DOE/PC/89854--T4

DOE/PC/89854--T4

DE92 011423

TECHNOLOGY REPORT
INDIRECT COAL LIQUEFACTION
FISCHER-TROPSCH SYNTHESIS
FOR
U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
FOR

DESIGN OF GENERIC

COAL CONVERSION FACILITIES

NO. DE-AC22-91PC89854

Prepared by

THE M. W. KELLOGG COMPANY

HOUSTON, TEXAS

Job 7508

OCTOBER 1991

TABLE OF CONTENTS

TABLE OF CONTENTS

TECHNOLOGY REVIEW
INDIRECT COAL LIQUEFACTION
FISCHER-TROPSCH SYNTHESIS

1.0 INTRODUCTION:

A comprehensive review of Fischer-Tropsch (F-T) technology, including fixed, fluidized, and bubble column reactors, was undertaken in order to develop an information base before initiating the design of the Fischer-Tropsch indirect liquefaction PDU as a part of the Generic Coal Conversion Facilities to be built at the Pittsburgh Energy Technology Center (PETC). The pilot plant will include a fixed bed and a slurry bubble column reactor for the F-T mode of operation.

The review encompasses current status of both these technologies, their key variables, catalyst development, future directions, and potential improvement areas. However, more emphasis has been placed on the slurry bubble column reactor since this route is likely to be the preferred technology for commercialization, offering process advantages and, therefore, better economics than fixed and fluidized bed approaches.

Large scale operations of fixed and fluidized bed F-T process have been in practice in South Africa since 1955. Also, a 11.5 tons/day demonstration plant, using a slurry bubble column reactor (5 ft. diameter x 28 ft. high) was successfully operated in Germany (Rheinpreussen Koppers) in 1950's. The developments in South Africa and in Germany were reviewed as they provide valuable insight and understanding of the process and technology.

Finally, as a part of the literature survey, contacts were established with a number of individuals, both in universities and private organizations, who are pursuing one or more important aspects of this technology. Such contacts provided useful insight and ideas that will be incorporated in the pilot plant design.

2.0 FISCHER TROPSCH REACTION

2.1 Feedstocks and Stoichiometry

The Fischer-Tropsch (F-T) synthesis is a catalytic hydrogenation process that produces saturated and unsaturated compounds of the homologous hydrocarbon series by using a mixture of synthesis gas containing carbon monoxide (CO) and hydrogen (H_2). The synthesis process can be described by two basic reactions: (1) hydrogenation of CO, and, (2) water-gas shift reaction.

(1) $CO + 2H_2 = (-CH_2-) + H_2O$

(2) $CO + H_2O = CO_2 + H_2$

The overall reaction is represented as:

(3) $2CO + H_2 = (-CH_2-) + CO_2$

The first reaction preferentially takes place on cobalt and nickel catalysts, the second and the third reactions on iron-based catalysts. The use of Co and Ni catalysts is desirable in cases where the syngas contains a high H_2/CO ratio. If the H_2/CO ratio in the syngas is low, then the water-gas shift reaction is desirable. In such a case Fe-based catalysts are preferred for the Fischer-Tropsch (F-T) reaction. Indeed, Withers et al. (1987) at Air Products have reported that for Co-based catalysts, H_2/CO usage ratio is almost always close to 2. On the other hand, Bukur et al. (1990) has observed with iron-based commercial Ruhrchemie LP 33/81 catalysts that the H_2/CO usage ratio varies between 0.56 to 0.77 depending upon operating conditions. Thus depending on the syngas composition, the appropriate catalyst and the reaction conditions can be chosen for maximizing the yields of the desired product.

In practice, however, which stoichiometry, (1) or (3), is of interest depends upon the gasifier that generates CO and H_2. The ratio of H_2/CO obtained from the gasifiers should match the ratio at which these gases are consumed. Some of the

advanced gasifiers (Shell, Texaco, Koppers Totzek, KRW) produce H_2/CO at a ratio of 0.5 to 0.67. Therefore, in recent years, the reaction (3) has been of great interest. A synthesis gas with a relatively high CO content (low H_2/CO ratio) can lead to the Boudouard reaction:

(4) $2CO = CO_2 + C$

Deposition of carbon on the catalyst particle is not desirable as it leads to catalyst deactivation. Gas phase reactors are most susceptible to carbon deposition on catalyst surface. In a slurry reactor any carbon formed would potentially disperse with the slurry instead of depositing onto the catalyst surface. Therefore for a low ratio of H_2/CO synthesis gas, slurry reactors offers an important advantage over gas phase reactors. Thus, when considered in conjunction with the modern gasifiers as the source of syngas, the slurry phase reactor has much appeal for F-T synthesis.

2.2 Product Distribution - Fischer-Tropsch Synthesis Products

F-T synthesis is generally non-selective in that it usually produces a spectrum of products, although one group of hydrocarbons or another can be maximized by an appropriate choice of catalysts and operating conditions (see Section 7.2.2). For example, the fluidized bed reactors at Sasol, operating at much higher temperatures than fixed bed reactors, maximize gasoline yields, while the fixed-bed process produces predominantly diesel and hydrocarbon waxes. High temperature operations, however, create a penalty due to production of more CH_4 than the fixed-bed operations.

The final processing or refining of gasoline range F-T products is rather simple. The light olefins can be oligomerized for high-quality gasoline. The diesel fraction is of excellent quality and required little upgrading. Diesel yields can be optimized by catalytic hydrocracking or by other processes applied to wax produced in the synthesis. Mobil has reported use of its ZSM-5 catalyst for upgrading F-T products into high-quality gasoline in a single step (Kuo, 1985).

3.0 REACTOR TYPES

The Fischer-Tropsch reactions are highly exothermic (2450 to 3050 kJ per cubic meter of syngas converted) and represents about 20 to 25% of the heat of combustion of feed. Since the equilibrium dictates the conversions, F-T reactions are favored at low temperatures, below 350°C. The challenge in the F-T reactor selection and design is to remove the large amount of heat and to maximize the yields of the desired product. In F-T synthesis reactors, internal coils are generally used to remove the reaction heat. The F-T synthesis can be carried out in gas phase or liquid phase reactor systems. Gas phase reactor systems, such as fixed bed, entrained beds and fluidized beds, have been demonstrated at commercial scale [Dry, 1981 and Geertsema, 1990]. Liquid phase reactor concept, popularly referred to as slurry phase reactors, has also been proposed and demonstrated [Kolbel and Ralek, 1980].

3.1 Fixed Bed Reactors

Fixed bed reactors have been demonstrated on industrial scale at Sasol and is referred to as the ARGE process. The ARGE process was developed by Ruhrchemie-Lurgi [Bussemeier, et al., 1985]. The development of the ARGE reactor was preceded by the demonstration of lamella reactors. The lamella reactor was rectangular and the reaction chamber occupied by a bundle of 630 tubes and 555 vertical iron plates (see Figure 3.1). The iron plates were arranged in parallel to each other at a distance of 7 mm. The plates served to transfer the heat to a system of horizontal cooling tubes in which pressurized water was circulated. The uniform filling with catalyst of the narrow interspaces of the lamella bundle demanded considerable care and expense. The removal of spent catalyst was also found to be difficult. Heat removal was found to be unsatisfactory despite the large cooling surface (4 m^2 per converted Nm^3 syngas).

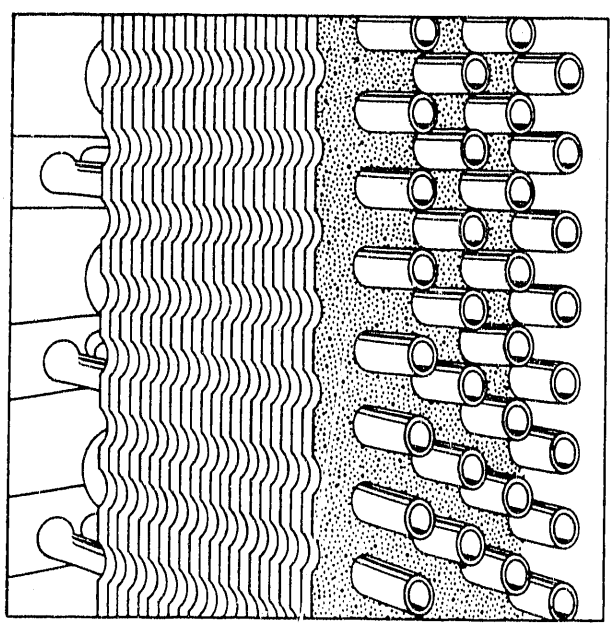

FIGURE 3.1: Section of lamella bundle [Bussemeier, et al., 1985].

An essential improvement in the removal of heat, in comparison of the lamella reactor was the development of the twin tube reactors [Bussemeier et al., 1986]. The twin tube reactor was built for a pressure of 12 atm and temperatures below 220°C. The catalyst was placed in the space (a distance of 10 mm) between the concentric tubes. The space outside the outer tube (44 mm diameter) and inside the inner tube (24 mm diameter) was filled with pressurized water for heat removal. The reactor contained 2044 pairs of tubes (4.5 m in length), the total catalyst volume was 10 m^3. Although the heat removal was improved, the fresh feed space velocity was still low at about 100 hr^{-1} (Nm^3 gas per m^3 catalyst per hour). On the basis of these results, intensified efforts at Ruhrchemie-Lurgi concerning heat removal problem lead to the development of the ARGE high capacity reactor. The ARGE reactor has been discussed in detail in section 4.0. One of the major significant achievements has been to be able to operate at high space velocity about 500 hr^{-1}, compared to about 100 hr^{-1} for earlier lamella and twin tubular reactors. This was achieved by the use of recycle gas which greatly improved the heat exchange characteristics of the reactor. The data from various fixed bed reactors is summarized in Table 3.1. Operating conditions of several commercial F-T synthesis plants using the gas phase fixed bed process is summarized in Table 3.2.

3.2 Bubble Column Slurry Reactors

Bubble column slurry reactors are suited for the liquid phase F-T synthesis. In the slurry reactor, synthesis gas enters at the bottom of the reactor. It flows upward through a tall catalyst-liquid slurry bed. The gas provides turbulence for keeping the catalyst in suspension. The turbulence also improves gas-liquid contact. The liquid used in slurry reactors should have low vapor pressure at the temperature being used. In F-T the liquid is conveniently a cut from the product spectrum, e.g., a high boiling point wax. The reaction heat is removed by circulating the slurry through external heat exchangers or by heat exchangers immersed directly into the slurry bed. Use of the slurry reaction medium provides uniform temperature in the reactor and good heat exchange capability, when compared with gas phase reactors [Frohning, et al., 1982].

TABLE 3.1. Data from Various Fixed Bed Reactors.
[Frohning, et al., 1982].

	Reactor		
	Lamella	Twin Tubular	Tubular, ARGE Process
Depth of catalyst layer (mm)	7	10	46
Length of catalyst layer (mm)	2500	4550	12000
Operating pressure (bar)	0.3	7–12	20–30
Operating temperature (°C)	180–195	180–215	220–260
Cooling surface [m^2/Nm^3 of converted $CO + H_2$]	4000	3500	230
Fresh gas feed (VVh)	70–100	100–110	500–700
Daily production per m^3 of catalyst (kg C_{2+}) (single stage)	190	210	1250

TABLE 3.2. Operating Conditions of Several Commercial FT Synthesis Plants Using the Gas Phase Fixed Bed Process [Frohning et al., 1982].

Characteristics of Process	Cobalt Normal Pressure Synthesis	Cobalt Medium Pressure Synthesis	Iron Medium Pressure Synthesis	ARGE High Capacity Synthesis
Process conditions				
Pressure (bar)	0.3	7–12	11	23–25
Temperature (°C)	180–195	180–210	190–230	220–250
H_2:CO ratio in fresh gas	2	2	1.25	1.3–2
Recycle:fresh gas ratio	No recycle	Generally no recycle	2	2.5
Number of stages	2	3	2	1–2
Fresh gas charge [$Nm^3/m^3 \cdot h$]	70–100	100–110	100–110	500–700
Type of heat removal	Water-cooled lamellas	Water-cooled twin tube	Water-cooled twin tube	Water-cooled tubes
Catalyst				
Composition (pbw)	100 Co, 8 MgO, 5 ThO_2, 200 kieselguhr	100 Co, 8 MgO, 5 ThO_2, 200 kieselguhr	100 Fe, 5 Cu, 5 K_2O, 25 SiO_2	100 Fe, 5 Cu, 5 K_2O, 25 SiO_2
Lifetime (months)	4–6	6–7	12	9–12
Reactors				
Catalyst charge (m^3)	10	10	10	40
Number of tubes	—	2044	2044	2,052
Dimensions of tubes (height × diameter, in (mm)	—[a]	4450 × 10[b]	4450 × 10[b]	12,000 × 46
Amount of catalyst per tube (l)	—	4.9	4.9	20
Production capacity per reactor (t of C_{2+} per day)	1.9	2.5	2.5	50

[a] Dimensions of reactor: 1500 mm wide, 2500 mm high, 5000 mm long.
[b] Inner tube 21 × 24 mm, outer tube 44 × 48 mm.

The slurry bed has an advantage over the fixed bed in that carbon deposition on the catalyst does not adversely effect its performance. Slurry reactors are operational over a broad temperature range using a low H_2/CO ratio synthesis gas. They also provide flexibility in the product spectrum and achieve high conversions per pass with stoichiometric consumption of the feed-gas components. Consequently there is little need for gas recirculation. The catalyst utilization efficiency ratio is also very high (one) [Kolbel and Ralek, 1980]. Thus the slurry bed reactor is potentially more flexible than the gas phase reactors. Details of the Reinpreussen-Koppers slurry bed demonstration plant has been discussed in detail in Section 5.0.

Van Vuuren (1987) lists the following as major shortcomings of the slurry reactor:

(a) Lower space time yield.

(b) Low octane gasoline is obtained from the slurry reactor. Mostly straight chain hydrocarbon products are obtained which need to be upgraded by isomerization and aromatization reactor using ZSM-5 or equivalent catalyst, to improve the octane value.

(c) Difficulties in separation of catalyst fines from the liquid reactor product.

The Bechtel study [Fox, et al., 1990], reports higher conversion per pass in slurry reactors than in fixed bed reactors. They report 80% conversion per pass for slurry reactors versus 37% for fixed bed reactors. Ultimate conversion of 95% is possible from fixed bed reactors but this requires recycle ratio of 2.34. Fixed bed reactors also require a high H_2/CO ratio compared to slurry reactors which can operate with H_2/CO ratio of as low as 0.6. Further more slurry bed reactors can be operated at higher temperatures because catalyst can be continuously replaced.

3.3 Fluidized Bed Reactors

Following the successful utilization of fluidized beds in catalytic cracking in the petroleum industry this technology was also applied to the F-T synthesis. There are two types of fluidized bed reactors, (a) the bubbling (or fixed) fluidized bed, and, (b) circulating fluidized reactors, which have been used for the F-T synthesis. In the bubbling fluidized bed (FB) reactor, the catalyst bed remains "stationary" in the reactor with gas passing upward through it; and in the circulating fluidized bed (CFB) reactor, the catalyst is entrained by the fast moving gas stream.

The FB reactor units were developed by Hydrocarbon Research and by Standard Oil of Indiana and led to the construction of the Hydrocol demonstration unit at Brownsville in 1950 [Dry, 1981]. The design capacity of the plant was 360,000 tons per year for two reactors. Each reactor had a width of 5 m, a height of 18 m and was loaded with about 200 tons of finely divided iron catalyst. The unit was operated at about 320°C, 27 atm and gas velocities above 20 cm/s were used [Dry, 1981]. The reaction heat was removed by heat exchangers immersed in the fluidized bed. The recycle to fresh gas ratio used was about 1.5 and conversions up to 96% were reported at high fresh feed space velocities (2,000 to 3,000 hr^{-1}). Many difficulties were experienced, the main problem apparently being lack of uniform fluidization of the entire catalyst bed leading to gas by-passing. The unit operated less than 35% of the designed capacity and was shut down in 1957. Based on this work Sasol designed and demonstrated a FB reactor [Dry, 1990]. The fluidized bed reactor has been reported to be cheaper to build and easier to operate than the Synthol CFB reactors. The performance of the fluidized bed reactor has been claimed to have met all the design expectations and it is claimed that conversion and selectivities were similar, and some aspects better, than the Synthol CFB unit [Dry, 1990]. Very little design and operational details are available in the literature on the fluidized bed at Sasol. More recent information indicates that development of FB by Sasol has been discontinued in favor of slurry reactor design.

The circulating fluidized bed reactor is similar to the FCC unit in the petroleum industry. The M.W. Kellogg Company developed the CFB unit and was scaled up from 10 cm ID to the 230 cm ID commercial units at Sasol I. The details on the CFB unit is available in Section 4.0

3.4 Others

Other reactor concepts such as the tube wall reactor and ebullating bed reactor have been proposed and have been studied in lab scale units [Thompson et. al, 1981]. The concept of the tube wall reactor originated at the U.S. Bureau of Mines and was based on the methanation reactors. The concept involved coating catalyst by a flame-spraying technique onto the surface of heat exchanger tubes. Designs differ in the placement of catalyst either on the inside or the outside tube surface. Major advantages claimed for the tube wall reactor are excellent temperature control and near isothermal operation. The main difficulty in applying the tube wall reactor to the F-T synthesis is getting enough catalyst surface area into the reactor. Since F-T catalysts generally exhibit low activity and very little internal surface, a large surface area is required. Although the study by Thompson et al. (1981) indicates a thermal efficiency of about 70% for the plant the process is not economically attractive. Consequently, little efforts have been made to demonstrate this technology.

Another concept for the F-T reactor is the ebullating bed reactor developed at the U.S. Bureau of Mines [Thompson, et al., 1981]. This concept is very similar to the slurry reactors, except the catalyst size used is between 2000 to 4000 microns (compared to 1 to 40 microns for slurry reactors). The larger catalyst size results in low catalyst activity (due to low surface area) and catalyst disintegration. The concept of ebullating bed reactors has been extensively demonstrated for direct coal liquefaction process, but not much work has been reported for F-T synthesis.

3.5 Comparison of Reactors

F-T synthesis have been conducted in various types of reactors, usually under differing process and reaction conditions and using a range of catalysts. Table 3.3 summarizes some characteristic data relating to different reactor technologies [Bussemeier, et al., 1986]. With respect to heat transfer and heat conductivity within the catalyst, fixed bed reactors exhibit disadvantage compared to other reactors. Axial and radial temperature gradients in the fixed bed reactors may result in hot spots, resulting in a partially uncontrolled synthesis, carbon deposition and recrystallization. Hot spots also favor methanation and cause damage to the catalyst. This disadvantage of the fixed bed can be minimized by increased syngas recycle.

Pressure drop at high syngas flow rates is least when using fixed bed reactors. With other reactor systems, the compression energy for the gas recycle is considerably higher. However, in the case of slurry reactors, gas recycle is not desirable as it results in decreasing the partial pressure of the reactants.

To obtain a narrow product spectrum, the reactor should be capable of operation with minimum backmixing. Since backmixing tends to favor consecutive reactions leading to a broad product spectrum. Thus from fixed bed and entrained bed reactors, a narrow product spectrum can be obtained. In slurry reactors the stirring effect of the ascending gas bubbles and in fluidized bed reactors the intense mixing of catalyst and syngas favor consecutive reaction of the primary product leading to a broader product spectrum and also to the formation of long chain hydrocarbons. Thus all processes with gas recycle should use syngas free of all reactive intermediates. When producing long chain saturated hydrocarbons, separation of intermediates or a low recycle ratio are normally disadvantageous for the composition of products.

Catalyst attrition due to mechanical stress is minimal in fixed bed; and to a certain extent, slurry reactors keep the catalyst loss at its lowest. On the other hand, entrained bed reactors and fluidized bed reactors are characterized by friction and

TABLE 3.3. Characteristic Data of Fixed Bed, Fluidized Bed and Entrained Bed and Liquid Phase FT Reactors [Bussemeier et al., 1986].

Characteristic Data	Reactor Type			
	Fixed-Bed	Entrained Fluidized-Bed	Fluidized-Bed	Bubble Reactor
Heat transfer velocity or heat removal through transferring surfaces	Slow	Medium up to high	High	High
Actual heat conductivity within the system	Poor	Good	Good	Good
Maximum reactor diameter as limited by heat removal	~8 cm[a]	No limitation	No limitation	No limitation
Pressure drop at high gas velocity	Small	Medium	High	Medium up to high
Residence time distribution of the gaseous phase	Narrow	Narrow	Broad	Narrow up to medium
Axial mixing of the gas	Small	Small	Large	Small up to medium
Axial mixing of the solid catalyst	None	Small	Large	Large
Catalyst concentration as volume portion of solid $(1 - \epsilon)^b$	0.55–0.7	0.01–0.1	0.3–0.6	Up to a maximum of 0.6
Particle size range of the solids (mm)	1–5	0.01–0.5	0.03–1	0.01–1
Mechanical stress of the solid by shock or friction	None	Great	Great	Small
Catalyst losses	None	2–4% per day due to abrasion	Not recoverable discharge due to abrasion	Small
Regenerability or exchangeability of the catalyst during synthesis	Interruption of synthesis necessary	Without interruption of synthesis by continuous purge and feed		

[a] A small increase seems to be possible if the heat transfer can be increased by higher gas velocities.
[b] ϵ = Relative, solid free particle interspace.

catalyst losses occurring due to abrasion. Regeneration or fresh catalyst loading during synthesis requires interruption of fixed bed reactors, whereas other reactor technologies allow this step to be conducted without interruption, i.e., via continuous purge and feed.

Space time yields is lowest for slurry phase reactors, followed by fixed bed reactors. Fluidized bed reactors have the highest magnitude of the space time yields. Slurry bed is least active due to retardation of the gas diffusion rate by the liquid phase [Dry, 1981].

Dry (1981) reported results of comparative tests on fixed, slurry and fluidized bed reactors and are summarized in Table 3.4. The fluidized and slurry bed tests were carried out in 5 cm ID and 380 cm long tubular reactors surrounded by Dowtherm jackets and topped by wider disengaging sections. The 12 m long 5 cm ID fixed bed reactors were water jacketed for isothermal operation. For each set of tests the same catalyst were used except for particle size differences as required by the reactor systems. The process conditions were also the same for each set.

Cases 1 and 2 show that slurry bed had a somewhat higher conversion than the fixed bed reactor. The smaller catalyst particle sizes in case of the slurry bed compensated for the lower mass of the catalyst charged. The selectivity in the case of the slurry bed shifted towards heavier products. This is consistent with the findings reported by Kolbel and Ralek (1980).

Cases 3 and 4 show that the fluidized bed has a higher activity than the slurry bed. The slurry bed contained less catalyst, but increased catalyst loading does not increase the conversion activity as the actual gas hold-up (and hence the effectiveness of the catalyst gas contact) is adversely effected. The lower activity of the slurry bed is due to lower rate of mass transfer of reactants from gas phase to the catalyst surface sites. There is little difference in the hydrocarbon selectivity spread between the two types of reactor.

TABLE 3.4. Comparison of Fixed, Slurry and Fluidized Bed Reactors [Dry, 1981].

Case	1	2	3	4	5 [b]	6 [b]	7	8	9
Bed type	Fixed	Slurry	Fluidized	Slurry	Fixed Isothermal	Fixed Adiabatic	Fixed Isothermal		Fixed Adiabatic
Catalyst type	Precipitated		Fused		Precipitated ca. 2.5 mm extrudates				
Particle size	ca. 2.5 mm	40–150 μm	<70 μm	<40 μm					
Catalyst load/kg Fe	2.7	0.8	4.2	1.0					
Catalyst bed height/m	3.8	3.8	2.0	3.8	1.6	1.45	1.6		1.45
Bed Inlet Temp./K	496	508	593	593	493	493	493	523	493
Bed Outlet Temp./K	509	511	598	601	496	529	496	528	526
H_2O Exit Pressure/MPa					0.020	0.025	0.039	0.041	0.055
Recycle to Fresh Feed ratio	1.9	1.9	2.0	2.0	25	25	25	25	25
Total Gas Linear Velocity/cm sec^{-1}	36	36	45	45	34	36	34	34	36
Conversion %									
$(CO + H_2)$ or $(CO + CO_2)$	46	49	93	79	75	88	60	75	67
Selectivity/% carbon atom									
CH_4	7	5	12	12					
C_3			14	14					
Gasoline	14	15	43	42	10	15	11	20	16
Hard wax	27	31	0	0	42	27	40	16	30
Rate of Activity decline/ % Conv. per day					0.37	0.78	0.46	0.83	1.6

[b] Cases 5 and 6 simulate the first stage of a multistage (successive catalyst beds) reactor system, while cases 7, 8 and 9 represent the third stage. Deactivation rates for cases to 4 are not given since the catalyst loadings are widely different in these cases.

Cases 5 to 9 simulate individual stages of a multistage reactor in which the fresh feed is split into roughly equal portions and fed separately to each successive catalyst bed. Cases 5 and 6 represent the first stages whereas cases 7, 8 and 9 simulate the third stage. The adiabatic reactor, because of the higher average catalyst temperature, has higher conversion. Also the product selectivity shifts to lower wax levels. When the temperature of the isothermal reactor is increased (case 8) it approximates the behavior of the adiabatic reactor (case 9). A major drawback of the adiabatic reactor is that the rate of activity declines markedly greater than for the isothermal reactor. This is due to the higher operation temperatures.

If the objective is to make high yields of wax, then the isothermal fixed and slurry bed reactors are more suited. Gas phase fluidized bed reactors are unsuited for wax production as the product deposition on the catalyst results in defluidization of the bed. The adiabatic operation of fixed beds is not suited for wax production as high bed temperatures result in rapid catalyst deactivation. If lighter hydrocarbons are desired, the fluidized bed has the highest production rate. Fixed bed reactors cannot operate at high temperatures at which fluidized bed can operate because of carbon deposition at higher temperatures leading to plugging of the fixed beds.

4.0 SOUTH AFRICAN EXPERIENCE IN FIXED AND FLUIDIZED BED TECHNOLOGIES

At the end of World War II all synthetic fuel production in Germany ceased. The only operating Fischer-Tropsch plant is situated in Sasolburg, South Africa, and has been in operation since 1955. Sasol I uses two type of reactors, fixed bed and circulating fluidized bed reactors. The fixed bed reactors produce mainly heavy liquid hydrocarbons and waxes, and the circulating fluidized bed reactors produce predominantly gaseous hydrocarbons and gasoline. The fixed bed reactors were jointly developed by Lurgi and Ruhrchemie and are referred to as the ARGE reactors. When scaled up, the ARGE reactors performed with little trouble. The circulating fluidized bed reactors were scaled directly from a 10 cm ID pilot unit by Kellogg and were the first units built. The performance of circulating fluidized bed was poor for several years. Some process and mechanical modifications including changes in the formulation of the catalyst resulted in a significant improvement in the performance of the fluidized bed reactors. These fluidized bed units are now known as the Sasol Synthol reactors.

The ARGE reactor at Sasol consists of 2050 tubes of 50 mm ID and 12 m long. The tubes are packed with catalyst and each tube contains approximately 20 liters of catalyst [Dry, 1983]. The ARGE reactor system at Sasol is shown in Figure 4.1 [Dry, 1983]. The tubes are immersed in water and the reactor temperature is maintained by controlling the steam pressure. The normal operating pressure is 27 atm and the temperature varies from 220 to 250°C. The Fischer-Tropsch reaction is highly exothermic (about 36 kcal per reacted carbon atom), and the high rate of heat removal from the catalyst particle is ensured by a high gas velocity. Recycle of tail gas has been reported to be desirable to increase both the conversion and the gas velocity [Dry, 1983]. The volume ratio of recycle to fresh feed is typically about 2. The synthesis gas enters at the top of the reactor where it is preheated and then flows through the reactor tubes. A large fraction of the

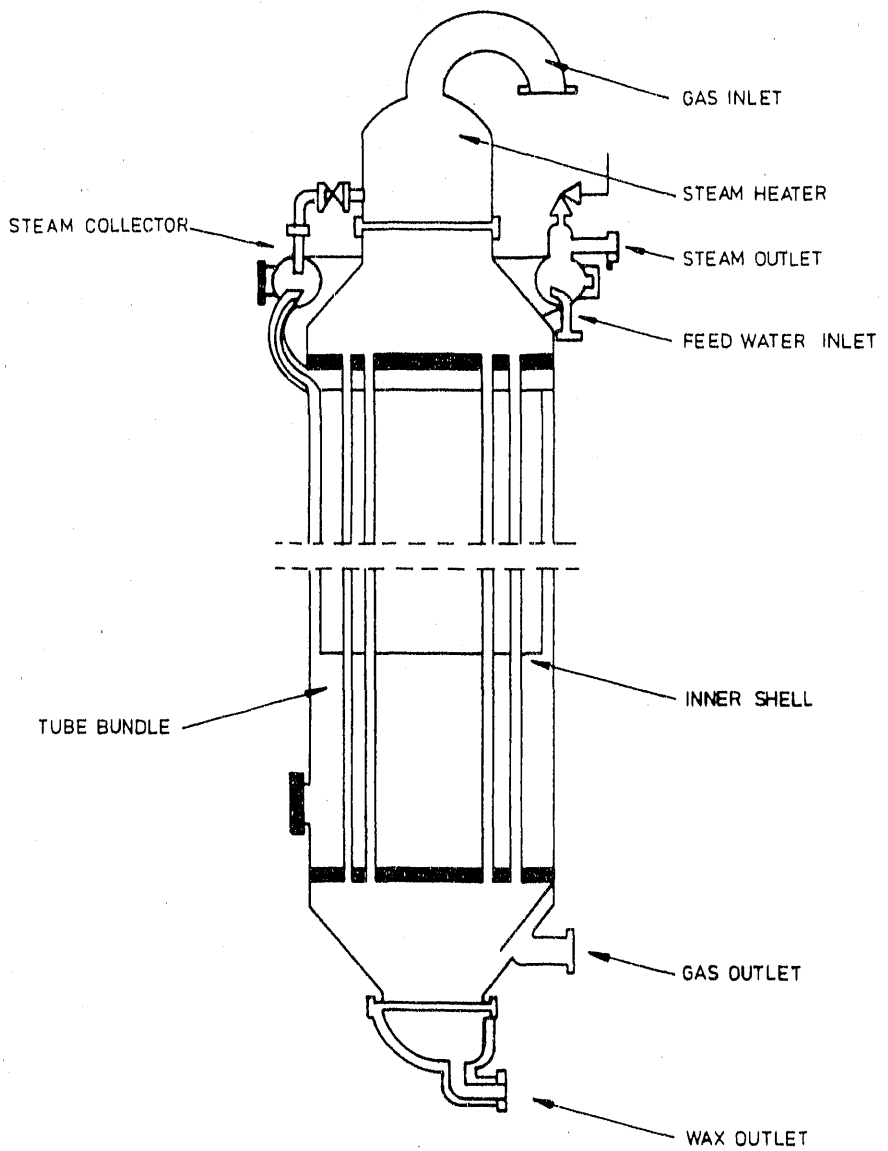

FIGURE 4.1. ARGE Commercial Fixed bed Fischer-Tropsch Reactor at Sasol. [Dry, 1981].

hydrocarbon product is in the liquid phase inside the reactor. The catalytic activity as well as selectivity for producing wax was found to decline with age. By progressively increasing the reactor temperature, the conversion could be maintained for about a year.

The Synthol reactors at Sasol I are about 50 m high with 2.3 m ID. Units at Sasol II and III are about 2.5 times as large as those in Sasol I. The Synthol reactor system is shown in Figure 4.2. The fresh feed and recycle gas enter the bottom of the reactor at about 165°C picking up hot catalyst from the base of the standpipe and rapidly transporting the catalyst into the reactor. The two banks of heat exchangers inside the reactor remove a large portion (about 30 to 40%) of the reaction heat. The rest of the heat is removed by the recycle and product gases, which leave the reactor at about 340°C. The entrained catalyst removed by the cyclones settles into the hopper and flows down the standpipe to be swept back into the reactor by the incoming feed gas. The rate of catalyst flow is controlled by the slide valve at the bottom of the standpipe. Dry (1983) reports that the formation of heavy hydrocarbons should be limited in fluidized bed reactors, because these would condense on the catalyst and result in defluidization of the bed. Table 4.1 compares the process conditions and product yields of these two reactors.

The operation of circulating fluidized bed reactors have been found to be challenging at Sasol [Dry, 1990]. Dense phase fluidization in the stand pipe was found to be critical to maintain the pressure differential and to ensure smooth flow. If catalyst defluidizes, unstable "slip-stick" flow results and could lead to choking of standpipe resulting in a loss of catalyst flow. High linear gas velocity is required in the riser and results in a high pressure differential across the reactor. Due to these factors the turn-down ratio is limited. High gas velocities also results in erosion of the reactor lining material. To reduce the costs and for easier operation, the use of bubbling fluidized bed was investigated at Sasol [Dry, 1990]. According to Dry (1990), bubbling fluidized bed was successfully demonstrated and scaled-up in 1989. Very few details are available on the Sasol bubbling fluidized bed reactor.

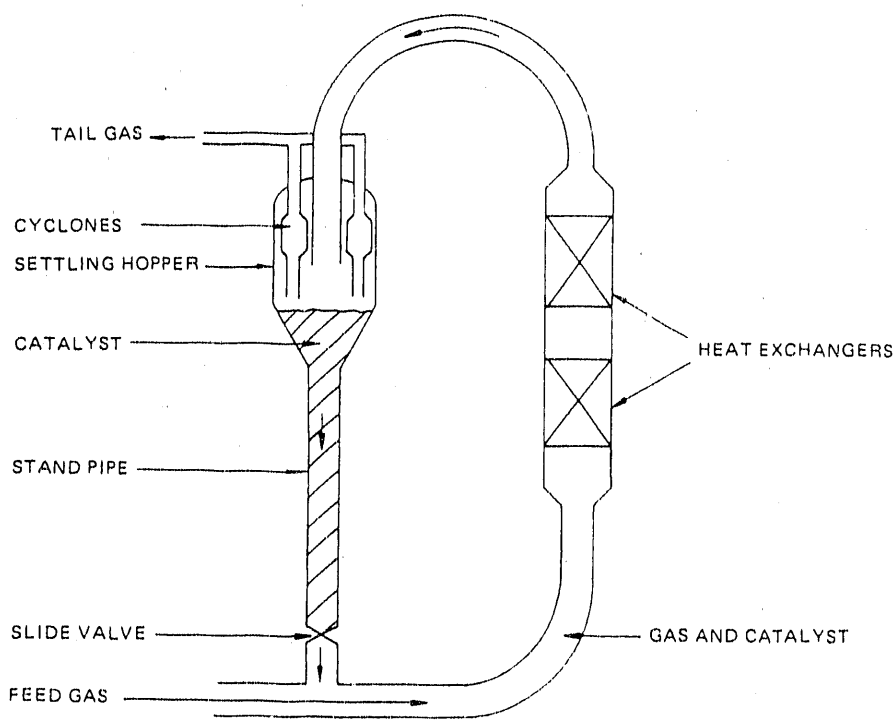

FIGURE 4.2. Synthol Circulating Fluidized Bed Reactor [Dry, 1981].

TABLE 4.1. Operating Conditions and Product Selectivity of Sasol Reactors. [Haag, et al., 1987].

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

5.0 RHEINPREUSSEN - KOPPERS SLURRY BED DEMONSTRATION PLANT

The process is briefly described by the flow chart of Figure 5.1 [Kolbel and Ralek, 1980]. The capacity of the 10 m^3 reactor demonstration unit has been reported to be 11.5 tons of hydrocarbon product per day based on syngas throughput of 2700 Nm^3/hr. The synthesis gas was produced in a Koppers water gas generator. CO_2 from the synthesis tail gas was added to the steam during the gas production period. The syngas contained an average H_2/CO ration of 0.67. The gas was purified over iron oxide to remove H_2S, and over a hot purifying mass (Lauta mass and soda) to remove organic sulfur compounds to a residual sulfur content of 1 to 2 mg of S/m^3. The syngas was compressed and preheated by the tail gas from the reactor. The feed enters at the bottom of the reactor through a gas distributor with jets about 2 to 3 mm in diameter. The reactor consists of a pressure-resistant steel cylinder with a diameter of 1.55 m and a height of 8.6 m. The height of the slurry is about 8 m. Up to 90% of the syngas is converted after a single pass. The reaction heat is removed by cooling tubes in the reactor. The internal heat exchanger ends about 1.3 m above the gas distributor. The reaction temperature is maintained by controlling the saturated steam pressure.

The carrier-free oxidized precipitated iron catalyst is finely milled in a liquid medium to a grain size of 5-50 micron and fed to the feeding tank. Before start-up, the reactor is charged with enough liquid medium to obtain the desired level. The tube exchanger in the reactor is used during the catalyst preparation to heat the suspension to the catalyst activation temperature. The catalyst suspension is introduced or withdrawn by means of pumps through nozzles at the bottom of the reactor from or to the stirred tank. The height of the suspension (8 m) is kept constant by a regulator either by filtering off the high fractions in the pressure filter or by adding higher-boiling synthesis products from containers. The reactor temperature is measured by 12 resistance thermometers attached at different heights, and recorded. Nine smaller nozzles mounted at different levels permit the removal of suspension samples from the reactor.

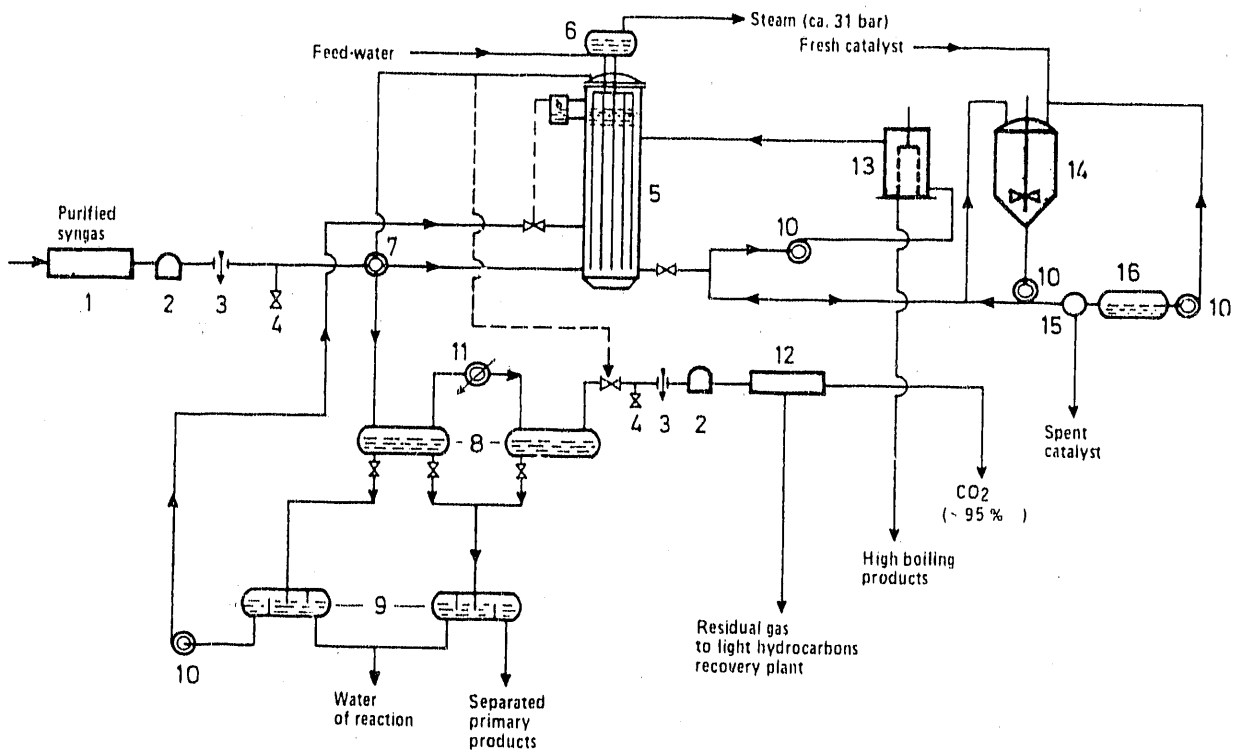

FIGURE 5.1. Process Flow Diagram of the Rheinpreussen-Koppers Liquid phase process [Kolbel and Ralek, 1980].

Key: (1) Compressor, (2) Gas Meter, (3) Valve, (4) Sampling, (5) Reactor, (6) Steam Drum, (7) Heat Exchanger, (8) Condenser, (9) Separating Tank, (10) Pump, (11) Cooler, (12) CO_2 Removal, (13) Pressure Filter, (14) Slurry Catalyst Tank, (15) Centrifuge, (16) Slurry Oil.

The products leave the reactor through a swan-neck and is cooled with fresh feed gas in a heat exchanger. Higher-boiling products partially condensed by the boiling range of the liquid medium are stored in containers. The F-T products are further cooled indirectly with water at about 30°C to condense synthesis water and products of the medium boiling range. After the carbon dioxide has been removed in the scrubber, the light-boiling and gaseous products are recovered. The carbon dioxide is cycled to the generator for the production of CO-enriched synthesis gases. In the case of a multistage of circulation process, most of the CO_2 and H_2O is removed from the outlet gas which is then recycled in the process.

If the production of low-molecular compounds is desired, the removal of the liquid medium is often greater than the addition due to synthesis. In this case the higher molecular weight product collecting in heat exchanger is recycled to the reactor by pumps. If the process is geared toward production of higher molecular weights, the catalyst-product mixture is separated in filter. The catalyst is recycled to the reactor. Water is removed from the catalyst free products in a separator. The separator yields oxygen-containing products, especially alcohols. The hydrocarbons are further separated into fractions by distillation, depending on their intended use. Tables 5.1 and 5.2 summarize the composition of the products obtained from the demonstration unit.

The Rheinpreussen demonstration unit has demonstrated that: a surface area of 50 m^2 is required for cooling coils for conversion of 1000 m^3 of syngas per hour, heat removal with internal cooling coils is possible with temperature gradient of $\pm$ 1°F, uniform catalyst distribution throughout the bed with micron size catalyst can be achieved, catalyst life of 400 Kg of hydrocarbon per Kg of Fe, and, low yields (about 4%) of methane and ethane.

TABLE 5.1. Composition and Properties of Products from the Demonstration Plant[a]. [Kolbel and Ralek, 1980].

	$CO + H_2$ [g/Nm^3]	Total C_{1+} Product (wt. %)	Olefin (%)	Av. Mol. Wt.	Specific gravity at 20°C	OH Number (mg KOH/g)	Acid Number (mg KOH/g)	Ester Number (mg KOH/g)
Methane + ethane	5.7	3.2	0	—	—	—	—	—
Ethylene	6.3	3.6	100	—	—	—	—	—
C_3	40.3	22.6	75–85	—	—	—	—	—
C_4	9.1	5.1	70–80	—	—	—	—	—
Fraction								
40–180°C	95.5	53.6	70	93.9	0.683	19.4	0.38	3.25
180–220°C	7.1	4.0	48	139.4	0.760	4.6	0.25	1.26
220–320°C	10.7	6.0	37	218.0	0.781	2.3	0.16	0.65
>320°C	3.3	1.9	7	300.5	0.811	0.0	0.45	1.05
Total	178.0	100.0						

[a]Process designed to produce gasoline.

TABLE 5.2. Variation of Product Composition from Liquid Phase Synthesis. [Kolbel and Ralek, 1980].

	Synthesis Aimed at Products of		
	Low Mol. Wt.	Medium Mol. Wt.	High Mol. Wt.
Yield C_{3+} (g/cm^3 CO + H_2)	162	175	182
Fractions	Share of total C_{3+} (%)		
C_3 + C_4	29.6	6.9	2.2
C_{5+} + to bp 190°C	63.0	40.0	7.1
190–320°C	6.2	25.7	8.3
320–450°C	1.2	18.3	33.0
>450°C	—	9.1	49.4

The Rheinpreussen demonstration unit (10,000 L suspension) was scaled up from a laboratory scale (6 L suspension). The most difficult task was uniform gas distribution when the ration of length to diameter of the reactors was decreased from 60:1 to 6:1. After the prevention of liquid circulation by specially constructed devices in the reactor, almost identical conversion and product spectra have been achieved together with increased reactor output. Table 5.3 compares the operating data and results of the demonstration unit with the laboratory scale reactor.

TABLE 5.3. Operating Data and Results from the Liquid Phase Synthesis[a] [Kolbel and Ralek, 1980].

	Reactor	
	Demonstration plant	Laboratory scale
Effective reaction volume		
Volume of suspension, incl. dispersed gas (l)	10,000	6
Catalyst (kg Fe)	880	0.4
Synthesis gas pressure (bar)	12	11
Synthesis gas (vol. ratio $CO:H_2$)	1.5	1.5
Quantity of synthesis gas [Nm^3/h]	2700	1.3
Linear velocity of compressed gas at operating temp., rel. to free reactor cross section (cm/s)	9.5	3.5
Total $CO + H_2$ consumed [Nm^3/h]	2300	1.1
Per m^3 reactor volume [Nm^3/h]	230	183
Per kg Fe [Nm^3/h]	2.6	2.45
Average synthesis temperature (°C)	268	266
CO conversion (%)	91	90
$CO + H_2$ conversion (%)	89	88
Products rel. to $CO + H_2$ feed		
Hydrocarbons [g/Nm^3]		
C_{1+}	178	176
$C_1 + C_2$	12	11
C_{3+}	166	165
Oxygen-containing products in process water [g/Nm^3]	3	2
Space-time yield of C_{3+} products, inc. O products, in 24 h (kg/m^3 reactor volume)	930	740

[a] Single-stage process with single pass using a precipitated iron catalyst.

6.0 HYDRODYNAMICS OF FISCHER-TROPSCH BUBBLE COLUMN REACTORS

6.1 General

In order to design/ or model a slurry bubble column reactor, a good understanding of the hydrodynamic behavior of such reactors is necessary. Parameters that are often required are: mean bubble diameter (Sauter mean), gas-liquid interfacial area, axial gas, liquid, and solids dispersion coefficients, gas hold-ups, gas-liquid and liquid-solid mass transfer coefficients, and heat transfer coefficients between the slurry and immersed heat transfer internals. A number of studies [e.g. Bukur, et al., 1990, Kuo, 1985, Deckwer et al., 1980] have been conducted on the subject in recent years. A major drawback of most of these studies is the use of small diameter reactors or columns. Hydrodynamics of such "narrow" reactors may not represent the behavior for commercial reactors and, therefore, uncertainty would exist in design scale-up. However, many have been carried out in wax media and at temperatures and pressures representative of F-T reactor conditions.

6.2 Flow Regimes

A bubble column reactor is characterized in terms of one of three flow regimes: slug flow, homogeneous bubbly flow, or churn turbulent flow. Figure 6.1 presents an approach to characterize the various flow regimes in two-phase and slurry column reactors as a function of the gas velocity and the reactor diameter. The transitions between the different flow regimes are not sharp. The exact limits depend on the height of the dispersion, the gas sparger, the liquid velocity, and the physico-chemical properties of the slurry (liquid) phase. A slurry column reactor can be treated as a two-phase bubble column (liquid-gas) reactor provided the size of the suspended particles is less than 50 micron and solids concentration is less than 16 wt%. Despite these limitations, Figure 6.1 provides a framework for describing flow regimes of slurry column reactors. A commercial F-T reactor, which would involve a relatively large diameter and a high superficial gas velocity is very likely to fall in the churn turbulent flow regime.

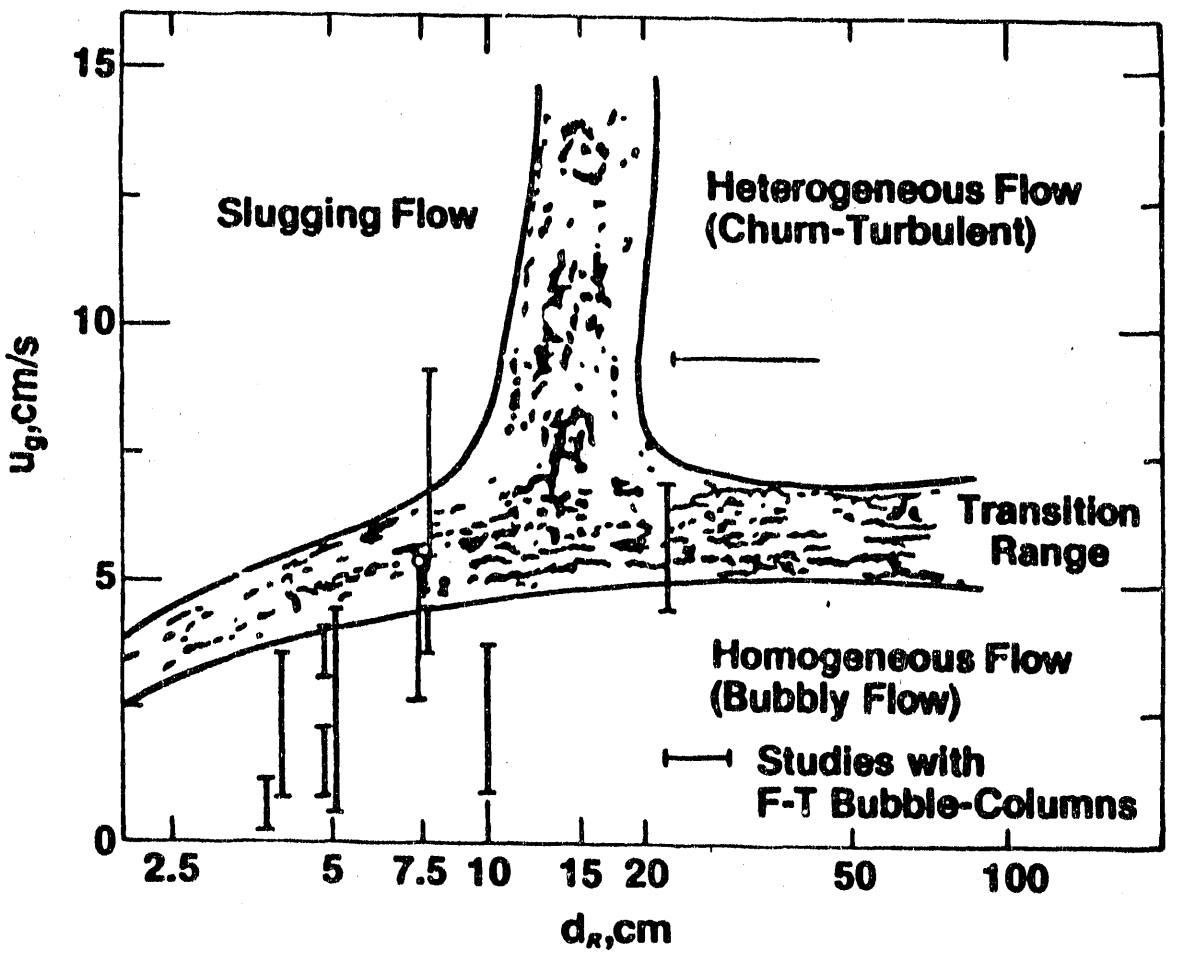

FIGURE 6.1. Flow Regimes for Bubble Columns.

Deckwer, et al., (1980) and Quicker and Deckwer (1981) have reported uniform bubble size distribution for gas velocities up to 4 cm/s. Uniform bubble size is indicative of homogeneous bubbly flow. Bukur, et al. (1990) and Kuo at Mobil (1985) have observed that for a 5 cm diameter column slug flow develops at a velocity of 2 to 3 cm/s. Bukur, et al. has also reported that with a 23 cm glass column homogeneous bubbly flow occurs for a velocity between 2 to 4 cm/s and churn turbulent regime appears at a higher velocity (up to 15 cm/s). For this latter flow, bubbles ranging from 1 mm to 100 mm have been observed.

6.3 Gas Hold-up and Bubble Size Distribution

The gas hold-up is a very important design parameter in that it determines, along with other variables, the reactor volume required for a given gas throughput. It also establishes the gas-liquid interfacial area, which in turn, is directly linked to mass transfer rate to the liquid phase. As a result, a substantial effort has been directed to the determination of this parameter for a variety of variables.

In a comprehensive study, using a molten hard paraffin as the liquid medium, Deckwer, et al. (1980) have examined the effects of column diameter, superficial gas velocity (up to 4 cm/s), temperature, pressure (0.4-1.1 MPa or 59 - 162 psi), and solids concentration (up to 16 wt%) on gas hold-up. Two columns, 4.1 and 10 cm diameters, both fitted with sintered metal plate distributor were used. The gas hold-up was found to be independent of column diameter, pressure, and temperature up to 240 C (464 F) and it decreased slightly with the addition of solids. Deckwer, et al. (1980) have also determined the Sauter mean bubble diameter to be 0.7 mm, and observed it to be independent of gas velocity. Using the hold-up and the Sauter mean diameter, the specific gas-liquid interfacial area was obtained and it was found to be three times that reported earlier by Calderbank et al. (1963) using a column of 5 cm diameter.

Quicker and Deckwer (1981) observed that for a 9.5 cm diameter column, a single nozzle distributor leads to a higher hold-up than a perforated plate kind and that there were no effect on bubble size distribution.

Researchers at Mobil [Smith et al., 1984 and Kuo, 1985] have conducted a comprehensive study of hydrodynamics of the slurry bubble column system. They studied the effects of distributor type, liquid static height, wax type, gas type, column diameter, and operating conditions on gas hold-ups. Wax type, distributor design, and temperature have been observed to have significant effect on gas hold-up. With sintered metal plate distributors, the effect of liquid static height was very pronounced--the hold-up being higher (up to 0.70) as the liquid height decreased. The column diameter had some effect on gas hold-up, but the effects of pressure and gas type were negligible. They also observed that bubble sizes produced by the orifice plate distributor were larger than those from a sintered metal plate. One drawback of all these results and reservations is that the tests were conducted with small inside diameter columns (3.2, 5.3 and 10.2 cm) with a large height for dispersion.

Bukur, et al. (1990) has performed systematic study on the subject using both FT-300 wax and various reactor waxes and two columns (5 and 23 cm diameter). The most important observation is that for the smaller column, under certain set of conditions, with FT- 300 wax, a stable foam layer exists above the dispersion, and this is referred to as the "foamy regime". For reactor waxes (Sasol and Mobil), however, "foamy regime" was not observed. For the larger column, with FT-300 wax, the foam broke up at velocities 3 to 5 cm/s and was not observed at a lower temperature. Use of hydrotreated wax is believed to result in foaming [Stiegel, 1991].

An important observation by Bukur, et al. (1990) is that Sauter mean bubble diameter varies depending upon the type of wax used, even though the gas hold-up is the same. For the FT-300 wax the diameter is 0.8 mm, whereas for Sasol wax it is 2 mm and for Mobil reactor wax the value is 4 to 5 mm. This observation would have important practical implications for design scaleup, as well as for technology development.

6.4 Mass and Heat Transfer

In a slurry F-T reactor, the reactants, CO and H_2, must first transfer from the bubbles to the liquid phase and then diffuse through the liquid, from liquid onto the solid catalysts and finally through the catalyst pores. However, compared to the intrinsic reaction rates, only the diffusion through the liquid phase is important in that it is the slowest step [Akgerman, 1988].

Zaidi et. al. (1979) measured values of the volumetric mass transfer coefficients, $K_l.a_g$ for carbon monoxide in a small bubble column reactor. The mass transfer coefficient, K_l, for carbon monoxide was determined by using the experimentally determined specific gas-liquid interfacial area, a_g, which, in turn, was obtained from data on gas hold-up and Sauter mean bubble diameter. The most important observation is that, $K_l.a_g$ obtained by such means matched fairly well with the value predicted by correlations developed by Calderbank and Moo-Young (1961) and by Hughmark (1967). Volumetric mass transfer coefficients have been determined for both carbon monoxide and hydrogen using stirred tank reactors [Albal et al., 1984; Ledakowicz et al. 1984; Deimling et al. 1984]. Here also, the values agree well with those predicted by correlation of Calderbank and Moo-Young (1961).

In view of agreement between experimentally determined values and predictions by correlations, mass transfer in F-T slurry reactor liquid can be predicted by available correlations in the literature.

In F-T synthesis heat transfer coils would be used in bubble column slurry reactor in order to remove the heat released from the highly exothermic reaction. Deckwer, et al. (1980) conducted tests in a 10 cm i.d. bubble column using paraffin wax as the liquid medium and up to 16 wt% alumina particles (less than 5 micron) as the solid phase and developed a correlation using this data. However, this correlation is applicable only for a superficial gas velocity up to 10 cm/s.

Saxena et al. (1991) performed extensive tests on hydrodynamics and heat transfer for slurry bubble column systems using 10.8 and 30.5 cm i.d. columns. The liquid media used are water and Therminol-66, which is a high molecular weight, high viscosity hydrocarbon heat transfer fluid. The heat transfer coefficients for air-water-red iron oxide (1.0 and 2.4 micron) solid (up to 30 wt%) decreased with increasing slurry concentrations. In this range the influence of particle size was negligible. For tube bundles, the coefficients were appreciably higher than single tubes.

Results with nitrogen-Therminol-red iron oxide system were much different from the air-water-red iron oxide system. The values for Therminol were an order of magnitude smaller than for water. Coefficients increased with increasing solids concentration and were smaller for tube bundles than for single tubes.

Saxena et al. (1991) has also observed that existing correlations cannot predict the observed results sufficiently closely, indicating that existing correlations are to be used only with caution for design or evaluation purposes.

Air Products (1991) has performed demonstration tests with the 22" ID LaPorte slurry methanol reactor and evaluated internal heat exchanger performance for slurry concentrations up to 46 wt% and superficial inlet velocity up to 16.8 cm/s. The slurry side coefficients were observed to be 295 to 321 Btu/(hr)(ft^2)(^oF) and the overall coefficient 44 to 96 Btu/(hr)(ft^2)(^oF). Furthermore, predicted overall coefficients, using Sieder-Tate and Deckwer correlations, were accurate within the range of uncertainty of the plant data. This observation regarding correlations is in contrast with what has been reported by Saxena et al. (1991).

Although the LaPorte plant is a methanol slurry reactor, operating experience and results would be useful for designing and scaling-up a F-T reactor also. This is particularly so because many of the operating parameters--temperature, pressure, solids concentrations, superficial velocity, particle sizes, exothermicity of the reactions--are not too far from those to be used for a F-T slurry reactor.

6.5 Effect of Liquid Velocity

Upward liquid velocity can have a major effect on bubble column slurry hydrodynamics. Bukur et al. (1990) has observed that even a small upward flow (2 cm/s) reduces the axial concentration profile of solids (Figure 6.2). In a 5 cm ID column, using iron oxide and FT-300 wax, concentration at the bottom is three times as much as that at the top (2.2 m from bottom) when the gas velocity in 2 to 12 cm/s. Indeed, magnitude of velocity has little effect on this gradient. But, with a liquid upflow as little as 2 cm/s, the gradient is uniform (Figure 6.2). This occurred with a solid particle size of 20 to 44 micron, an average concentration of 20 wt%, and a 2 mm orifice in a 5 cm ID column.

Another important effect of liquid flow is that gas hold-up is lower with liquid flowing upward. As observed by Bukur et al. (1990), for 5 and 21 cm columns, with moderate gas superficial velocity, the gas hold-up could be 20 to 50% lower with liquid flow than without it (Figure 6.3). With a foaming liquid, the hold-up can decrease drastically with a small upward flow of liquid. For example, Shah et al. (1985) observed that for a foaming ethanol-water mixture, hold-up declines from 0.8 to 0.2 with an upward velocity of 0.77 cm/s.

6.6 Foaming

Mobil (Kuo, 1985) has performed hydrodynamic study using small diameter columns (3.2 and 5.3 cm) and waxes from different sources (FT-200, FT-300, Mobil's run CT-256-4, CT-256-5) and observed foam formation, that was severe in some cases. It seems that wax type, distributor design, and gas velocity have major effect on severity of foam build-up. With sintered metal plate (SMP) distributor having 15 and 60 micron pores and a 3.2 cm column a great deal of foam forms with hold-ups as high as 70 vol% at superficial velocity above 0.8 and 1.4 cm/s. This occurred with FT-200 wax at 200 C (392 F). No foam was observed, however, with CT-256-5 wax used with a 5.3 cm i.d. column and four different gas distributors.

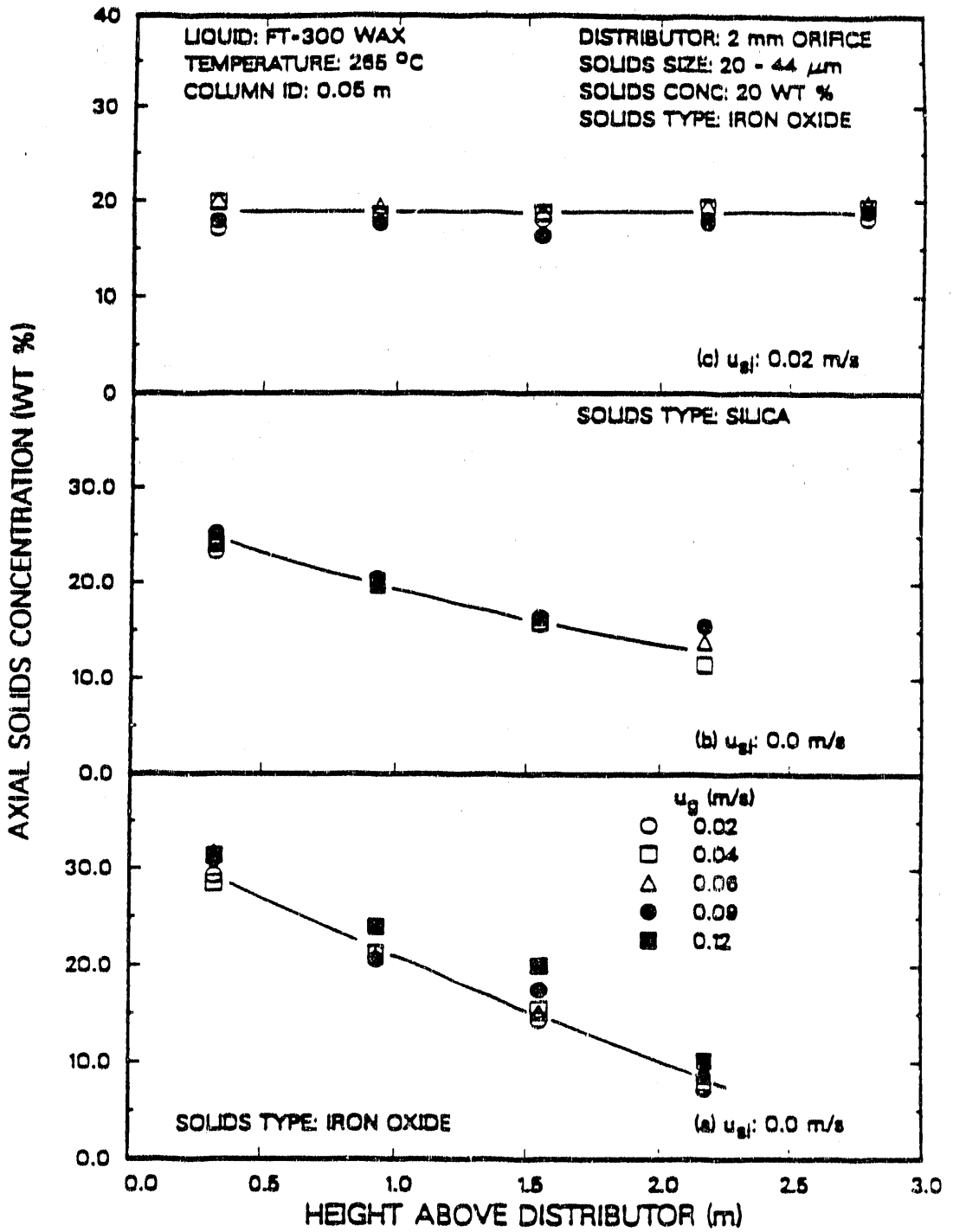

FIGURE 6.2. Effect of Axial Position and Superficial Gas Velocity on Solids Concentration [Bukur et al., 1990].

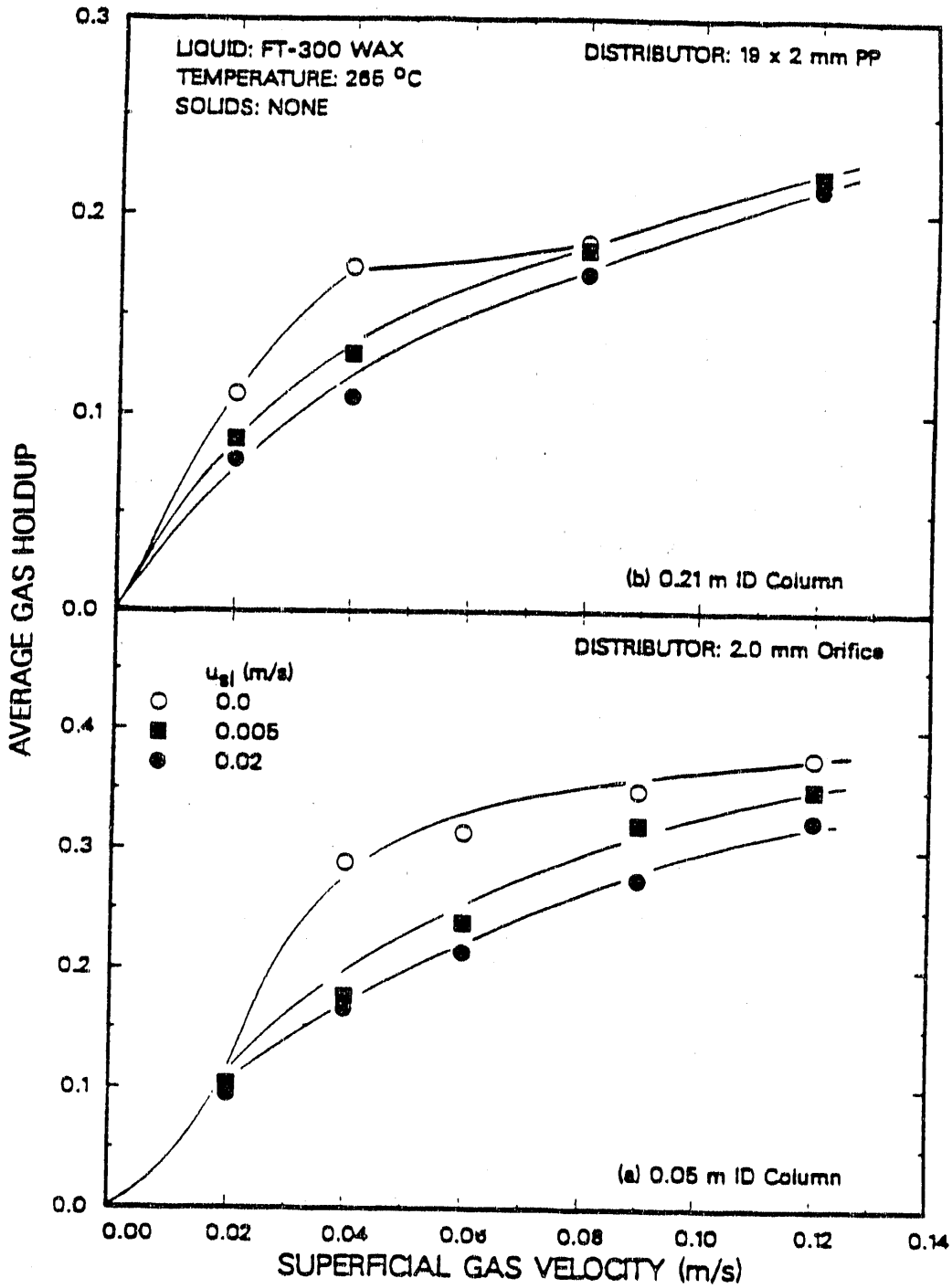

FIGURE 6.3. Effect of Superficial Gas Velocity on Average Gas Holdup [Bukur et al., 1990].

Bukur et al. (1990) has reported formation of foams in his extensive tests on hydrodynamics using waxes with iron oxide and silica dispersed in them, but nowhere as much as encountered by Mobil. Furthermore, Deckwer et al. (1980) studied hydrodynamics thoroughly, using paraffin wax at 250 -300 C (482-571 F) but did not observe foam formation. Hydrotreated waxes are believed to increase the foam formation [Stiegel, 1991].

From the review of literature information on foam formation phenomena, it seems that whether foam would form in a large commercial or demonstration reactor for a given set of conditions and equipment (distributor) chosen is not certain at all. This is an area where additional research is necessary to understand the factors, that lead to foam formation and ways to prevent it. Such knowledge would be directly useful for design and operation of a F-T reactor.

7.0 FISCHER-TROPSCH CATALYSTS

7.1 Types of Catalysts

The most widely used F-T catalysts, either for commercial/semi-commercial operation or for small scale development work has been an unsupported iron (Fe) containing potassium (K), and copper (Cu) as promoters. Precipitated, fused, and sintered forms of iron catalysts, usually with promoters have been tested and used. Other catalysts known to promote conversion of synthesis gas to F-T hydrocarbons are cobalt (Co), ruthenium (Ru), copper (Cu), and manganese (Mn). More recently, Bukur et al. (1990) have tested catalysts containing varying quantities of silica (SiO_2): 100 Fe/5 Cu/4.2K/x SiO_2 (x = 0,8,24,100, all numbers in parts by weight). Activity, selectivity, and stability of these iron/silica catalysts are influenced by the presence of SiO_2.

Examples of catalysts chosen in large scale operations are that fused magnetite has been used in the Sasol entrained bed F-T reactors. Precipitated Fe catalysts have been successfully used in Germany, both for fixed bed and for slurry reactor in 1950's [Kolbel and Ralek, 1980].

Experience, so far, indicates that Fe-based catalysts are the best in terms of activity and selectivity of the desired products. Furthermore, based on test data, precipitated Fe catalyst is likely to be used in the slurry phase commercial reactor for F-T synthesis.

Royal Dutch/Shell in its Malaysian fixed-bed F-T reactor is reportedly going to use dual catalyst and Statoil in its 30 bbl/day pilot plant may be using Cu and rhenium (Re) on aluminum oxide (Al_2O_3) as one of the catalysts. Rhenium is known to improve dispersion of catalyst [Srivastava, 1991].

With an aim toward identifying and developing better catalysts in terms of activity and selectivity, Air Products (DE-AC22-80PC30021) has screened a large number of formulations, consisting of two broad groups. One was more conventional

precipitated and supported catalytic metals, and the other consisted of molecular cluster compounds on a variety of supports. Clusters were chosen as catalytic precursors based on the premise that they would decompose at the operating temperatures, which are sufficiently high, and form fragments of controlled particle size. Based on this screening, two catalysts, one from each group, showing best results, were chosen for further tests. These are a co-precipitated Fe/Cu/K-based catalyst and a Co-carbonyl on zirconia-promoted alumina composition.

7.2 Catalyst Activity and Selectivity

7.2.1 Anderson-Schulz-Flory Distribution

In F-T synthesis, product selectivity to different fractions (light hydrocarbons, gasoline, diesel, and wax) is in accord with the Anderson-Schulz-Flory (ASF) distribution [Anderson, 1984] of molecular weights. The F-T synthesis is a polymerization reaction, the monomer being a C_1 species derived from CO, and the process involves chain growth. The molecular weight distribution is characterized by a parameter, α, which is the probability of chain growth. This parameter is a measure of probability of addition of a carbon atom to a chain. A second parameter used in the distribution equation is the carbon number, n, which is the average number of carbon atoms in the molecules in a product fraction. The distribution is given as:

$$\log (W_n/n) = n\log\alpha + \log\left[\frac{(1-\alpha)^2}{\alpha}\right]$$

where W_n = weight fraction of product with carbon number n.

According to this equation, a plot of ln (Wn/n) vs. n will generate a straight line having a slope logα. The magnitude ofα, thus obtained corresponds to the characteristics of catalyst used, and operating variables employed. Using ASF distribution relations, one can calc ilate the maximum yields of various products functions as shown in Figure 7.1 -- naximum gasoline range hydrocarbon (C_{12}-C_{18}) yield 48% and maximum diesel yield 30%.

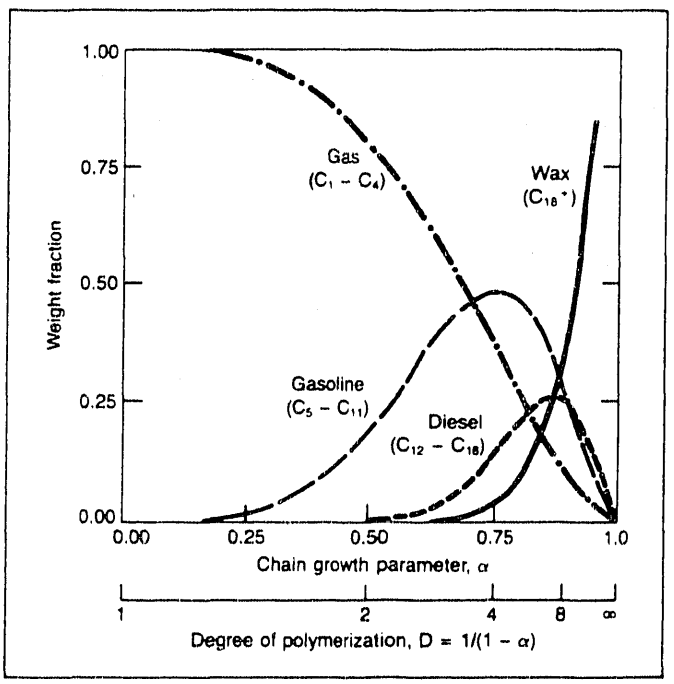

FIGURE 7.1 Product Selectivity as a function of Chain Growth Parameter. [Srivastava et al., 1990].

One way of changing α would be to formulate a catalyst leading to a desired product distribution, such as more wax formation or less light hydrocarbon. Indeed, Royal Dutch/Shell has developed a proprietary catalyst with a high α and, therefore, a high selectivity toward heavier products, including heavy wax, and this has been shown semi-quantitatively in Figure 7.2.

A second approach would be to formulate catalysts that generate products deviating from ASF distribution and leading to higher fractions of desired products. Some studies in the literature indicate ASF distribution with different α's for different carbon ranges. Such distributions referred to as "double α" may be due to two different types of catalytic sites present with different chain growth probabilities [Srivastava et al., 1990]. Air Products' effort to do so led to two catalysts -- a co-precipitated Fe/K - derived catalyst and a Co-carbonyl on zirconia-promoted alumina formulation showed apparent deviation for ASF distribution (Air Products DE-AC22-80PC-30021). Research in this direction should be continued in order to discover more active and selective catalysts, that can potentially lead to major improvement of the technology.

7.2.2 Comparison of Catalyst Activities and Selectivities

Overall trends of selectivities of different F-T catalysts are well known. This can be summarized as:

Catalyst	Predominant Product
Fe	olefin/wax
Ni	CH_4
Co	paraffin/wax
Ru	wax

Among them, Fe-based catalysts have been most widely used because of its high activity, both for F-T synthesis and for water gas shift (WGS) reaction, and it is inexpensive. Such catalysts have been used routinely and extensively in the Sasol

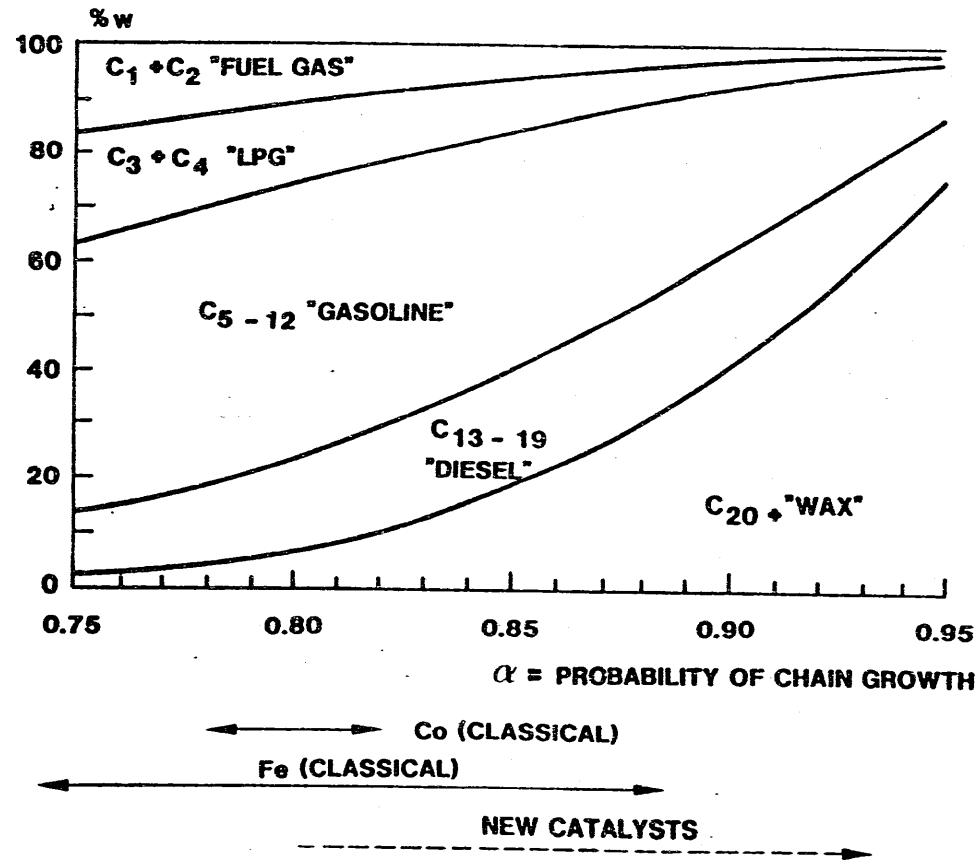

FIGURE 7.2. Product Selectivity with Different Catalysts having Different Chain Growth Parameters.

plants. The typical state-of-the-art selectivities obtained in the Sasol fixed and fluidized bed reactors is given in Table 7.1 Note that two reactors operate at two different temperatures. As the catalyst ages, the hard wax selectivity in the case of fixed-bed reactors decreases and the selectivities at the opposite end of the spectrum (C_1 to C_4 hydrocarbons) increases. The same phenomenon, but to a lesser degree, occurs in the case of fluidized catalysts. At fixed operating temperatures, the overall activity of the catalysts also decreases with age.

A comparison has been made of activities and various products selectivities of iron-based catalysts (Table 7.2) investigated by different groups, either in a stirred tank slurry reactor (usually autoclave) or in a bubble column slurry reactor.

This comparison includes Kolbel's (Kolbel et al. 1955) results as observed in the Rheinpreussen BCSR in the 1950's. Catalyst activity (89% conversion) and selectivity of 53.6% (to gasoline) claimed by this group are the best reported, but no one else has been able to duplicate these results. Mobil's observations (Kuo, 1985) are close to Kolbel's results but still fall significantly short, particularly in terms of selectivity to gasoline.

Mobil's results are promising with two catalyst formulations. They were able to shift selectivity either to distillate (with run CT-256-3) or to wax (with run CT-256-13), although the operating conditions in terms of temperature, pressure, space velocity and synthesis gas compositions are the same.

Comprehensive studies have been carried out at Sasol to establish the effect of supports on the performance of a series of precipitated iron catalysts ($Fe/Cu/K_2O$). Unfortunately, only a limited range of data has been revealed because of proprietary reasons. Nevertheless, SiO_2 was found to be the best support in terms of both activity and selectivity. A second support material (CaO_2, Cr_2O_3, Al_2O_3, V_2O_5, ThO_2, MgO or SiO_2) added to SiO_2, showed results inferior to SiO_2 alone. Dry (1981) emphasizes that a careful balance between K_2O as promoter and SiO_2 as a support is necessary in order to maximize the desired activity and

TABLE 7.1 Selectivity of Sasol Commercial Operations*
[Dry, 1981]

Product	ARGE, Fixed bed at 220°C (428°F) %	CFB, Synthol at 325°C (617°F) %
CH_4	2	10
C_2H_4	0.1	4
C_2H_6	1.8	4
C_3H_6	2.7	12
C_3H_8	1.7	2
C_4H_8	3.1	9
C_4/H_10	1.9	2
C_5 to C_{11} (gasoline)	18	40
C_{12} to C_{18} (diesel fuel)	14	7
C_{19} to C_{23}	7	
C_{24} to C_{25} (medium wax)	20	4
> C_{25} (hard wax)	25	
Water-soluble nonacid chemicals	3	5
Water-soluble acids	0.2	1

* Carbon atom basis

TABLE 7.2. Comparative Catalyst Performance and Tests Data.

	TAMU Bukur (1988)	UOP Abrevaya & Shah (1990)	Rheinpreussen Plant Kolbel, et al. (1955)	MIT Satterfield (1987)		Mobil (Kuo, 1985) CT-256-3	CT256-13
Catalyst	100 Fe/0.3 Cu/0.5K	Precipitated Fe + Promoter	Fe/Cu/K_2O	Ruhrchemie	C73	Fe/Cu.K_2O	Fe/Cu/K_3O
Reactor Type [a]	STSR	STSR	BCSR	STSR	STSR	BCSR	BCSR
Conditions							
Temperature, C	265	275	268	263	263	260	258
Pressure, atm	15	21	12	25	8-15	15	15
SV, Nl/g-Fe/h	1.6	0.9	3.4	2.0	1.0	2.6	2.4
H_2/CO Ratio	0.72	0.70	0.67	0.70	0.70	0.67	0.67
Activity							
CO + H_2, Conv., %	71.0	83.0	89.0	33.6	56.0	86.8	82.2
Mol/g-cat/h	0.034	--	0.106	0.021	0.039	0.070	0.061
Nm^3/kg-Fe/h	1.13	0.75	3.02	0.67	0.56	2.25	1.97
Selectivity, wt %							
C_1	3.2	6.2	3.2 ($CH_4 + C_2H_6$)	5.7	11.6	7.8	2.7
C_2-C_4	11.4	34.8	31.3	27.0	39.6	24.5	11.1
C_5-C_{11}	20.4	28.6	53.6	40.0[c]	39.5[c]	41.5	18.1
C_{12}-C_{18}	65.0[b]	11.20	10.00	27.3[d]	9.30[d]	15.4	10.2
$C_{19}+$	--	19.20	1.9	--	--	10.8	57.9
Product yield							
g-HC/Nm^3 converted	220	--	178	172	183	197	206
g-HCl/g-Fe/h	0.25	--	0.57	0.05	0.10	0.37	0.41

[a] STSR - stirred tank slurry reactor, BCSR - bubble column slurry reactor
[b] $C_{12}+$
[c] C_5-C_{12}
[d] $C_{13}+$

hydrocarbon product selectivity. The rationale is that acidic SiO_2 neutralizes basic K_2O, thereby reducing the promoted action due to K_2O which suppresses formation of light hydrocarbons. Furthermore, high surface-area supports reduce direct contact between iron and potassium because the latter may not cover the entire surface. If this happens, promoter action of K_2O would be less effective. Bukur et al. (1990) have examined the influence of SiO_2 and Al_2O_3 supports on the activity and selectivity of precipitated iron catalysts by using a fixed bed reactor at 1.5-3.0 MPa (221-442 psi) and 220-250 C (428-482 F). Their results show that for F-T synthesis and WGS, activity decreased with increasing support content, but the catalyst was more stable. Product selectivities changed with increasing SiO_2 content of the catalyst, whereas no significant changes were observed with two Al_2O_3- containing catalysts. The total olefin content and the fraction of branched hydrocarbons both decreased, whereas the fraction of internal olefins increased with an increase in the SiO_2 catalyst.

7.3 Catalyst Activation and Pretreatment

F-T catalyst needs pretreatment prior to its use for synthesis. The ferric iron must be converted to the metallic or iron-carbon bonding state before the catalyst can be utilized. Such bonding states are obtained by reduction with CO, H_2 or CO + H_2 mixture or by consecutive treatment with CO and H_2. Pretreatment or activation conditions have been observed to have significant effects on subsequent catalyst activity, selectivity, and stability. Bukur et al (1990) has reported that in a laboratory fixed-bed reactor Ruhrchemie LP 33/81 catalyst (commercial state-of-the-art formulation) activated with CO had the lowest methane and the highest $C_{12}+$ selectivity, whereas H_2 reduction at 280 C (536 F) resulted in the highest methane and the lowest $C_{12}+$ selectivity. However, H_2 reduction makes the catalyst more stable.

Kolbel and Ralek (1980) and Mobil workers [KuO, 1985] used carbon monoxide-rich synthesis gas mixtures for in-situ pretreatment of unsupported precipitated Fe/Cu/K catalysts. However, this procedure did not lead to reproduceable results

during studies at PETC [Zarochak and McDonald, 1987], and at TAMU [Bukur et. al., 1988] with Fe/Cu/K catalyst. Relatively rapid catalyst deactivation and change of selectivity with time onstream were observed in studies at PETC for Fe/Cu/K. Similar trends, but much less severe, were reported by Bukur et al.

Subsequent study at PETC shows that during the F-T synthesis, catalyst deactivation in a slurry reactor was moderate with the synthesis gas composition H_2/CO ratio > 0.86 but was noticeably more rapid for gas with H_2/CO ratio < 0.8.

Underlying causes of the effects of pretreatment on catalyst properties are far from well-understood. They may have to do with the catalyst composition and phase changes occurring during pretreatment. Characterization of catalysts before and after pretreatment and following synthesis test would be necessary to develop explanation for pretreatment effects.

7.4 Catalyst Deactivation Due to Poisons

F-T catalysts, particularly Fe-based ones, are known to be easily deactivated by poisons such as sulfur compounds [Anderson, 1984]. In a fixed-bed reactor, the section near the inlet is deactivated by sulfur, whereas the section toward the outlet is deactivated by carbon deposition. A recent study [Chaffe et al., 1989] has shown that coprecipitated Fe-Mn catalyst was two orders of magnitude more sulfur-tolerant than Fe-based catalysts that have been employed commercially.

Literature information [Anderson, 1984 and King, 1938] suggests that Co-containing catalysts are more sulfur tolerant than Fe-based formulations. Herrington and Woodward (1939) observed that addition of small quantities of H_2S or CS_2 increased the yield of liquids and decreased the gaseous hydrocarbons. Madon and Taylor (1979) tested Co catalysts poisoned with varying quantities of H_2S and observed that most of the poisoned solids were as active as the fresh ones. The selectivity of producing C_5+ hydrocarbons at 197°C (387°F) and 0.6-1.6 MPa (88 to 235 psia) seemed independent of sulfur content.

It seems that poisoning effects of sulfur and other components on F-T catalysts are not sufficiently understood and even less so when the reactor is a slurry one. As a part of F-T catalyst research, additional work is necessary for further elucidation of this important phenomenon.

7.5 New or Modified Catalysts

Air Products [Withers, Jr. et al., 1987] has developed Co-based catalysts using a slurry reactor and reported high bulk activity and selectivity. A formulation with 3.5% Co and 6.6% Zr on silica produced the best results. The activity does not seem to be as high as that observed by Mobil for its Fe/Cu/K_2O catalyst used in run CT-256-13 [Kuo, 1985], but the achievable selectivity to gasoline and diesel are higher than for the Mobil catalyst. Syngas conversion was 25 to 71%, with the bulk activity ranging from 16 to 54 mol syngas/Kg/hr. Selectivity to gasoline range (C_5-C_{11}) products was 20 to 45% and to diesel (C_{12}-C_{18}) was 17 to 32% in the slurry reactor.

This catalyst has been successfully tested in an extended slurry-phase run with 6 months on-stream and a concomitant 10% loss in activity. Exxon [Rice 1987, 1988 and Fiato 1987] has reported some catalyst formulations that show promise for high selectivity in a slurry reactor. A novel approach -- pyrolysis by using laser -- to produce fine-particle promoted or supported iron-carbide-based catalyst was developed. Exxon has used both catalysts to produce various heavier hydrocarbons with high selectivity from syngas in a slurry reactor.

8.0 MASS TRANSFER AND KINETICS FOR FISCHER-TROPSCH REACTION SYSTEMS

The Fischer-Tropsch kinetics is complex due to interaction of large number of parameters such as pressure, temperature, fresh gas composition, residence time, heat and mass transfer, and catalyst (including catalyst type, catalyst support, catalyst activation during preparation and catalyst age). The composition of the reaction products of Fischer-Tropsch synthesis (ratio of alkanes to alkenes, chain length distribution, formation of water or carbon dioxide) is kinetically controlled and does not correspond to the composition predicted by thermodynamics [Bussemeier et al., 1986]. According to thermodynamics, the main products should consist of methane and carbon dioxide [Storch et al., 1951]. The hydrogenation of CO is achieved by simultaneous chemisorption of H_2 and CO on metallic sites of the catalyst surface. H_2 is believed to be chemisorbed dissociatively, whereas, CO is believed to be bounded to the catalyst metal (Co, Fe, or Ru) by C-metal bond. This bond results in weakening the C-O bond, ultimately resulting in hydrogenation of the CO molecule.

In heterogeneous catalysis, such as the Fischer-Tropsch synthesis, interactions of CO and H_2 with the catalyst particle are important and any factor hindering such an interaction may result in the reaction being diffusion limited. The mass transfer of the reactants to the external catalyst surface and the desorption of the products are believed to be relatively fast and do not determine the net reaction rate [Frohning et al., 1982]. This is explained by relatively high activation energy for the FT reaction (20 to 25 kcal/mol). However, under normal FT conditions the activity of the catalyst is dependent on the particle size of the catalyst [Dry, 1981]. This indicates that mass transfer within the pore structure of the catalyst is of considerable importance. The reactants dissolve in this liquid and diffuses into the catalyst pores where they react. The reaction creates a concentration gradient leading to an increase in the diffusion. Thus, the kinetics of the reaction and diffusion are coupled. Within the catalyst particle, the concentration of the

reactants decrease (due to the reaction) and that of products increase as the distance from the catalyst surface increases. High concentration of products such as CO_2 and H_2O results in the oxidation of the inner catalyst surface. Since the catalyst is active only in reduced state, only the area surrounding the pore opening (up to a depth of 0.1 mm) remains active [Anderson et. al., 1964].

The FT reactions occur via a complex path and thus the published equations for the FT and the related methane synthesis do not present a uniform picture. Table 8.1 summarizes various kinetic equations reported for each of the four main metal catalyst [Dry, 1981]. Table 8.1 indicates that the order of reaction with respect to hydrogen varies from zero to two, and for CO from one to minus one. Vannice (1976) in his review reports that when the H_2/CO molecular ratio is between one and three, the order with respect of H_2 is about one and the order with respect to CO is between zero and minus one half. The partial pressure of water plays an important role in case of Fe catalysis due to the water-gas shift reaction. If water competes with CO and H_2 for catalyst sites, then it plays a role in the kinetics, this has been seen in case of Ni catalyst by Saletore (1977). Variation in the rate expression reveals the complex nature of the reaction. For Co, Fe or Ru catalysts, the apparent activation energies cover the range from 20 to 25 kcal/mol, indicating that the FT reaction is not diffusion limited. Dry (1981) reports that for FT reaction over iron catalyst, the rate is proportional only to the partial pressure of H_2 in case of a differential reactor; whereas in an integral reactor the rate is proportional to $pH2.pCO/(pCO + a.pH2O)$; where a is a constant obtained from regression. Thus information generated in differential reactor would be of little value for designing commercial integral reactors.

When the F-T reaction is carried out in a slurry reactor syngas is bubbled through a slurry of finely divided catalyst suspended in heavy-oil medium whose composition may or may not change with time depending upon the product selectivity variation and time. In this three phase reactor, a discontinuous gas phase in form of bubbles moves relative to a continuous "homogeneous" slurry phase. The syngas reactants

TABLE 8.1. Some Kinetic Equations for CO Hydrogenation over Various Metal Catalysts [Dry, 1981].

Metal	Kinetic equation	Ref. No
Ni	$r = kp_{CO}p_{H_2}^{0.5}$	[185]
	$r = kp_{CO}/(1 + kp_{CO})^2$	[186]
	$r = kp_{H_2}^{0.9}p_{CO}^{-0.2}$	[187]
	$r = kp_{H_2}^{0.85}p_{H_2O}^{-0.9}$	[188]
Co	$r = k$ (i.e. independent of reactant pressures)	[189]
	$r = kp_{H_2}^2/p_{CO}$	[190]
Fe	$r = kp_{H_2}^{0.6}p_{CO}^{0.4} - fr^{0.5}p_{H_2O}^{0.5}$	[56]
	$r = kp_{H_2}/(1 + ap_{H_2O}/p_{CO})$	[2]
Ru	$r = kp_{H_2}^2$	[191]
	$r = kp_{H_2}^{1.33}p_{CO}^{-0.13}$	[192]
	$r = kp_{H_2}^2p_{CO}/(1 + mp_{CO} + np_{H_2})^3$	[193]
	$r = kp_{H_2}^{1.5}p_{CO}^{-0.6}$	[157]

[185] = Lee et al., 1970
[186] = van Herwijnen et al., 1973
[187] = Luyten and Jurgens, 1945
[188] = Saletore and Thomson, 1977
[189] = Anderson et al., 1949
[190] = Brotz, 1949
[56] = Anderson et al., 1964
[2] = Anderson, 1956
[191] = McKee, 1967
[192] = Karn et al., 1960
[193] = Phung Quach and Rouleau, 1978
[157] = Ekerdt and Bell, 1979

must diffuse through the liquid phase to the catalyst surface in order for the F-T synthesis to occur. The general approach has been to consider the specific mass transfer and kinetic rate processes that are taking place.

In the slurry, the effective H_2/CO ratio the catalyst sees is controlled by the vapor-liquid equilibrium, chemical reaction rate and mass transfer rate. Due to the reaction stoichiometry and the difference in the rates of diffusion for CO and H_2, the H_2/CO ratio at the catalyst surface may be different than the corresponding ratio in the inlet gas stream. Akgerman (1990) has examined variation in the H_2/CO ratio at the catalyst surface and the inlet gas stream as a function of the rate controlling step. If the reaction is slow and is the rate determining step, then the concentration is uniform and the effective H_2/CO ratio the catalyst surface sees is the ratio of solubilities of H_2 and CO in the liquid phase. Based on the available information in the literature, Akgerman (1990) estimated the solubility ratio of H_2/CO to between 0.5 and 1.12 (depending on the values of the Henry's Law constants) for a gas stream with H_2/CO ratio of 0.7 Thus for a chemical rate controlling the reaction, the effective H_2/CO concentration the catalyst surface sees is not much different from a gas phase reaction.

On the other hand, if the reaction is mass transfer controlled, then the effective ratio of H_2/CO at the catalyst surface depends on the diffusion coefficient of H_2 and CO in the liquid. Assuming that the ratio of the diffusion of H_2 to CO is 3.0, Akgerman (1990) estimated the mass flux ratio of H_2/CO to be between 1.5 and 3.36 (depending on the values of the Henry's Law constant) for a gas stream with H_2/CO ratio of 0.7. Thus for a mass transfer controlled reaction, the catalyst sees a higher H_2/CO ratio than the gas phase. If the process is gas-liquid mass transfer controlled, then the H_2/CO ratio at the catalyst surface depends on the mass transfer coefficients of H_2 and CO. Based on various correlations for mass transfer coefficients available in the literature, Akgerman (1990) estimates the ratio of mass transfer coefficients of H_2/CO to be between 1.5 and 2.0 (depending on the mass transfer coefficient calculation) for a gas stream with H_2/CO ratio of 0.7. Thus for a gas-liquid mass transfer control, the H_2/CO ratio at the catalyst surface is higher than the ratio in the gas phase.

Since the rate of mass transfer from the gas-liquid interface is proportional to the interfacial area, both the solids loading and bubble hydrodynamics are extremely important. Details of the bubble hydrodynamics is discussed in Section 6.0. An increase in the solids loading has been reported to result in a decrease in the gas-liquid interfacial area and results in a decrease in the effective rate of mass transfer [Akgerman, 1990].

The intrinsic kinetics associated with various F-T slurry reactions have been presented by Kuo (1981 and 1983) and Satterfield et al. (1983) and are summarized in Table 8.2 [Saxena et al., 1986]. In Kuo's (1981) expressions, r_{H2} is the hydrogen conversion rate. The Satterfield et al. (1983) expression gives the rate of H_2 plus CO conversion based on the following F-T reaction:

$$n\,CO + (m+n)\,H_2 \text{ ------> } C_nH_{2m} + n\,H_2O$$

where n is 3 and m is 3.5, based on the average organic product composition of C_3H_7. At low conversion, the partial pressure of H_2O is negligible and the Satterfield et al. equation in Table 8.2 simplifies to the first order form proposed earlier by Anderson (1956). Kuo (1983) considered two consecutive reactions, the Fischer-Tropsch reaction (r_1) followed by the water-gas shift reaction (r_2). Earlier Kuo (1981) had included the loading factor for the active component (Fe) to stress the significance of the water-gas shift reaction. The interpretation of the intrinsic kinetic rate constant requires the concentration of the reactants in the liquid phase, catalyst loading, residence time of the reactants, the degree of mixing of the fluid phases and the order of reaction [Saxena et al., 1986]. Since the order of reaction with respect to H_2 changes with the extent of conversion, Saxena et al. (1986) recommend caution when applying intrinsic rate expressions to conversion results in a F-T slurry reactor, especially at high conversions.

TABLE 8.2. Intrinsic Kinetic Rate Expressions for Fischer-Tropsch Catalyst. [Saxena et al., 1986].

Investigators	Kinetic Expression	Rate Constant
Satterfield *et al.* [1983]	$r_{H_2+CO} = a'b'P_{CO}P_{H_2}^2/(P_{H_2O} + b'P_{CO}P_{H_2})$	$a' = 2.39 \times 10^8 \exp(-19700/RT)$ $b' = 9.50 \times 10^8 \exp(-24000/RT)$ a' = μmol/g cat-min-kPa b' = kPa^{-1} $T = K$, $R = 1.987$ cal/K P_{CO} = Partial pressure CO, kPa P_{H_2} = Partial pressure H_2, kPa P_{H_2O} = Partial pressure H_2O, kPa
Kuo [1981]	$r_{H_2} = k_c'''(1-\varepsilon_g)(1-V)w_{Fe}C_{HL}$	$0.84 < k_{H^-} < 2.3$ ε_g = Gas holdup, cm^3 gas/cm^3 expanded slurry V = Volume raction catalyst in slurry, cm^3 catalyst/cm^3 slurry w_{Fe} = Iron concentration in liquid phase, gFe/cm^3 liquid C_{HL} = Liquid phase H_2 concentration, mol H_2/cm^3 liquid k_c''' = cm^3 liquid/g Fe-s
Kuo [1983]	$r_1 = k_1[H_2][CO]/([CO] + k_3[H_2O])$ $r_2 = k_2([CO][H_2O] - [H_2][CO_2]/k_4)/([CO] + k_3[H_2O])$	$k_1 = 0.50$ cm^3 liquid/g Fe-s $k_2 = 1.35$ cm^3 liquid/g Fe-s $k_3 = 0.2$ $k_4 = 37.5$ [ ] = Volumetric concentration in liquid phase

9.0 CATALYST WAX SEPARATION

One of the challenges of operating the slurry reactors is the separation of sub-micron to 50 micron sized catalyst particles from the product wax. The separation of catalyst-wax is necessary to avoid catalyst loss and avoid problems in wax upgrading. Catalyst-wax separation may be performed inside or outside the slurry reactor [Zhou, 1991]. Zhou (1991) has recently reviewed various catalyst-wax separation techniques and concluded that internal filters are subject to plugging risks and not suited for commercial plants. The concept of using high gradient magnetic separation has a potential of being used inside or outside the reactor. This technique is feasible as F-T catalysts are ferromagnetic. Preliminary results indicate the solids content can be reduced down to less than 0.015 wt% [Zhou, 1991]. In a laboratory scale study, Mobil demonstrated that the solids content can be reduced from 0.13 wt% to less than 0.015 wt%. Thus the magnetic separation technique can be employed as a catalyst-wax separator and also as a polishing technology. Although the magnetic separation technology has been demonstrated to a limited extent at the laboratory scale and holds the potential for success at the commercial scale, it is expensive and the technology is still in infancy.

Other potential techniques to separate catalyst-wax mixture include: (a) vacuum distillation and thermal cracking of vacuum bottoms, (b) chemical conversion of iron catalyst, (c) sedimentation by gravity, (d) centrifuges, and (e) pressure filtration. The first two techniques are unsuitable for F-T synthesis as it results in loss of catalyst. Sedimentation, centrifuges and pressure filtration are more suited for catalyst-wax separation in the F-T synthesis. Gravity sedimentation or settling is a commonly used simple and inexpensive device for catalyst-wax separation. This usually requires a long settling time of 1 to 3 hours to reduce solids content of reactor wax down to 0.1 wt% [Zhou, 1991]. The British Greenwich F-T pilot plant operated a gravity settling system fairly well [Farley and Ray, 1964]. However the efficiency of separation was low and was considered to be due to hindered agglomeration. The mechanical difficulties of operating the pilot plant were mainly those of efficient separation of catalyst and wax to maintain a constant level in the reactor.

Mobil used an on-line catalyst settling system and believes that it was demonstrated [Kuo, 1985]. Mobil's on-line catalyst-wax separation system can continuously withdraw up to 7 kg of clean reactor wax containing less than 0.1 wt% solids per day. The residence time in the settler is less than 3 hours. Mobil also noticed an increase in the catalyst size and is believed to be due to agglomeration or by the growth of heavy polymers on the outside of the catalyst particle. But the mechanism for the particle growth remains unclear [Kuo, 1985]. The particle growth was not reported in the British study [Farley and Ray, 1964]. Gravity settling can remove bulk of the catalyst from the wax, but a complete removal of catalyst particles could take an unacceptable long time. According to Zhou (1991), essentially no study was specifically specifically done on settling performance of the F-T catalyst-wax system.

Hydroclones offer a simple and inexpensive means of solid-liquid separation. Hydroclones have been used in the petroleum refining industry in somewhat similar fashion were catalyst fines are separated from the fractionator bottom slurries. Hydroclones have an advantage as the same size units employed in the pilot plant can be used in parallel in commercial plant, so there is no problem associated with scale-up. Hydroclones do not produce an overflow with very low solids content and therefore the overflow needs to be further clarified through other means, such as filtration to meet the solids content requirement for wax processing. Hydroclones may be used to recover bulk of the catalyst from the slurry stream to be recycled back to the reactor. A combination of hydroclone and filters appears the most feasible method to remove the solids from the wax in cost effective manner. Mobil had proposed such a system for removal of catalyst in their conceptual process design [Kuo, 1985]. However, the hydroclone system has not been demonstrated for F-T slurry separation [Zhou, 1991]. An investigation of the hydroclone efficiency, reliability and economics for the slurry F-T catalyst-wax separation is desirable.

Centrifuges are similar to the hydroclones in the mechanism of separation, expect that external energy is used to generate the centrifugal force required for catalyst-wax separation. This is usually a batch operation and is not preferred for continuous use in commercial operations.

Pressurized filtration is another important solid-liquid separation technique. The advantages of filtration is that it has a high efficiency of solids separation with reasonable particle size. However, poor mechanical history, high capital and operating costs, intermittent operation and difficulty in catalyst recovery makes filtration undesirable to remove solids from a slurry with a high solids loading. However it is an excellent device for small scale operation and for use in series with hydroclones or settlers. Pressurized filters have been used in the Rheinpreussen-Koppers Demonstration Plant [Kolbel and Ralek, 1980].

10.0 FUTURE DIRECTION

The F-T reactions are highly exothermic and non-nselective. The exothermicity of the reaction can be handled by a proper reactor design and depending on the H_2/CO ratio of the feed and the H_2/CO usage ratio, an appropriate reactor and catalyst with/without CO shift can be selected. The non-selective nature of the F-T reaction can be reduced by improvements in catalyst formulations which should be capable of yielding reproduceable results. Precipitated iron catalysts with promoters are perhaps the most promising catalyst. Programs funded by PETC and presentations at the Proceedings of the Liquefaction Contractors' Review Meeting (September 1991) indicate that significant efforts are in progress towards development of a poison resistant and selective catalyst with high activity, longevity and attrition resistance.

The source of H_2/CO for most demonstration and commercial facilities has been coal. Advanced coal gasifiers produce H_2/CO ratio of 0.5 to 0.67. The ratio can be modified to suit the H_2/CO usage ratio in gas phase reactor by adding a shift convertor prior to the reactor. The use of shift convertor is not necessary for slurry phase reactor as the catalyst will have CO shift capability.

The direction of the F-T reactor technology can be inferred from the work conducted at Sasol. The fixed bed ARGE reactor and the entrained bed reactor technologies have been commercially proven in mid 1950's. Although these technologies were proven, Sasol developed and commercialized bubbling fluidized bed technology in 1989 [Dry, 1990]. This development was undertaken to improve the economics of the technology. More recent information from Sasol indicates that the development of bubbling fluidized bed has been discontinued in favor of slurry reactor design. These developments indicate that slurry reactor promises to be the technology of the future for F-T synthesis. The most comprehensive study on the slurry reactor, other than the original Kolbel's work, has been made by Mobil. Mobil's work was hampered by a variety of operational problems and only

a few runs lasted long enough to obtain reliable information on the product distribution and catalyst deactivation [Srivastava, et al., 1990].

Air Products and Chemicals is currently operating a process development unit at LaPorte, which is capable of producing about 9 tons/day of methanol in slurry phase reactor of 22 in ID. Air Products plans to operate this unit for F-T synthesis in mid 1992. The F-T test to be conducted at LaPorte is expected to provide additional insight into the future direction of the slurry reactor technology.

There are engineering problems associated with the design and scale-up that need to be resolved. These include: exploring the fouling of heat exchange tubes due to catalyst deposition, catalyst separation from the wax and a better understanding of heat and mass transfer and hydrodynamic parameters. The ability to understand and engineer these factors into a workable reactor design are critical to the commercialization of the F-T slurry reactor technology.

11.0 SCALE-UP OF BUBBLE COLUMN FISCHER-TROPSCH REACTORS

The scale-up of a slurry reactor is a rather complex problem since in most cases reactor performance depends significantly upon the prevailing hydrodynamics, transport and mixing characteristics of the reactor. As discussed earlier (Section 6.0), the variations in these characteristics with the reactor scale-up are not well understood [Shah and Deckwer, 1985]. The applicability of the hydrodynamic and mixing models used for correlating the reactor performance can also depend on the scale of the reactor. Since the apparent reaction rate depends upon various transport resistances, as discussed in Section 8.0, the controlling resistance can also depend on the scale of the reactor. This implies that the reactor performance model used for small-scale reactor may not be useful for the large-scale reactor. On the other hand, German researchers have been successful in scaling up the laboratory scale reactor from 6 L suspension to 10,000 L suspension in a demonstration unit [Kolbel and Ralek, 1980]. The most difficult task was reported to be the uniform distribution of gas when the ratio of length to diameter of the reactor was decreased from 60:1 to 6:1.

The proper design and scale-up of a slurry reactor is facilitated by a good reactor design. A procedure normally followed for this purpose is shown in Figure 11.1 [Shah and Deckwer, 1985]. Application of the procedure requires the definition of throughput, nature of the reaction system, and the product yield structure desired. In addition it is desirable to have specifications on reactor geometry, adjustable reactor operating conditions and process data. The desired production rate, reactor geometry and the process data fix the bounds of the adjustable operating condition such as phase velocities, temperature, pressure and the direction of flow. The hydrodynamics is dictated by the reactor geometry, process data and adjustable operating parameters.

In design of a multiphase reactors, the non-adjustable are important parameters. These non-adjustable parameters include phase holdup, the interfacial areas, the heat and mass transfer properties, and the dispersion coefficients or the mixing parameters. These parameters are also dependent on the reactor geometry,

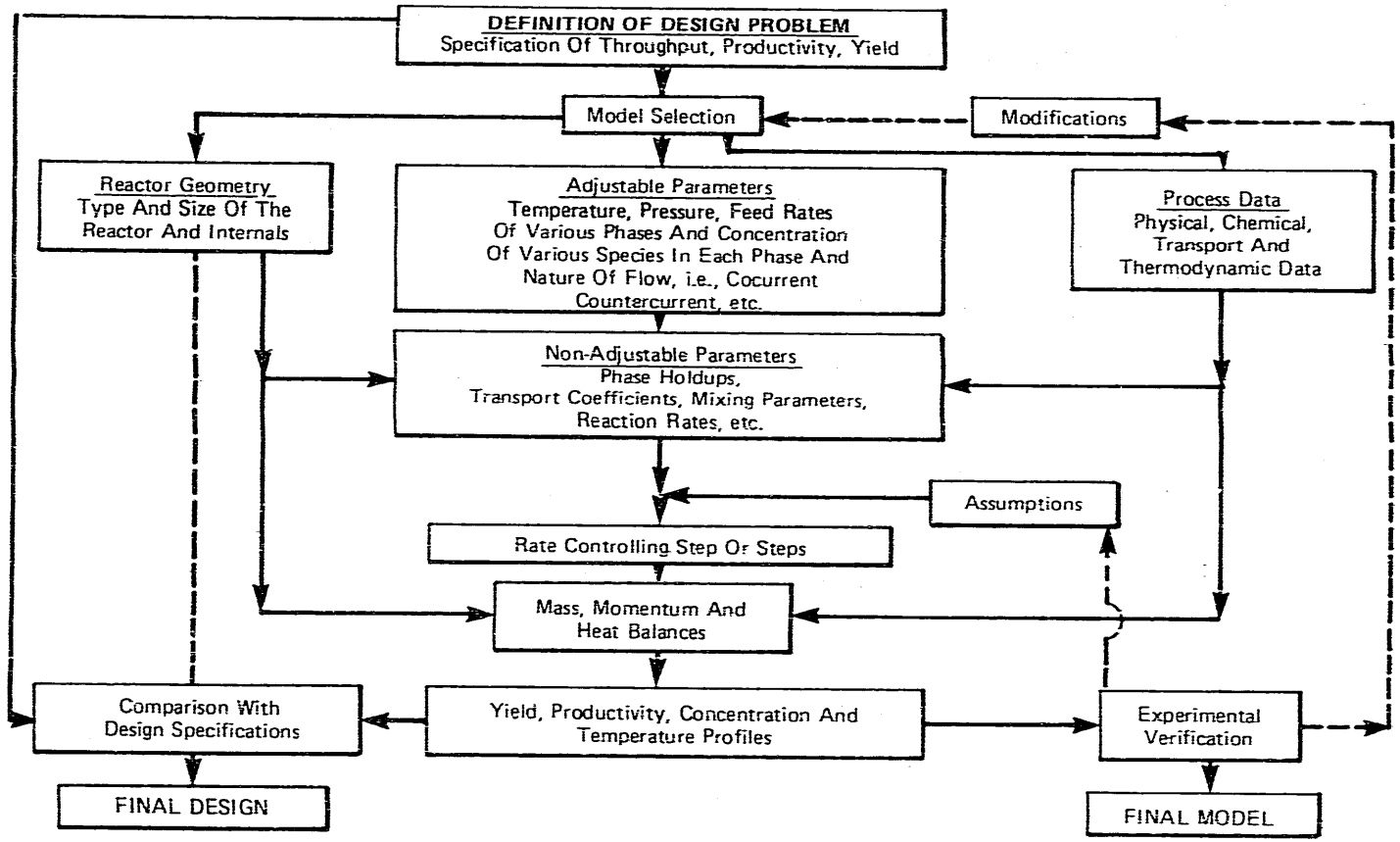

FIGURE 11.1. A Flow Path for the Design and Modeling of Reactors [Shah and Deckwer, 1985].

adjustable operating conditions and process data. Various methods of estimating these parameters have been discussed in detail in Section 6.0.

Based on the physical and chemical phenomena occurring within the reactor, reactor geometry and reaction parameters, the adjustable and non-adjustable, the reactor model equations are derived. As mentioned in Section 6.0, a number of researchers have been involved in developing reactor models to design slurry reactor for F-T synthesis [Bukur et al., 1990, Deckwer et al., 1980, Kuo, 1985, Saxena et al., 1986, Shah and Deckwer, 1985]. Work is also at progress at Viking Systems International to develop a model to design slurry reactor for indirect liquefaction [Prakash and Bendale, 1991]. The models can then be used to scale-up the reactor. Reactor scale-up usually implies an increase in the reactor diameter, length, and gas velocities. These changes are accompanied by changes in the flow regime, phase holdup characteristics, axial and radial mixing and transport coefficients (Section 6.0). Shah and Deckwer (1985) have reviewed the scale-up of slurry reactors and summarized the effect of scale-up variables on the non-adjustable parameters, and is shown in Table 11.1. Table 11.1 shows the effect of increase in a number of independent scale-up variables on the hydrodynamic, transport and mixing characteristics of the bubble column.

TABLE 11.1. General Trends of Reactor Scaleup Variables on Bubble Column Reactor Dynamic Variables [Shah and Deckwer, 1985].

Effect on/Increase in	Reactor Length	Reactor Diameter	Gas Velocity	Liquid Velocity[a]	Solids Concentration
Flow regime	Generally no change except near transition boundary	May change	May change (around 5–10 cm/sec)	Most likely will not change under practical range of operation	May change at high solids concentration and for large particle size
Gas holdup	For very tall bubble columns holdup may decreases due to coalescence	Essentially no change	Increase	Essentially no change	May change-effect is complex and not well known yet
Gas–liquid interfacial area	May decrease in tall bubble column	Essentially no change if proper gas distributor is used	Increase	Essentially no effect unless liquid velocity is large	Effect not known—depends on particle size and concentration—decreases for larger particles and concentrations
Volumetric gas–liquid mass transfer coefficient ($k_L a$)	May decrease along column length	Essentially unchanged	Increase	No or small change	Effect is quite complex—depends on particle size and concentration usually decreases
Gas-phase dispersion	No observed effect	Increase	Increase	No observed effect	Not known—most probably only small effect under the practical range of operations
Liquid-phase dispersion	Observed increase along length	Increase	Increase	No observed effect	No effect under most practical conditions—may show effect for large particles
Solid-phase dispersion	No observed effect	Increase	Increase	No observed effect	Small effect at large concentrations
Slurry-wall heat	No observed effect	Increase	Increase	Some increase	Small increase may show optimum

[a]Generally liquid velocity range of 0–3 cm/sec is considered to be of most practical importance. Gas to liquid velocity ratio in most practical operations is of the order of 10 to 1.

12.0 RECOMMENDATION

For the proposed pilot plant, the objective is to convert syngas generated from coal to hydrocarbon fuels. The H_2/CO ratio generated from modern coal gasifiers is in the range 0.5 to 0.67. Syngas rich in CO is unsuitable for fixed bed reactors as this leads to carbon deposition and different H_2/CO usage ratio. Thus for a fixed bed reactor a CO shift reactor would be needed to increase the H_2/CO ratio, in order to match the H_2/CO usage ratio with the feed H_2/CO ratio and to minimize catalyst deactivation due to carbon deposition. This would result in added cost. Use of slurry reactor, on the other hand, eliminates the need for the CO shift reactor. Furthermore when compared to a fixed bed reactor, a slurry reactor, has a high conversion per pass, requires about one fourth the cooling surface area, can operate over a wide temperature range (200 to 350°C compared to 200 to 250°C for fixed beds), and for a given throughput the volume of the reactor system is lower. Heat transfer limitations of the fixed bed also results in thermal gradients causing coke formation and catalyst deterioration. Due to low conversion and heat transfer limitations, gas recycle is required for fixed bed systems. This results in additional costs due to recompression of gas. Another drawback of the fixed bed reactor is that for catalyst regeneration and reloading of fresh catalyst requires shut down of the system. Whereas, a slurry reactor this step can be conducted without interruption. Thus both the capital and operating costs of the slurry reactor system is much more attractive, when compared to the fixed bed system. A review of the literature indicates that most of the current work on catalyst development is geared towards the slurry reactor technology. Very little has been reported in the recent literature on the development of catalyst for fixed bed reactor technology. Based on these findings, building of the fixed bed reactor system for the proposed pilot plant study is not recommended.

The three critical factors needed to further develop and commercialize the slurry phase F-T technology are: (1) the compactness of the reactor, (2) improvements in catalyst activity and selectivity, and (3) catalyst-wax separation. It is recommended

that a more active and more selective catalyst such as those formulated by Air Products should be investigated. Further work needs to be done in catalyst pretreatment procedures, promoters, and examination of its effect on conversion, product distribution and selectivity. Improvements in the physical attrition, activity and poison resistance properties of the catalyst is also needed.

Based on the information available in the literature, the following conditions are recommended for operating and designing the slurry reactor:

Conditions	Operating Range	Normal Operation
Temperature, °C	200-380	250
Inlet Pressure, psig	300-550	400
Space Velocity, Nl/hr-kg Fe	1200-6000	3400
Catalyst Loading, wt%	4-50	15
Superficial Gas Velocity, cm/s	3-30	10

For compactness of reactor an increase in conversion along with high solids loading and higher superficial gas velocities is required. Although solids concentration of up to 20 wt% has been used, work at Air Products indicates that upto 50 wt% is feasible for methanol synthesis. Over 35 wt% solids has been theorized to make the slurry reactions mass transfer limited. For F-T synthesis it is expected that the solids loading will be less than that of methanol synthesis. Hence the recommended range for solids loading is 4 to 50 wt%. Increased solids loadings can result in an increase in viscosity of the suspension causing a decrease in the interfacial area and ultimately resulting in reduced conversion. Use of bimodal catalyst size distribution should also help in reducing the slurry viscosity.

Superficial gas velocities of up to 12 cm/sec have been successfully used in the F-T synthesis without loss in conversion. Air products has used superficial gas velocities of up to 22 cm/sec for methanol synthesis. With improvements in catalyst activity and reaction time, and with improvements in technology to limit

backmixing, it is expected that velocities of up to 30 cm/sec should be possible. Therefore the recommended range for superficial gas velocity is 3 to 30 cm/sec.

A commercial slurry bed reactor would operate in churn turbulent flow regime. Based on the information available, the recommended diameter for the pilot plant slurry reactor should be at least 4" ID to avoid wall effects. The L/D ratio in the pilot plant studies is generally greater than 35, while in commercial reactor the L/D ratio is in the range 5 to 10. The recommended L/D ratio for the slurry reactor is between 40 and 50 for the proposed pilot plant.

The design of gas distributor for smaller and uniform bubbles is critical. Use of sintered metal plate has been found to be capable of producing small and uniform bubbles compared to gas nozzles. However, sintered metal plates require a greater pressure drop.

Catalyst-wax separation is another important factor that needs to studied. Three methods: (1) settling, (2) pressure filters and (3) hydroclones followed by pressure filters, appear to be promising conventional methods and needs to be evaluated. Catalyst particle size, slurry viscosity and differences in the densities of catalyst and wax determine the efficiency of separation. Since the catayst size is of the order of sub-micron to micron range, use of solvent extraction coupled with the aforementioned physical separation is recommended for further evaluation.

13.0 LITERATURE CITED

Air Products and Chemicals, Inc., "Catalyst and Reactor Development For a Liquid Phase Fischer-Tropsch Process," Final Report, Task 2, DOE/PETC Contract No. DE-AC22-80PC30021. (Author's name not given.)

Air Products and Chemicals, Inc., "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation and Support Studies," Topical Report. Task 2.0, Run E-5, Gas Hold-up and Equipment Evaluation Studies. DOE/PETC Contract No. DE-AC22-87PC90005. (Author's name not given.)

Akgerman, A., Final Report, DE-AC22-84PC70032, 1988.

Akgerman, A., "Slurry Reactor Design Studies", in Final Report- Slurry Reactor Design Studies, DOE Report No. DE-AC22-89PC89867, 1990.

Albal, R. S., Y. T. Shah, N. L. Carr, and A. T. Bell, "Mass Transfer Coefficients and Solubilities for Hydrogen and Carbon Monoxide under Fischer-Tropsch Conditions," Chem. Eng. Sci., 39, 305 (1984).

Anderson, R.B. et al., J. Am. Chem. Soc., 71, 183 (1949); Ref. 189 in Dry (1981).

Anderson, R.B., Catalysis Vol IV, Ed. P.H. Emmett, Reinhold, NY, 1956.

Anderson, R.B., F.S. Karn and J.F. Schulz, U.S. Bur. Mines. Bull., 614 (1964).

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

Bhatt, B.L., D.M. Herron and E.C. Heydorn, "Development and Demonstration of a One-Step Slurry Phase Process for the Co-Production of Dimethyl ether and Methanol", Proceedings of Liquefaction Contractors' Review Meeting, Pittsburgh, PA, 1991.

Brotz, W., Z. Elektrochem., 5, 301 (1949); Ref. 190 in Dry (1981).

Bukur, D. B., X. Lang, S. A. Patel, W. H. Zimmerman, M. P. Rosynek, and H. P. Withers, Texas A&M Univ. (TAMU), Proc. 8th Indirect Liquefaction Contractors' Review Meeting, Pittsburgh, 1988.

Bukur, D. B., S. Ledakowice, and M. Rama Krishna, "Fischer-Tropsch Synthesis Over Iron/Silica Catalysts," DOE Contractors' Review Meeting, Pittsburgh, PA Nov 6-8, 1990.

Bukur, D. B., X. Lang, D. Mukesh, W. H. Zimmerman, M. P. Rasynek, and C. Li, "Binder/Support Effects on the Activity and Selectivity of Iron Catalysts in the Fisher-Tropsch Synthesis," Ind. Eng. Chem. Res., 1990, 29, 1588-1599.

Bukur, D. B., J. G. Daly, and S. A. Patel, "Hydrodynamics of Three-phase Slurry Fischer-Tropsch Bubble Column Reactors," Final Report, DOE-AC22-86PC90012, July 1990.

Bussemeier, B., C.D. Frohning and B. Cornils, Fischer-Tropsch Synthesis, in Encyclopedia of Chemical Processing and Design, Vol 22, 81 (1983).

Calderbank, P. H. and M. B. Moo-Young, "The Continuous Phase Heat and Mass Transfer Properties of Dispersions," Chem. Eng. Sci. 16, 39 (1961).

Calderbank, P. H., F. Evans, R. Farley, G. Jepson, and A. Poll, "Rate Process in the Catalyst - Slurry Fischer-Tropsch Reaction," Catalysts in Practice - Instn. Chem. Engs., 66 (1963).

Chaffe, A. L., I. Campbell, and N. Valentine, Appl. Catal., 47, 253, 1989.

Deckwer, W-D, Y. Louisi, A. Zaidi, M. Ralek, "Hydrodynamic Properties of the Fischer-Tropsch Slurry Process," Ind. Eng. Chem. Process Des. Dev., 19, pp. 699-708, 1980.

Derbyshire, F. and D. Gray, Coal Liquefaction in Ullmann's Encyclopedia of Industrial Chemistry, Volume A7, 197 (1986).

Dry, M.E., The Fischer-Tropsch Synthesis, Chapter 4 in Catalysis- Science an Technology, Ed. J.R. Anderson and M. Boudart, Springer-Verlag, NY, 1981.

Dry, M.E., The Sasol Fischer-Tropsch Process, in Applied Industrial Catalysis, Ed. B.R. Leach, Academic Press, NY, 2, 167-213 (1983).

Dry, M.E., "Experience with Fluidized Bed Fischer-Tropsch Reactors at Sasol", Proceedings of the Indirect Liquefaction Contractors' Review Meeting, November 6-8, 1990.

Ekerdt, J.G. et al., J. Catalysis, 58, 170 (1979); Ref. 157 in Dry (1981).

Farley, R. and D.J. Ray, J. Inst. Petrol., 50(482), 27 (1964).

Fiato, R. A., G. W. Rice, S. Misco, S. L. Soled, U.S. Patent No. 4,687,753, 1987 (assigned to Exxon).

Fox, J.M., B.D. Degen, G. Cady, F.D. Deslate and R.L. Summers, "Slurry Reactor Design Studies", Final Report to U.S. DOE, Report No. DE-AC22-89PC89867, June 1990.

Frohning, C.D., H. Kolbel et al., Fischer-Tropsch Process, in Chemical Feedstocks from Coal, Ed. J. Falbe, John Wiley, NY, 1982.

Geertsema, A., "Chemicals from the Sasol Plants", Proc. Seventh Annual Pittsburgh Coal Conf, p571 (1990).

Haag, W.O., J.C.W. Kuo and I. Wender, "Gasification for Synthesis of Fuels and Chemicals", in COGARN Report on Coal Gasification, DOE/ER-0326 (1987).

Herrington, E.F.G. and L.A. Woodward, Trans. Faraday Soc., 35, 958 (1939).

Hughmark, G.A., "Hold-up and Mass Transfer in Bubble Columns, " Ind. Eng. Chem. Pro. Des. Dev. 6, 218 (1967).

Karn, F.S. et al., J. Phys. Chem., 64, 446 (1960); Ref. 192 in Dry (1981).

King, J.G., J. Inst. Fuel, 11, 484, 1938.

Kolbel, H., Ackerman, P., and Engelhardt, H., "Proceedings 4th World Petroleum Congress," Section W/C, P. 227, Corlo Colombo Publishers, Rome 1955.

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

Kuo, J.C.W., "Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline", U.S. DOE Quarterly Report No. DOE/PC/30022-2, January-March 1981, April 1981.

Kuo, J.C.W., "Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline", U.S. DOE Final Report No. DOE/PC/30022-10, 1983.

Kuo, J.C.W., "Two-stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels, "Mobil Corp., U.S. DOE Technical Report, DE-AC22-83PC60019, 1985.

Lee, A.L. et al, ACS Div. Fuel Chem., Preprints, 14, 126 (1970); Ref. 185 in Dry (1981).

Luyten, L. et al., Bull. Soc. Chim. Belges., 54, 303 (1945); Ref. 187 in Dry (1981).

Madan, R.J. and W.F. Taylor, Adv. Chem. Ser. 178, 93 (1979).

McKee, D.W., J. Catalysis, 8, 240 (1967); Ref. 191 in Dry (1981).

Phung Quach, T.Q. et al., J. Appl. Chem. Biotechnol., 28, 378 (1978); Ref. 193 in Dry (1981).

Prakash, A. and P.G. Bendale, "Design of Slurry Reactor for Indirect Liquefaction Applications", Proceedings of the Liquefaction Contractors' Review Meeting, Pittsburgh, PA, 1991.

Quicker, G. and W.D. Deckwer, "A Further Note on Mass Transfer Limitations in the Fischer-Tropsch Slurry Process, "Chem. Eng. Sci., 36, 1577 (1981).

Rice, G.W., R.A. Fiato, S.L. and Soled, U.S. Patent No. 4,659,681, 1987; 4,688,647, 1987; 4,788,222, 1988, assigned to Exxon.

Saletore, D.A. et al., IEC Process Des. Dev., 16, 70 (1977); Ref. 188 in Dry (1981).

Satterfield, C.N., T. Bartos, G.A. Huff, R. Hanlon, D. Matsumoto and H. Stenger, "Fischer-Tropsch Synthesis in Slurry Reactor Systems, U.S. DOE Quarterly Report No. DOE/PC/40771-10, August-October, 1983.

Saxena, S.C., M. Rosen, D.N. Smith and J.A. Ruether, "Mathematical Modeling of Fischer-Tropsch Slurry Bubble Column Reactors", Chem. Eng. Commun., 40, 97 (1986).

Saxena, S.C., N.S. Rao, R. Vadivel, S. Shrivastav, A.C. Saxena, B.B. Patel, et al. "Heat Transfer Investigations in a Slurry Bubble Column," DOE/PETC, DE-AC-22-86-PC90008, 1991.

Shah, Y.T., S. Joseph, D. N. Smith, and J. A. Ruether, "On the Behavior of the Gas Phase in a Bubble Column With Ethanol-water Mixture," Ind. Eng Chem. Pros. Des. Dev., 24, 1140, 1985.

Shah, Y.T. and W.D. Deckwer, "Fluid-Fluid Reactors", in Scale-Up of Chemical Processes, Eds. A. Bisio and R.L. Kabel, John Wiley, NY, 1985.

Smith, J., K.M. Gupte, T. M. Leib, and J.C.W. Kuo, "Hydrodynamics Studies of Fischer-Tropsch Bubble Column Systems, "AIChE Summer National Meeting, Philadelphia (1984).

Srivastava, R.D., Private Communication, 1991.

Srivastava, R.D., V.U.S. Rao, G. Cinquegrane and G.J. Stiegel, "Catalysts for Fischer-Tropsch", Hydrocarb. Proc., 62, 59, (1990).

Stiegel, Gary, Private Communication, 1991.

Storch, H.H., N. Golumbic and R.B. Anderson, The Fischer-Tropsch and Related Syntheses, Wiley, NY, 1951.

Thompson, G.J., M.L. Riekena and A.G. Vickers, "Comparison of the Fischer-Tropsch Systems- Phase I Final Report", U.S. DOE, DE-AC01-78ET10159 (1981).

Wender, I. and K.S. Seshadri, The Indirect Liquefaction of Coal", Report submitted to PETC.

Withers, Jr., H.P., K.F. Eliezer and J.W. Mitchell, "Novel Fischer-Tropsch Slurry Catalysts and Process Concepts for Selective Transportation Fuel Production," DOE/PETC DE-AC22-84PC70030, December 1987.

van Herwijnen, T. et al., J. Catalysis, 28, 391 (1973); Ref. 186 in Dry (1981).

van Vuuren, D.S., "Assessment of the Techno-Economic Potential of Fischer-Tropsch Slurry Reactors", CSIR Report No. CENG 655 (1987).

Zaidi, A., Y. Louisi, M. Ralek, and W. D. Deckwer, "Mass Transfer in the Liquid Phase Fischer-Tropsch Synthesis," Ger. Chem. Eng., 2, 94, 1979.

Zarochak, M.F. and M.A. McDonald, Proc. 7th Indirect Liquefaction Contractors' Review Meeting, Pittsburgh, 1987.

Zhou, P.Z., "Status Review of Fischer-Tropsch Slurry Reactor Catalyst/Wax Separation Techniques", U.S. DOE Report No., DE-AC22-89PC88400 (Subtask 43.02), Feb 1991.

APPENDIX A: DISCUSSION WITH PROF. DRAGOMIR BUKUR

On 17 July 1991, a discussion was held with Prof. Bukur current status of bubble column slurry reactor technology for Fischer-Tropsch (F-T) synthesis, major design parameters, future direction, key technical issues to be resolved before commercialization occurs, and Kellogg's reactor concept. Almost 2-1/2 hours were spent on the subject. A summary is outlined below:

- Bukur thinks that a slurry F-T reactor should have a high superficial velocity--it is almost a necessity in cases where a high solid concentration is to be used. A magnitude of 8 to 10 cm/sec or even higher can be used. Regarding the effect of velocity on bubble size, it has been established that bubble size increases with increasing velocity and that larger bubbles are not desirable for enhanced mass transfer. But, there will always be smaller bubbles present in the swarm. Therefore, higher superficial velocity is the direction to take.

- He said that slug flow occurs only in small diameter reactors and should not be a concern for an 8" diameter PDU proposed for PETC.

- Catalyst pretreatment is very important, but no well-defined procedures have emerged yet. Pretreatment methods would most likely vary from catalyst to catalyst. Storage behavior of pretreated catalysts has not been studied. Bukur believes that it should be possible to store activated catalyst, if it is kept under reducing or inert atmosphere with wax. He does not expect storage temperatures to have any effect on activity. Pilot plant work by Mobil indicates need for pre-activation even for make up catalysts.

- Mobil's reported axial variation of catalyst concentration must be evaluated in the context of other variables. With an appropriate choice of conditions, such variation can be eliminated.

- Causes of bed slumping, observed in Mobil pilot plant work are unknown. This is related to catalyst agglomeration, which is a complex phenomenon and not well-understood at all. Furthermore, settling tendency is a strong function of particle size, more so than velocity.

- Foaming: He said that foaming decreases with an increasing superficial velocity and reactor diameter. He believes that foaming should not be a concern in design of an Indirect Liquefaction PDU.

- Attempts are being made to develop new catalysts (Fe-containing zeolites) to control Schulz-Flory distribution up to a carbon number of 11. Supported catalysts have also been tried. These new catalysts may have promise but he does not know. UOP is active in new catalysts development.

- Rheinpreussen demonstration work is a bench mark in this technology. Others have confirmed most of Rheinpreussen's results except catalyst selectivity. Indeed, Mobil repeated these observations, but could not reproduce selectivity.

- His major concern regarding commercialization of Fischer Tropsch technology is separation of catalyst from wax product. Use of larger particles may not help as catalyst disintegrates during reaction. The catalyst size, therefore, decreases with a prolonged operation. Millipore is developing new filters which should be evaluated for possible applications with F-T technology.

- Bukur had following comments on MWK's suggested reactor design:

  •New design concept, uncharted territory, which, to his knowledge, has not been studied by any group. Although design and scale-up principles of distillation towers are well known, this is a reactor with relatively high concentration of solids. It is not a distillation column.

  •Internals (trays) and pumpback arrangement is complicated when compared to the simple bubble column reactor.

  •Effect of catalyst removal from reactor and pumping on catalyst performance is a major concern to him. He feels that catalyst should not be removed from the reaction environment. By doing this, catalyst may get deactivated. Attrition due to pumping is another concern.

APPENDIX B

LAPORTE METHANOL PLANT VISIT:

SUMMARY OF DISCUSSION AND OBSERVATIONS

On 13 Aug 1991, Kellogg members from PETC Pilot Plant project visited Air Products/DOE Alternate Fuels Demonstration Unit (AFDU) in LaPorte in order to obtain information regarding design features, Air Products' experience, and operating problems, if any. Such information would be useful in designing the pilot plant and avoiding potential pitfalls. Members from Kellogg and Air Product employees who met are as follows:

Kellogg	Air Products
R. Daze	Ed. G. Heydorn, LaPorte Pilot Plant, Manager, Host
G. Henningsen	John L. Henderson, Technology Manager
P. Sadhukhan	

Mr. Henderson took us around the plant. Outline of the discussion and observations from the tour are summarized.

- Air Products experience spans about 8 years.
- Early use of bubble caps as gas distributors did not work well - large bubbles and bubble coalescence were the main problems.
- Sparger worked very well - generating small bubbles, which are desirable. Also, with sparger, no plugging problems encountered. When spargers are restarted following catalyst settling during shutdown, they worked as well as before solids settling.
- Up to 50% solids (catalyst) concentration has been used successfully. With such a high solid loading, slurry looks like mud. The highest superficial gas velocity used with 50% solids concentration is 0.7 ft/sec (21.3 cm/sec).
- Latest reactor operating mode (LP-3) used coils inside and does not need any external circulation of slurry. No coil erosion or solids build-up problems have been observed. Earlier operations (LP-2) used coils outside with slurry circulation for heat transfer. Currently coils occupy only 4% of reactor cross-section. For Fischer-Tropsch synthesis outside coil should not be ruled out due to higher heat generation per mole of synthesis gas.
- A gamma ray device is used to measure reactor bed density - the device can slide vertically so measurement can be made at any axial position.

- No foaming has been observed or detected in the reactor during operation.
- Catalyst was the "precursor" used for making pellets of fixed-bed methanol catalyst. Catalyst bulk activity in terms of (kg methanol formed)/(kg catalyst hr) is higher than in fixed bed.
- Early operations with ebullating bed mode did not work due to catalyst pellet disintegration.
- The company has developed procedures for testing catalysts in a stirred autoclave and for predicting activity expected in LaPorte reactor using the autoclave data. Such predictions and observations usually match well.
- Slurry pump is centrifugal (Lawrence pump) that worked well. Over the years, Air Products developed proprietary expertise in pump seals and slurry handling. Mineral oil return pumps are capable of handling slurry, albeit there are usually little solids in the oil collected.
- Plant has been operated successfully both in methanol and methanol-dimethyl ether modes.
- One more oxygenate mode run is planned before the proposed F-T operation. However, actual sequence of oxygenate and F-T operation is subject to change.
- Slurry reactor is essentially isothermal - - few degrees difference between the top and bottom locations. Isothermal in radial direction too.
- The plant is very well maintained.

END

DATE
FILMED
5/11/92