systems because of the difficulty in providing adequate heat transfer. For example, the packed bed reactors used in Germany had to be designed such that catalyst was no further than 5-mm from a cooling surface (1). Tube wall reactors, where catalyst is flame-sprayed on the tube side of heat exchangers, have been developed at the Pittsburgh Energy Technology Center (5). Although these reactors are able to control the heat of reaction, large surface areas are required to achieve acceptable gas conversions.

Entrained bed reactors have been used at SASOL for 30 years. They are designed and operated to produce mainly gasoline boiling range products (19). Fluidized beds, using cobalt based catalysts, have been used successfully at ASU for biomass-derived pyrolysis gas liquefaction to liquid fuels (31).

There are two types of three-phase reactors: oil-recirculation reactors and slurry reactors. Oil-recirculation reactors were developed by the U.S. Bureau of Mines in the 1950's (54). The pelleted catalyst in these reactors is fluidized by a recirculating flow of liquid oil. Slurry reactors are similar, except that the catalyst is finely divided. The catalyst is kept suspended in the liquid by the gas flow through the reactor; the liquid phase is usually, but not necessarily, stationary (28).

The estimated costs and performance of commercial scale entrained bed, tube wall, slurry, and oil-recirculation reactor systems are compared in Figure 7 (49). The major advantage to the slurry system is that it gives gasoline and diesel yields similar to the other systems, at lower investment and catalyst costs. The low investment costs can be attributed to the uncomplicated construction required of the slurry reactors.