

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) CO₂ 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 CO₂ and H₂O 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 m² is required for cooling coils for conversion of 1000 m³ of syngas per hour, heat removal with internal cooling coils is possible with temperature gradient of +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						

^aProcess 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.

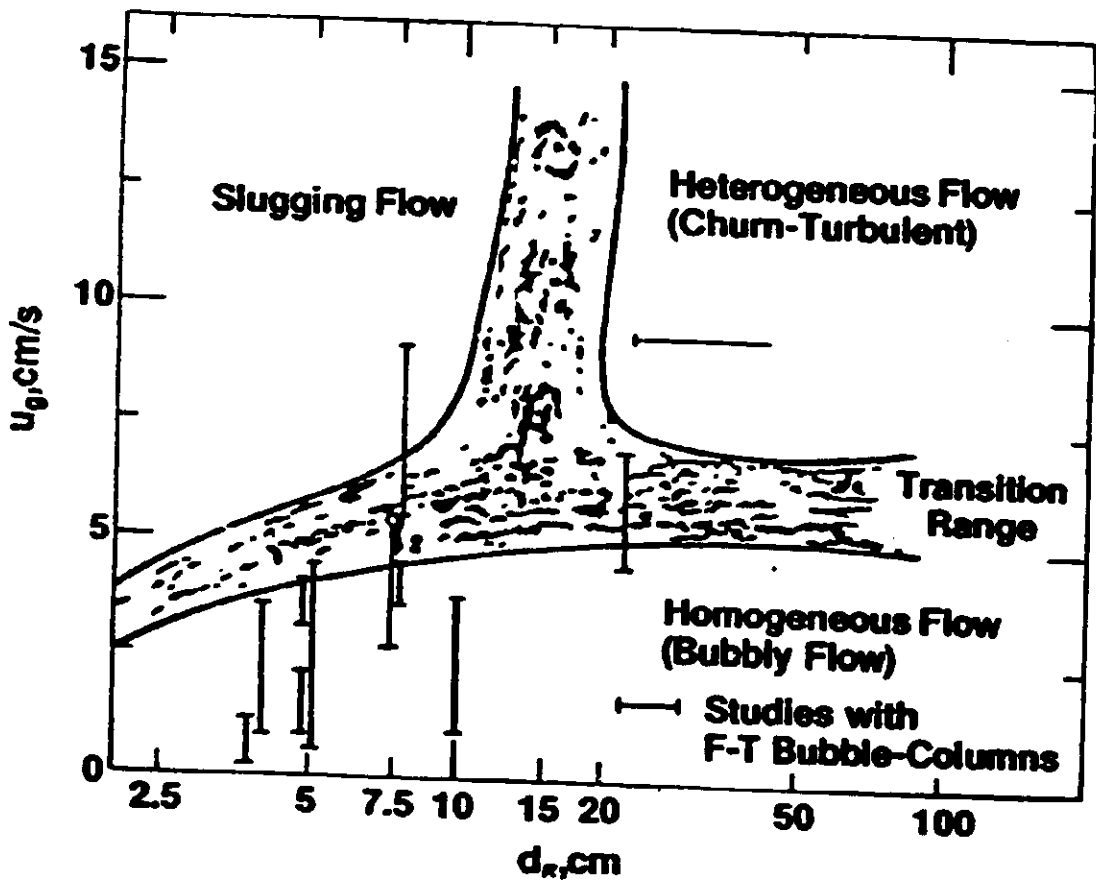


FIGURE 6.1 Flow Regimes for Bubble Columns.

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 H₂, 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)(ft²)(°F) and the overall coefficient 44 to 96 Btu/(hr)(ft²)(°F). 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 is 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 50 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.

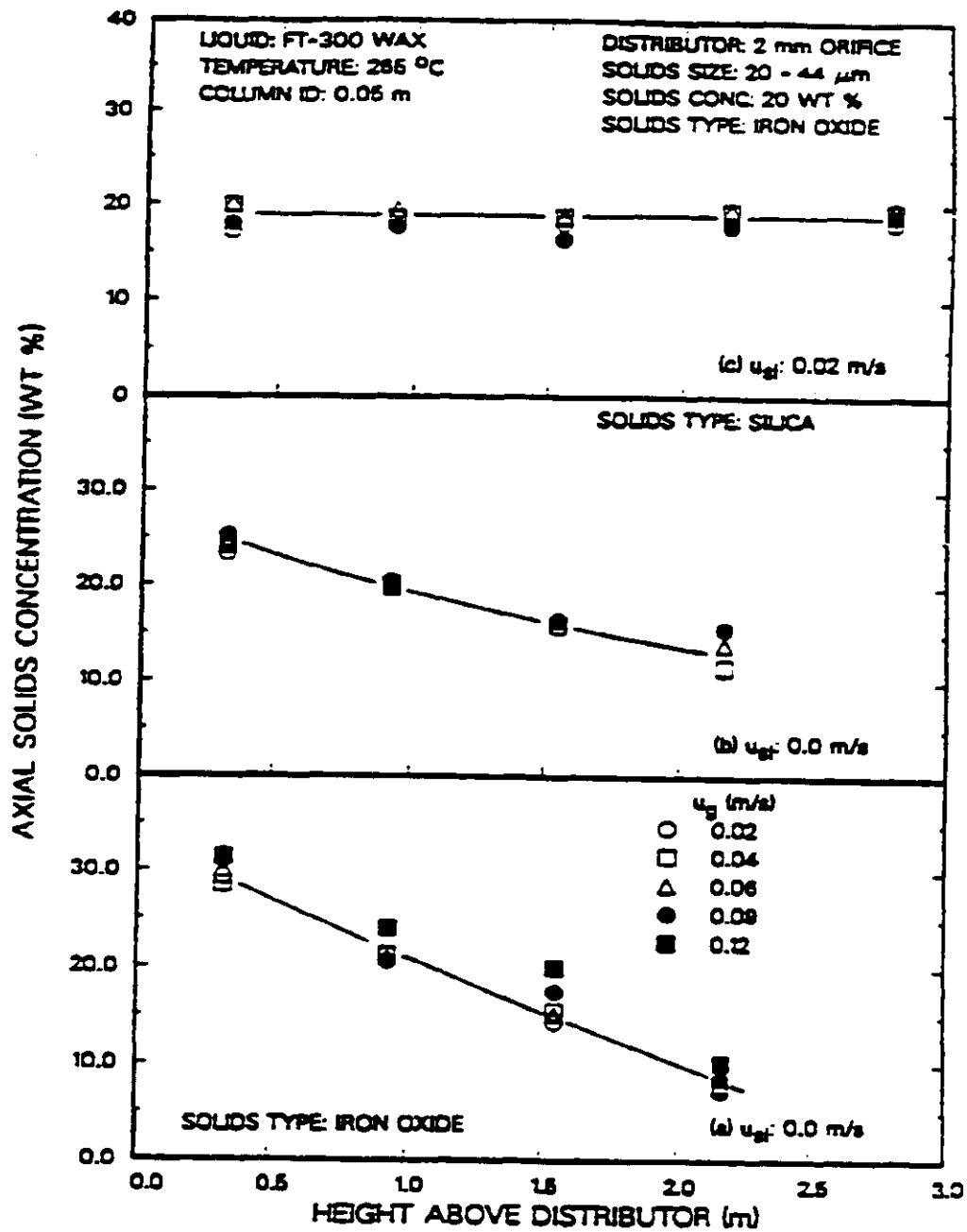


FIGURE 6.2. Effect of Axial Position and Superficial Gas Velocity on Solids Concentration [Bukur et al., 1990].

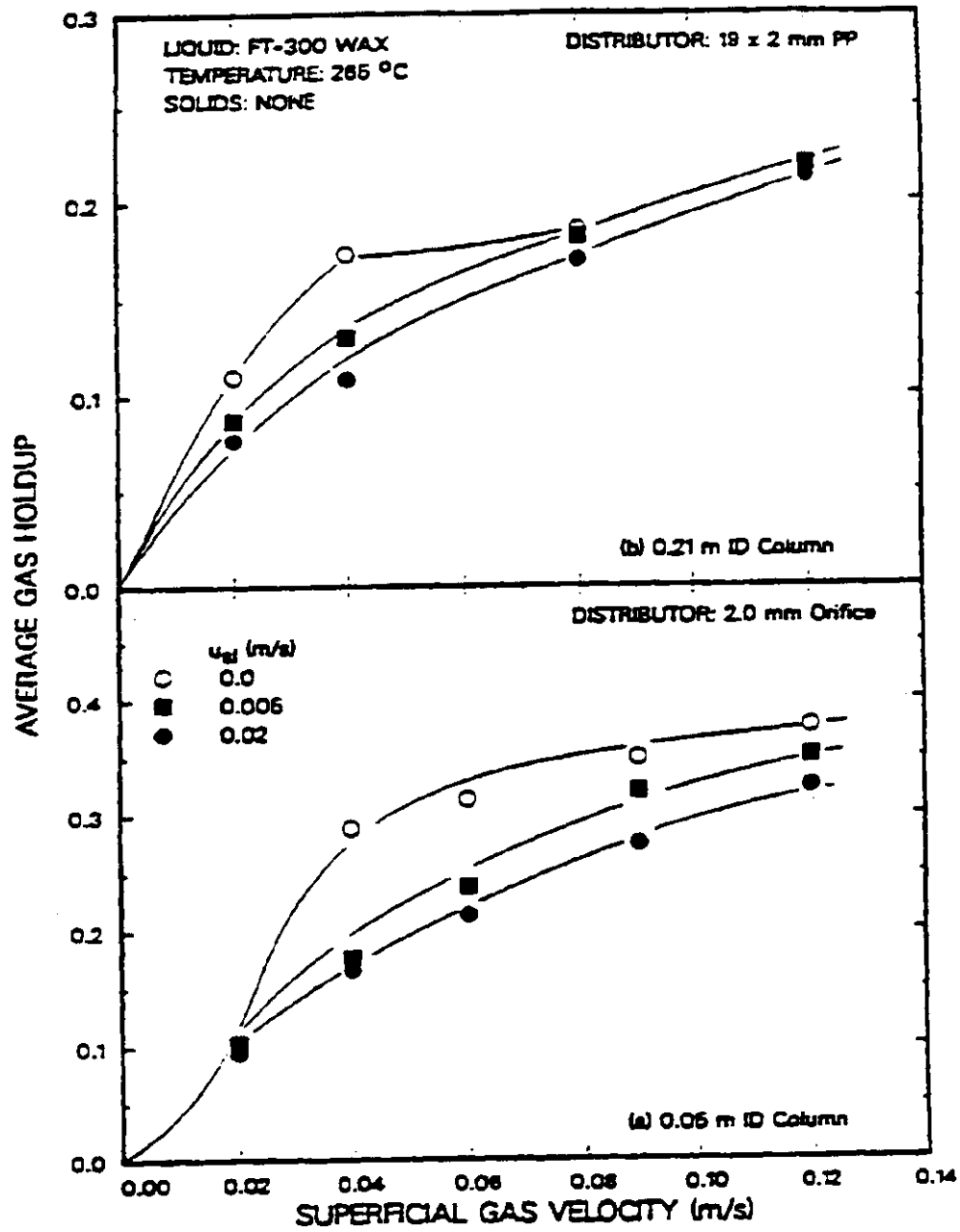


FIGURE 6.3. Effect of Superficial Gas Velocity on Average Gas Holdup [Bukur et al., 1990].

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 (SiO₂): 100 Fe/5 Cu/4.2K/x SiO₂ (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 SiO₂.

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 (Al₂O₃) 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 C₁ 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 $\ln (W_n/n)$ vs. n will generate a straight line having a slope $\log \alpha$. The magnitude of α , thus obtained corresponds to the characteristics of catalyst used, and operating variables employed. Using ASF distribution relations, one can calculate the maximum yields of various products functions as shown in Figure 7.1 – maximum gasoline range hydrocarbon (C₁₂-C₁₈) yield 48% and maximum diesel yield 30%.

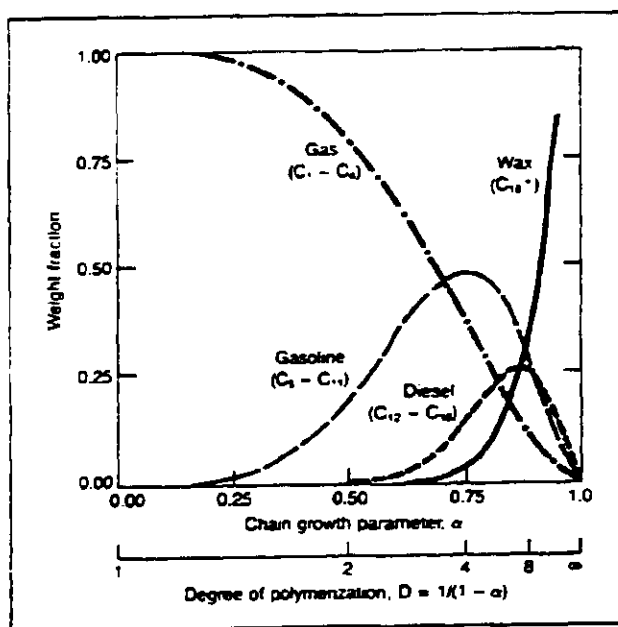


FIGURE 7.1 Product Selectivity as a function of Chain Growth Parameter.
[Srivastava et al., 1990].

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:

<u>Catalyst</u>	<u>Predominant Product</u>
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

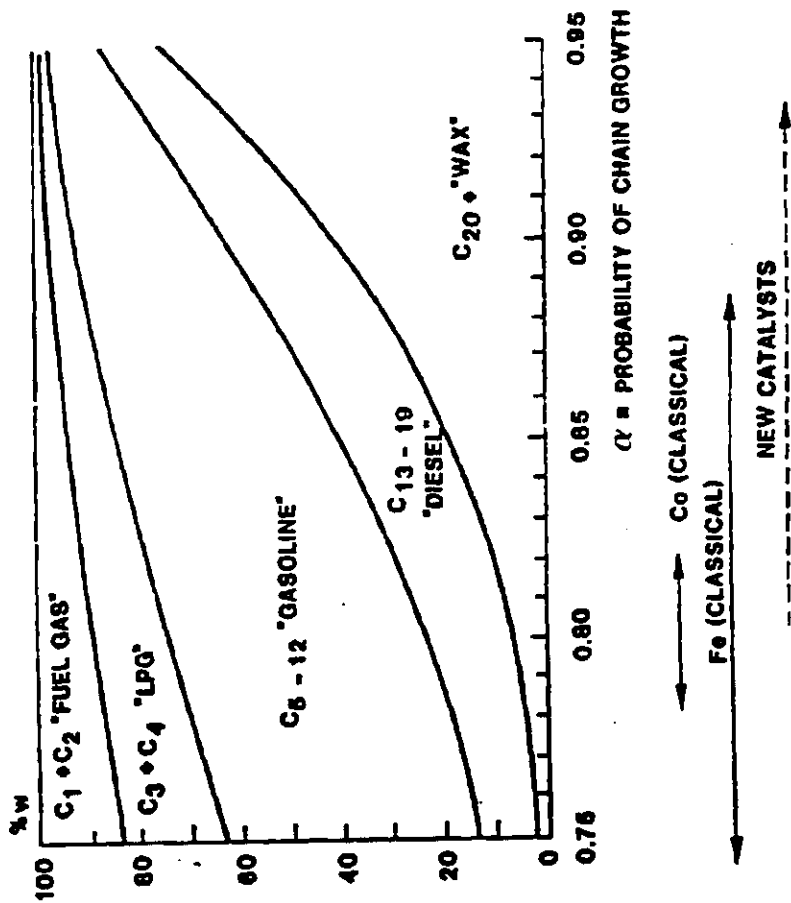


FIGURE 7.2. Product Selectivity with Different Catalysts having Different Chain Growth Parameters.

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 (C₁ to C₄ 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/K₂O). Unfortunately, only a limited range of data has been revealed because of proprietary reasons. Nevertheless, SiO₂ was found to be the best support in terms of both activity and selectivity. A second support material (CaO₂, Cr₂O₃, Al₂O₃, V₂O₅, ThO₂, MgO or SiO₂) added to SiO₂, showed results inferior to SiO₂ alone. Dry (1981) emphasizes that a careful balance between K₂O as promoter and SiO₂ as a support is necessary in order to maximize the desired activity and

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

<u>Product</u>	ARGE, Fixed bed at 220°C (428°F)	CFB, Synthol at 325°C (617°F)
	<u>%</u>	<u>%</u>
CH ₄	2	10
C ₂ H ₄	0.1	4
C ₂ H ₆	1.8	4
C ₃ H ₆	2.7	12
C ₃ H ₈	1.7	2
C ₄ H 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.

Catalyst	TAMU Bukur (1988)	UOP Abrevaya & Shah (1990)	Rheinpreussen Plant Koibel, et al. (1955)	MIT Satterfield (1987)	Mobil (Kuo, 1985) CT-256-3	CT256-13
	100 Fe/0.3 Cu/0.5K	Precipitated Fe + Promoter	Fe/Cu/K ₂ O	Ruhrchemie C73	Fe/Cu/K ₂ O	Fe/Cu/K ₂ O
Reactor Type a	STSR	STSR	BCSR	STSR	BCSR	BCSR
Conditions						
Temperature, C	265	275	268	263	260	258
Pressure, atm	15	21	12	8-15	15	15
SV, Ni/g-Fe/h	1.6	0.9	3.4	2.0	2.6	2.4
H ₂ /CO Ratio	0.72	0.70	0.67	0.70	0.67	0.67
Activity						
CO + H ₂ , Conv., %	71.0	83.0	89.0	33.6	56.0	82.2
Mol/g-cat/h	0.034	..	0.106	0.021	0.039	0.061
Nm ³ /kg-Fe/h	1.13	0.75	3.02	0.67	0.56	1.97
Selectivity, wt %						
C ₁	3.2	6.2	3.2	5.7	7.8	2.7
			(CH ₄ + C ₂ H ₆)			
C ₂ -C ₄	11.4	34.8	31.3	27.0	24.5	11.1
C ₅ -C ₁₁	20.4	28.6	53.6	40.0 ^c	41.5	18.1
C ₁₂ -C ₁₈	65.0 ^b	11.20	10.00	27.3 ^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	197	206
g-HCl/g-Fe/h	0.25	..	0.57	0.05	0.37	0.41

a STSR - stirred tank slurry reactor, BCSR - bubble column slurry reactor

b C₁₂ +

c C₅-C₁₂

d C₁₃ +

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 $\text{CO} + \text{H}_2$ 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 $\text{C}_{12}+$ selectivity, whereas H_2 reduction at 280 C (536 F) resulted in the highest methane and the lowest $\text{C}_{12}+$ 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 reproducible 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 $197^\circ C$ ($387^\circ F$) 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/K₂O 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 (C₅-C₁₁) products was 20 to 45% and to diesel (C₁₂-C₁₈) 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.