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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

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Prepared by

THE M. W. KELLOGG COMPANY

HOUSTON, TEXAS

Job 7508

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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) $CO + 2H_2 = (\text{-}CH_2\text{-}) + H_2O$

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

The overall reaction is represented as:

(3) $2CO + H_2 = (\text{-}CH_2\text{-}) + CO_2$

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).

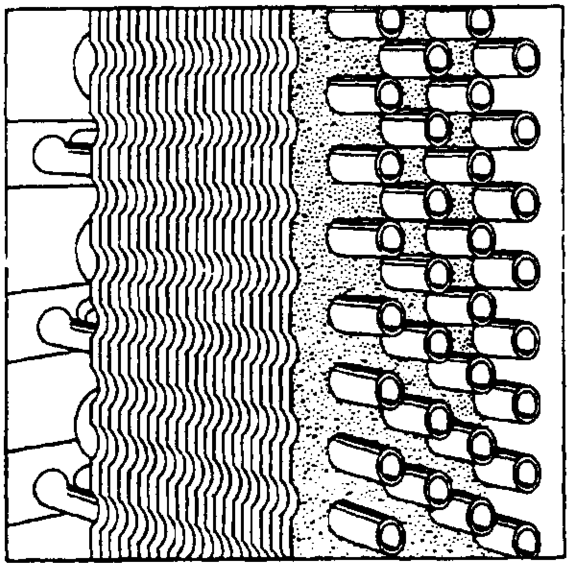

FIGURE 3.1: Section of lamella bundle [Bussemeier, et al., 1985].

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

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[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 Fluid-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[a]	6[a]	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

[a] 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

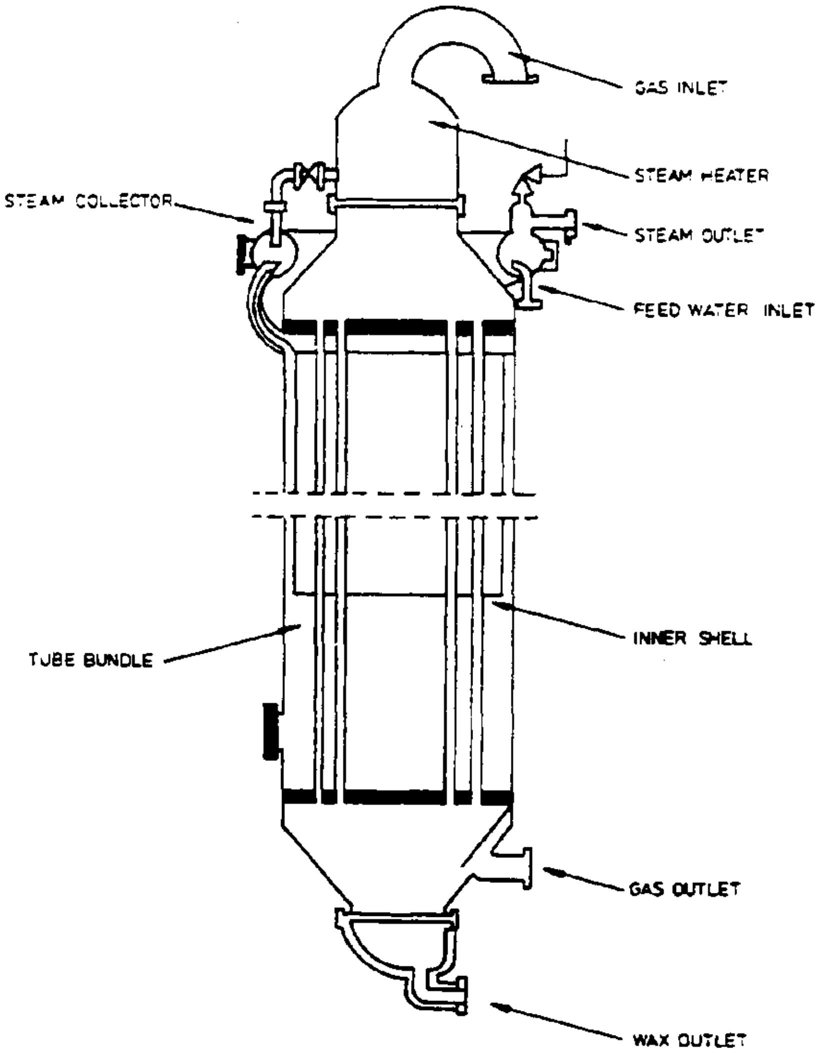

FIGURE 4.1. ARGE Commercial Fixed bed Fischer-Tropsch Reactor at Sasol. [Dry, 1981].

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.

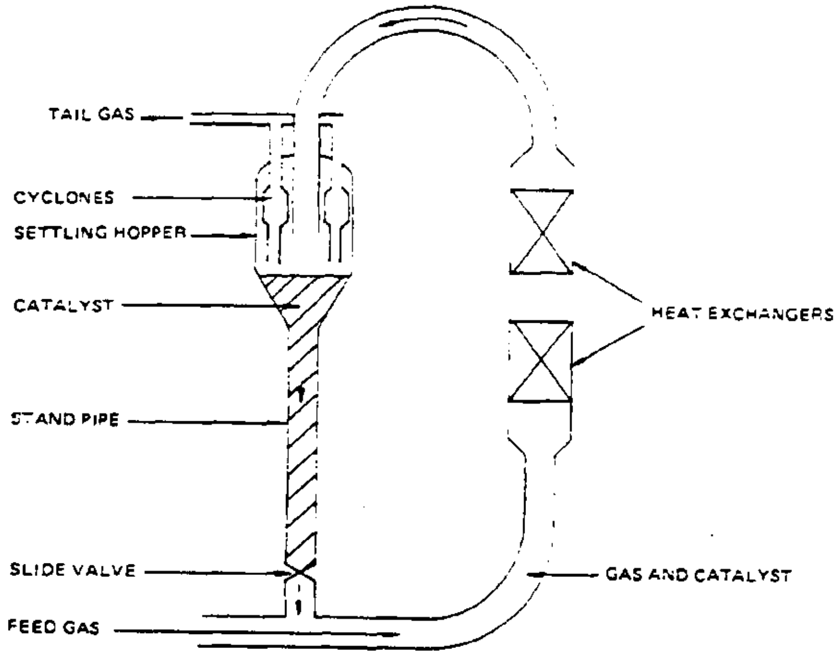

FIGURE 4.2. Synthol Circulating Fluidized Bed Reactor [Dry, 1981].

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 x height, m	3x17	2.2x36	3x75
C_1	5.0	10.0	11.0
$C_2^=$	0.2	4.0	
C_2	2.4	6.0	7.5
$C_3^=$	2.0	12.0	
C_3	2.8	2.0	13.0
$C_4^=$	3.0	8.0	
C_4	2.2	1.0	11.0
C_5-C_{12}	22.5	39.0	37.0 (C_5-191°C)
C_{13}-C_{18}	15.0	5.0	11.0 (191-399°C)
C_{19}-C_{21}	6.0	1.0	3.0
C_{22}-C_{30}	17.0	3.0	(399-521°C)
C_{30}	18.0	12.0	0.05 (>521°C)
Nonacid chemicals	3.5	6.0	6.0
Acids	0.4	1.0	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.