

## 4. ASSESSMENT OF SLURRY-PHASE REACTION SYSTEMS IN FISCHER-TROPSCH SYNTHESIS

### 4.1 INTRODUCTION

The major technological problems associated with Fischer-Tropsch processing are rapid and efficient removal of the reaction heat and the ability to process synthesis gas of low hydrogen-to-carbon monoxide ratio. The rapid and efficient removal of the reaction heat (which amounts to  $1-1.5 \times 10^7$  kJ per ton of hydrocarbon product) is necessary to avoid local overheating of the catalyst, which favors (undesired) methane formation and the lay down of carbonaceous deposits. The formation of these deposits, which results in catalyst deactivation and eventual catalyst pore and reactor plugging, is also favored by low  $H_2/CO$  ratios (1). Paradoxically, operation at low  $H_2/CO$  ratios is preferred because it reduces the production cost of the synthesis gas (2,3). This cost typically amounts to 80% of the total production cost (4) and therefore necessitates high product yields per unit volume of synthesis gas used ( $g/Nm^3$ ) for the economical production of chemical raw materials by Fischer-Tropsch processing. Past improvements in reactor technology have been directed toward this goal, and have, at the same time, solved the above-mentioned processing problems.

This chapter briefly reviews the various reactor types that have been developed for this purpose and compares some of the key features of the three major reactor technologies, focusing on their ability to handle low  $H_2/CO$  feed ratios. Problems in scale-up and design of slurry-phase reactors are identified and discussed in terms of flow regime, degree of phase mixing, and design parameters.

A list of symbols used in this section is given on page 4-29.

## 4.2 REACTOR DEVELOPMENTS

To solve the problems associated with Fischer-Tropsch synthesis, various types of reactors were developed, differing mainly in the way heat is removed and gas and catalyst are contacted. A classification of these various reactor types, based on catalyst mobility and the number of phases involved in the process, is given in Table 4-1. Extensive discussion on the historical development, key features, and technical limitations of these reactors is available in the literature (4-12).

Some of these reactor technologies soon appeared unsatisfactory, either because of poor temperature control due to the low linear gas velocities used [the lamellar and concentric tube reactor (6)] or because of pressure drops that were too high, due for instance, to agglomeration of crumbled catalyst [the trickle-bed "oil-recycle" reactor (5,11)]. Other reactor technologies, though conceptually innovative [for example, the tube wall reactor (10)], were considered too expensive (9). While only two of these reactor technologies are currently used industrially [the fixed-bed ARGE reactor and the fluidized-bed Synthol reactor at Sasol (6,7)], some technologies (the ebullating-bed reactor, the fluidized-bed Hydrocol reactor, and the bubble-column slurry reactor) never had the opportunity to demonstrate their competitiveness, often because of the unfavorable economics of the indirect coal liquefaction route at the time they were developed. These alternative technologies, however, still deserve consideration. As a matter of fact, work is currently being undertaken by Sasol to critically assess the advantages offered by fluidized-bed reactor technology without catalyst entrainment. Because of its potentially high throughput, high conversion, and good temperature control (6), further industrial development of this type of reactor seems to be worthwhile.

The ebullating-bed reactor technology, on the other hand, could principally offer operating advantages similar to those of the slurry-phase reactor (9) if the problem of catalyst attrition can be solved (5). The slurry-phase bubble-column reactor, however, uncontestedly remains the most attractive alternative to the existing technology because of its numerous generic advantages (Table 4-2). Slurry-phase operation, however, also has disadvantages, including supplementary

Table 4-1

Reactor Technologies Applied to Fischer-Tropsch Synthesis

Reactors With Stationary Catalyst:

- Two-phase:
- Lamellar reactor
  - Tubular reactors:
    - concentric tube reactor
    - tube wall reactor (PETC)
    - fixed-bed reactor (Ruhchemie/Lurgi: ARGE)
- Three-phase:
- Trickle-bed reactor (BASF, U.S. Bureau of Mines)

Reactors with Mobile Catalyst:

- Two-phase:
- Fluidized-bed reactor:
    - without catalyst entrainment (HRI: Hydrocol)
    - with catalyst entrainment (Kellog: Synthol)
- Three-phase:
- Slurry reactor:
    - bubble column reactor (Kölbel)
    - continuous stirred tank reactor
  - Ebulating-bed reactor (U.S. Bureau of Mines)

Table 4-2

Major Generic Advantages of Slurry-phase Operation

- REACTOR:
- Simple vessel design
  - High reactor efficiency
  - No reactor plugging problems
- CATALYST:
- High specific external surface area [ $m^2_{cat}/m^3_{slurry}$ ] and reduced internal diffusion resistance due to small particle size
  - Easy replenishment of catalyst; continuous regeneration is feasible
  - No special mechanical strength requirements; attrition of the catalyst is not undesirable
  - Potentially longer life
- OPERATION:
- Excellent temperature control: the large liquid-phase heat transfer coefficients and liquid mass, which acts as a thermal sink, eliminate temperature excursions; heat recovery is practical
  - High flexibility under operating conditions

resistance to mass transfer introduced by the inclusion of a third phase, namely the solvent medium; problems in efficient separation of the solids from the liquids; and, most dramatically, the present lack of reliable scale-up rules. Hence, to critically assess whether slurry-phase operation is a superior operation mode, its comparison to the commercial fixed-bed and fluidized-bed technologies must be as objective and as comprehensive as possible.

An objective assessment of the relative merits of slurry-phase, fixed-bed, and fluidized-bed technologies is extremely delicate because it depends primarily on the basis for comparison. Some authors compare these technologies at identical operating conditions (6,13), but the comparisons are limited by the range of the least flexible technology (in this case the fluidized-bed technology), and sometimes even include identical catalyst particlesizes (13). Others prefer to optimize each technology separately to meet a given productivity (9) or to maximize the yield of a given product slate (for example, diesel versus gasoline). Recognizing that these different approaches might result in contradictory conclusions, an attempt has been made to compare the three major reactor technologies--entrained fluidized-bed, tubular fixed-bed, and the developing slurry-phase operation--in the most general terms (Table 4-3), as carefully distilled from a survey of the most pertinent sources (3,4,6-9,13-19).

As seen in Table 4-3, fluidized-bed operation requires significantly higher reaction temperatures than either fixed-bed or slurry-phase operation. This is necessary to avoid condensation of the heavier hydrocarbons on the catalyst and, hence, to prevent the inevitable agglomeration of the catalyst particles. Some important consequences of this high-temperature operation are that the achievable product range is restricted to low-molecular-weight products (gas and gasoline) and that the risk of possible carbon formation is increased. Besides causing more rapid deactivation of the catalyst, increased carbon formation results in a more difficult fluidization of the catalyst due to the increase in weight. To avoid this risk, synthesis gas of a substantially higher  $H_2/CO$  feed ratio must be used. One of the reasons fixed-bed operation necessitates higher  $H_2/CO$  feed ratios than slurry-phase operation is the potential plugging of fixed-bed

Table 4-3

Comparison of Tubular Fixed-bed, Fluidized-bed with  
Catalyst Entrainment, and Slurry-phase Bubble-column Operation

<u>Technology</u>	<u>Tubular fixed bed reactor</u>	<u>Fluidized bed with entrainment</u>	<u>Slurry phase bubble column</u>
<u>Operating conditions</u>			
temperature (°C)	220-250	320-340	260-275
pressure (bar)	25	20-23	11-12
H <sub>2</sub> /CO feed ratio	1.3-2.0	2.0-2.8	0.5-0.7
recycle/feed ratio	2.2-2.5	2.0-2.5	/
catalyst: particle size (mm)	1-5	0.05-0.2	0.03-0.07
charge (ton)*	highest	800	90
<u>Operability</u>			
temperature control	poor	good	good-excellent
pressure drop at high U <sub>G</sub>	small	medium	medium up to high
flexibility	intermediate	low	high
catalyst: continuous replacement	very difficult	simple/expensive	feasible/problematic
losses	none	2-4% per day	small
lifetime	6-9 months	44 days	yet unknown

Table 4-3  
(continued)

Comparison of Tubular Fixed-bed, Fluidized-bed with

Catalyst Entrainment, and Slurry-phase Bubble-column Operation

<u>Technology</u>	<u>Tubular fixed bed reactor</u>	<u>Fluidized bed with entrainment</u>	<u>Slurry phase bubble column</u>
<u>Conversion/yields</u>			
syngas conversion (%)	50-70	80-85	> 90
space time yield (kgHC/m <sup>3</sup> . hr)	comparable to slurry phase	highest	comparable to fixed bed
catalyst efficiency (kgHC/m <sup>3</sup> cat. .hr)	lowest	highest	intermediate
<u>Selectivity</u>			
C <sub>4</sub> - formation	low	high	as fixed bed or lower
gasoline production	lowest	high	comparable to fluidized bed
product range	full range	restricted to low molecular weight	full range
<u>Profitability</u>			
relative investment cost* (reactors, vessels, heat exchangers)	intermediate	100	45
relative catalyst cost*	highest	100	51
thermal efficiency (%) (steam generation, BFW heating)	lowest	85	91

\*Based on conversion of 793 10<sup>3</sup> std m<sup>3</sup> of syngas/hr (UOP, 1982)

reactors due to excessive carbon deposition, which results in intolerable pressure drops. Other reasons are discussed in more detail below. There is, however, no obvious reason why slurry-phase reactors can be operated at lower total syngas pressures. The pressure values given reflect only the average working pressures used in most of the slurry-phase Fischer-Tropsch synthesis studies. Also, the high pressure drops claimed for slurry-phase reactors at high superficial gas velocities (18) are surprising. In fact, very little work has been published on the estimation of pressure drops in bubble-column reactors. One of the most comprehensive studies is that of Jourdani (20).

Jourdani states that the total pressure drop in a bubble column not only accounts for the pressure loss due to the static head of the solvent medium, roughly equal to:

$$\Delta p = L_s \epsilon_L \rho_L g \quad (4.1)$$

but also accounts for the frictional losses due to the flow of gas and (eventually) liquid. The latter losses are believed to depend on the superficial velocities and densities of both the gas and the liquid phase, in addition to the column diameter. The general observation is an increase in pressure drop upon an increase in the superficial velocity of either the gas or the liquid phase.

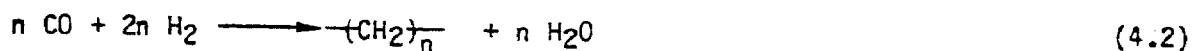
The high operational flexibility of slurry-phase reactors, as extensively discussed by Kolbel (4), enables a gasoline yield comparable, or even superior, to that of fluidized-bed operation (3,9,13), although this has been contradicted by Dry (6). All authors, however, generally agree that the highest space-time yield (kg hydrocarbon product/m<sup>3</sup><sub>R</sub>-hr) and catalyst efficiency (kg hydrocarbon product/m<sup>3</sup><sub>cat</sub>-hr), sometimes referred to as reactor and catalyst performance (21), are achieved in fluidized-bed operation. However, a study on the process economics, based on a required conversion of 793 x 10<sup>3</sup> std m<sup>3</sup> of syngas/h (9), indicates a distinct advantage of slurry-phase operation (Table 4-3). The conclusion drawn from this most general comparison of reactor technologies is that slurry-phase operation appears to be a most attractive alternative to the existing technologies, especially when compared to tubular fixed-bed technology.



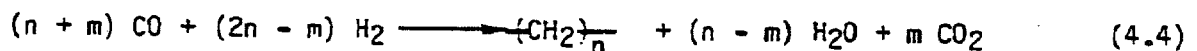
### 4.3 HYDROGEN-TO-CARBON MONOXIDE RATIO IN SLURRY-PHASE OPERATION

As already mentioned, the use of synthesis gas with a low H<sub>2</sub>/CO ratio is desirable in view of the savings in production cost (2,3). However, lower H<sub>2</sub>/CO feed ratios also imply an increase in the average molecular weight (decreased methane formation) and olefin content of the hydrocarbon product, as well as an increased tendency toward coke formation in the reaction mixture (1,22). Because of potential catalyst deactivation, reactor plugging, or catalyst de-fluidization, coke formation constitutes the major reason that fixed-bed and fluidized-bed reactors are unable to accept low H<sub>2</sub>/CO feed ratios as supplied by so-called "second generation" coal gasifiers [Texaco, Shell-Koppers, BGC Lurgi (3)]. Slurry-phase reactors, on the other hand, are claimed to be able to withstand such low ratios without appreciable catalyst deactivation (23). Apart from the unlikely occurrence of reactor plugging, the ability of slurry-phase reactors to accept syngas of low H<sub>2</sub>/CO ratio is basically due to the intrinsic water-gas shift activity of the catalysts used, the high degree of back-mixing in the liquid phase, and the substantial differences in diffusivities (and solubilities) of the reactant gases in wax media (22,24). This statement is discussed in more detail below.

The Fischer-Tropsch synthesis of hydrocarbons is often conveniently represented by the following two stoichiometric reactions:



Upon combination, these reactions yield the following expression for the "overall" reaction:



The number of moles of hydrogen converted per mole of carbon monoxide  $[(2n-m)/(n+m)]$ , conventionally called the usage ratio (U), depends on the extent to which the ("internal" or "intrinsic") water-gas shift (Equation 4.3) occurs.

Hence, the limits for the usage ratio are obtained for  $n = m$  ( $U_{min}$ ) and  $m = 0$  ( $U_{max}$ ), and therefore:

$$0.5 < U = (2n-m)/(n+m) < 2.0 \quad (4.5)$$

Usage ratios greater than 2.0 or smaller than 0.5, though theoretically possible in the case of highly excessive  $C_3^-$  or oxygenate formation, rarely occur with conventional Fischer-Tropsch catalysts.

The necessity of high catalyst activity toward the water-gas shift, which essentially translates into low usage ratios (low  $n-m$  values), is best understood from the relationships between the feed ( $I$ ), usage ( $U$ ), and exit ( $E$ )  $H_2/CO$  ratios, and the hydrogen ( $X_{H_2}$ ), carbon monoxide ( $X_{CO}$ ), and syngas ( $X_{CO} + H_2$ ) conversions (Table 4-4). The set of Equations 4.12 to 4.14, or its equivalent, Equations 4.12' to 4.14', are easily found by appropriate elimination of the gas concentrations from the definition relations, Equations 4.6 to 4.9. These equations also combine readily into Equation 4.15, which expresses the exit  $H_2/CO$  ratio solely as a function of the syngas conversion and the feed and usage ratios. Equation 4.15 is particularly convenient, since a quick comparison of its numerator and denominator immediately leads to Equation 4.16, which essentially states that the exit ratio will exceed the feed ratio whenever the usage ratio is lower than the feed ratio. This observation, already reported in different terms by Satterfield (22), is illustrated in Figure 4-1 for several theoretically possible values of the usage ratio at a feed ratio  $I = 1.5$ . Note that  $I = E$  at  $(X_{CO} + H_2) = 0$ .

It should be emphasized that Equations 4.12 through 4.16 generally apply to the gas-phase effluent of any type of reactor, provided an "overall" usage ratio has been calculated, for example, from the exit conversions or from the inlet and outlet gas concentrations (Equation 4.10). Local values of the usage ratio may, however, differ, depending upon local temperatures and concentrations. Equation 4.16b, if valid at the reactor outlet, may not be met throughout the reactor. The high degree of mixing usually prevailing in the liquid phase of slurry reactors allows the assumption of uniform conditions in the liquid phase, and, hence, of a constant value for the usage ratio throughout the reactor. If mass (and heat) transfer limitations are negligible, the liquid-phase concentrations

Table 4-4

Some Useful Relationships Between the Feed (I), Usage (U), and Exit (E) H<sub>2</sub>/CO Ratio, and the Hydrogen (X<sub>H<sub>2</sub></sub>), Carbon Monoxide (X<sub>CO</sub>), and Syngas (X<sub>CO+H<sub>2</sub></sub>) Conversion

$$X_{H_2} = \frac{(H_2)^{in} - (H_2)^{out}}{(H_2)^{in}} \quad (4.6) \quad \left| \quad I = \frac{(H_2)^{in}}{(CO)^{in}} \quad (4.9)$$

$$X_{CO} = \frac{(CO)^{in} - (CO)^{out}}{(CO)^{in}} \quad (4.7) \quad \left| \quad U = \frac{(H_2)^{in} - (H_2)^{out}}{(CO)^{in} - (CO)^{out}} \quad (4.10)$$

$$X_{CO+H_2} = \frac{(H_2)^{in} + (CO)^{in} - (H_2)^{out} - (CO)^{out}}{(H_2)^{in} + (CO)^{in}} \quad (4.8) \quad \left| \quad E = \frac{(H_2)^{out}}{(CO)^{out}} \quad (4.11)$$

$$X_{CO+H_2} = \frac{X_{CO} + IX_{H_2}}{1 + I} \quad (4.12) \quad \left| \quad X_{CO} = \frac{I - E}{U - E} \quad (4.12^b)$$

$$U = I \frac{X_{H_2}}{X_{CO}} \quad (4.13) \quad \left| \quad X_{H_2} = \frac{U}{I} \left( \frac{I - E}{U - E} \right) \quad (4.13^b)$$

$$E = I \frac{(1 - X_{H_2})}{(1 - X_{CO})} \quad (4.14) \quad \left| \quad X_{CO+H_2} = \frac{(I - E)(1 - U)}{(U - E)(1 + I)} \quad (4.14^b)$$

$$E = I \frac{(1 + U) - \frac{U}{I} (1 + I) X_{CO+H_2}}{(1 + U) - (1 + I) X_{CO+H_2}} \quad (4.15)$$

$$E = E \text{ as } X_{CO+H_2} \nearrow \text{ if } U = I \longrightarrow X_{H_2} = X_{CO+H_2} = X_{CO} \quad (4.16a)$$

$$E \nearrow \text{ as } X_{CO+H_2} \nearrow \text{ if } U < I \longrightarrow X_{H_2} < X_{CO+H_2} < X_{CO} \quad (4.16b)$$

$$E \searrow \text{ as } X_{CO+H_2} \nearrow \text{ if } U > I \longrightarrow X_{H_2} > X_{CO+H_2} > X_{CO} \quad (4.16c)$$

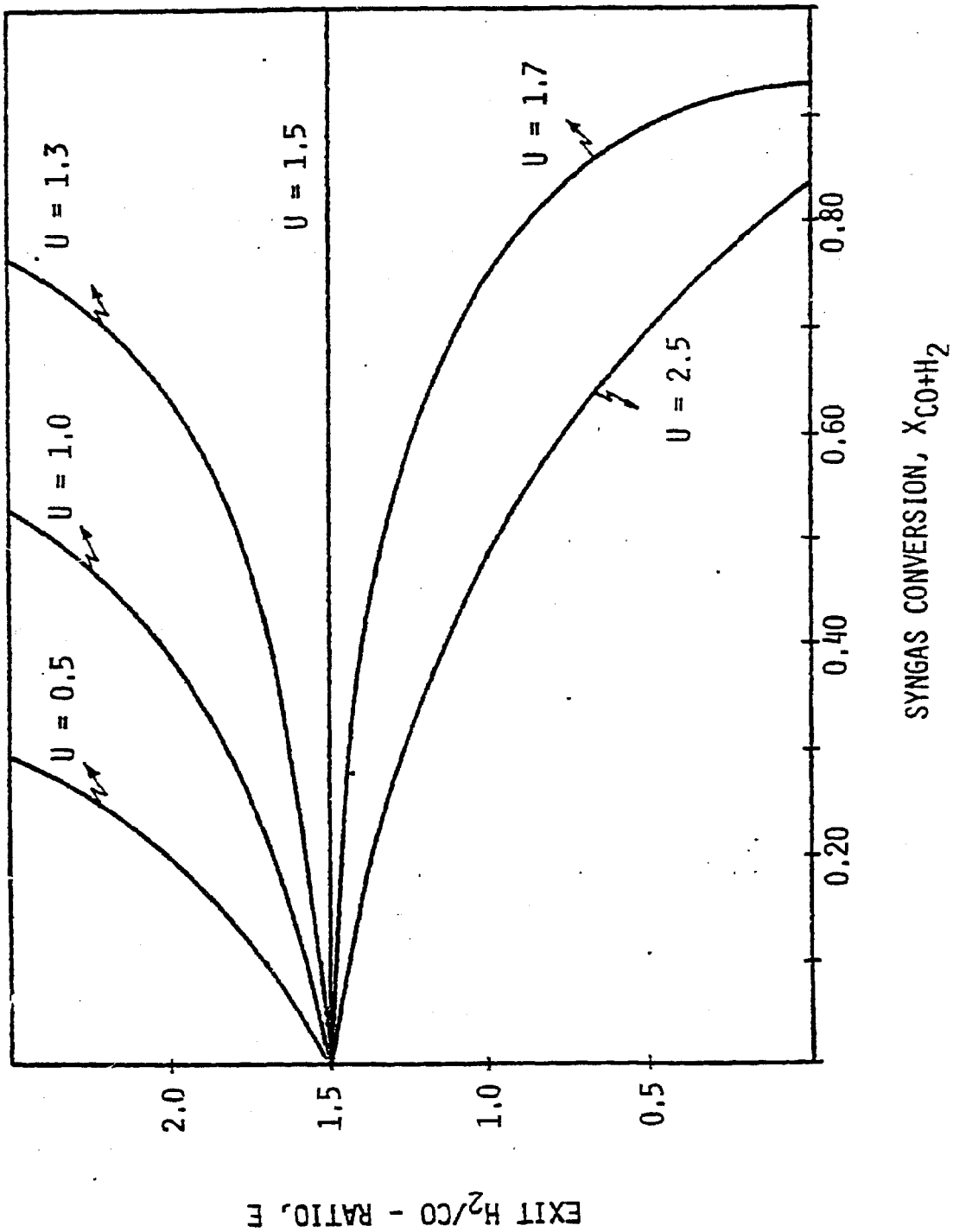


Figure 4-1. Relationship between the Exit  $H_2/CO$  Ratio and the Syngas Conversion for Assumed Values of the Usage Ratio and Feed  $H_2/CO$  Ratio of 1.5

correspond to saturation at the exit gas-phase concentrations (22). It can therefore be stated that in Fischer-Tropsch slurry reactors, with sufficient liquid mixing and negligible mass transfer limitations, the actual  $H_2/CO$  ratio in the liquid phase exceeds the feed ratio whenever  $U$  is lower than  $I$ . Consequently, a tendency toward decreased carbon formation can be expected when operating in the slurry phase. Table 4-5 shows that this condition is indeed fulfilled for the catalysts used in published Fischer-Tropsch studies.

Rates of synthesis in slurry-phase operation are usually limited by external liquid-side mass transfer, even though there is no agreement on the magnitude of its contribution (30). But even when resistance to mass transfer is considered, formerly derived statements still hold because of the higher diffusivity and solubility of hydrogen (as compared to carbon monoxide) in wax media. The impact of the differences in diffusivity and solubility of the reactant gases on their gas-phase and liquid-phase concentrations has been extensively discussed by Stern and co-workers (24). They simulated the slurry-phase operation of the methanation reaction:



Perfect mixing in the liquid phase and plug flow for the gas phase were assumed, and the external liquid-side mass transfer was considered the major resistance to the reaction. Some of their conclusions are illustrated in Figure 4-2, which shows the gas-phase and liquid-phase concentrations of the reactants as a function of the normalized axial reactor coordinate,  $\xi$ . While the  $H_2/CO$  gas-phase ratio ( $\theta_{G,H_2}/\theta_{G,CO}$ ) sharply decreases at low  $\xi$  values and never exceeds the  $H_2/CO$  feed ratio ( $I = 1$ ), the liquid-phase  $H_2/CO$  ratio ( $\theta_{L,H_2}/\theta_{L,CO}$ ) is more than twice the feed ratio. This results primarily from the much higher diffusivity of, and mass transfer coefficient for, hydrogen, which, at the considered conditions, amounts to 37 times the diffusivity of carbon monoxide.

It should be stressed that the above-mentioned considerations apply equally to other gas/liquid/solid reactor systems, such as the ebullating-bed reactor, provided that sufficient mixing is achieved in the liquid phase. Similar considerations are also applicable to slurry-phase alcohol (methanol) synthesis.

Feed and Usage Ratio of Hydrogen to Carbon Monoxide for

Several Slurry-phase Studies of the Fischer-Tropsch Reaction

Authors	$\frac{I}{U}$	$\frac{X_{H_2}}{X_{CO+H_2}}$	$X_{CO+H_2}$	$X_{CO}$	Catalyst	
Schlesinger et al. (1951)	1.0	0.67	0.28	0.35	0.42	pptd. Fe catalyst;
	1.0	0.61	0.48	0.64	0.79	Fe/Cu/K <sub>2</sub> O = 100/10/1
Hall et al. (1952)	3.27	2.82	0.571	0.592	0.662	fused Fe catalyst;
	2.44	2.34	0.924	0.935	0.962	with 0.7% K <sub>2</sub> O, 3.4% MgO
Schlesinger et al. (1954)	1.0	0.81	0.639	0.714	0.789	nitrated fused Fe catalyst
Kolbel et al. (1956)	0.67	0.63	0.86	0.89	0.91	unsupported pptd. Fe;
	0.67	0.63	0.85	0.88	0.90	Fe/Cu/K <sub>2</sub> O = 100/0.1/0.05-0.5
Mitra and Roy (1963)	1.33	1.19	0.671	0.705	0.750	pptd. Fe catalyst; Fe/Cu/
	1.30	1.24	0.896	0.915	0.939	MgO-(CaO)/K <sub>2</sub> O/Kieselguhr; 100/10/4/3.5/50
Forley and Roy (1964)	0.703	0.616	0.327	0.354	0.373	pptd. Fe catalyst;
	0.662	0.565	0.538	0.594	0.631	Fe/Cu/K <sub>2</sub> O = 100/1.6/2
Kunugi and Sakai (1968)	0.59	0.59	0.808	0.808	0.808	pptd. Fe catalyst;
						Fe/Cu/K <sub>2</sub> CO <sub>3</sub> = 100/0.3/0.6-1.2
Forney et al. (1975)	1.00	0.62	0.45	0.59	0.73	Fe catalyst with;
						Fe/Cu/K <sub>2</sub> O = 100/10/1
Mobil (1982)	0.687	0.580	0.602	0.668	0.713	"I-B" with
	0.673	0.635	0.839	0.868	0.888	Fe/Cu/K <sub>2</sub> O

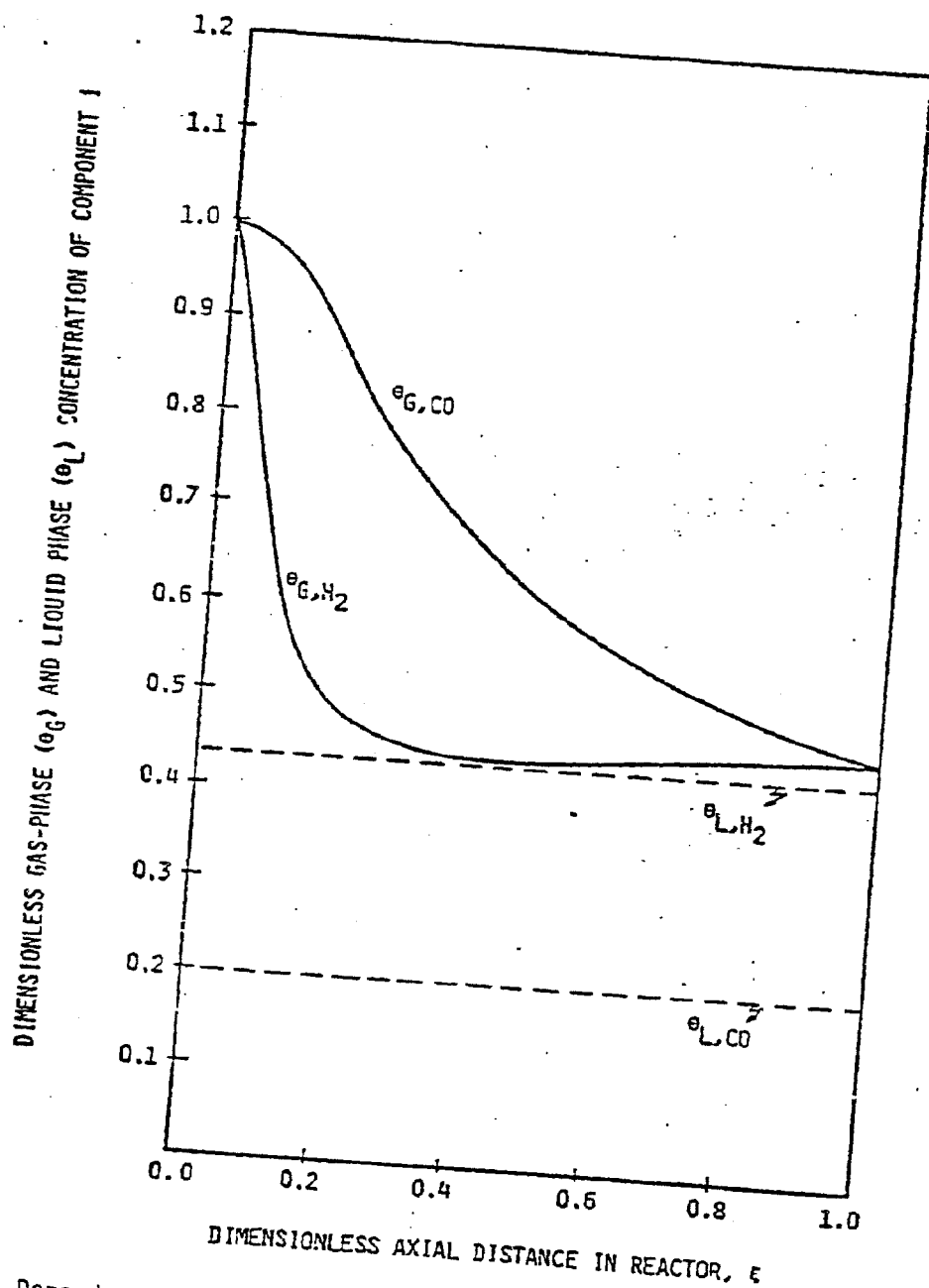


Figure 4-2. Dependence of the Gas and Liquid Concentrations of H<sub>2</sub> and CO on the Axial Reactor Distance. Calculated for the reaction  $2 H_2 + 2 CO \rightarrow CH_4 + CO_2$  at 270°C with  $\tau_G = 70s$  and  $\tau_L = 700s$ .

Reference: (24)

One last practical conclusion that can be drawn from the equations in Table 4-4 is that the highest conversions (100%) are obtained for usage ratios equal to the feed ratio. The maximum achievable yield of hydrocarbon product (kg hydrocarbon/Nm<sup>3</sup> syngas), on the other hand, is found at 100% syngas conversion ( $I = U$ ) and zero carbon dioxide production ( $m = 0$  or  $U = 2$ ). It can easily be verified that this maximum achievable hydrocarbon yield amounts to 208.6 kg hydrocarbon per Nm<sup>3</sup> synthesis gas.

#### 4.4 IDENTIFICATION OF SCALE-UP AND DESIGN PROBLEMS

One of the major reasons that slurry-phase operation of Fischer-Tropsch synthesis has not yet been commercialized is the limited knowledge of the extent to which some factors (such as the reactor geometry, gas distribution, phase properties, and operating conditions) affect the hydrodynamic behavior of the reactor system. This knowledge is essential, as the scale-up and design of reactor systems requires a reliable modeling of their hydrodynamic behavior, including such phenomena as flow regime, back-mixing, interfacial areas, sedimentation, and convective heat transfer.

This section identifies some of the most crucial problems in the scale-up of slurry-phase bubble-column reactors and identifies research areas that deserve consideration.

##### 4.4.1 Flow Regimes

A major problem in the scale-up of slurry-phase bubble-column reactors is the assessment of the proper type of flow regime under which the reactor should be operated. This is of critical importance as it also determines the applicability of the correlations used for some essential design parameters, such as the gas holdup.

Some insight into the possible flow regimes in three-phase (gas/liquid/solid) systems can be gained from the better understood two-phase (gas/liquid) systems,



because three-phase systems essentially behave as pseudo-two-phase systems provided the catalyst concentration and size are small (21). For such systems it is known that at low superficial gas velocities, the gas flow is characterized by bubbles rising in a rather undisturbed fashion in the column. This hydrodynamic situation, in which the interaction between the bubbles is small and their size distribution narrow, is usually referred to as homogeneous, or bubbly, flow (Figure 4-3a)(21). Upon increasing the superficial gas velocity to values dependent on several factors, coalescence of the bubbles starts to occur. An equilibrium between coalescence and break-up of the bubbles is established, and the flow regime is denoted as heterogeneous, or churn-turbulent (Figure 4-3b). Among the pseudo-homogeneous dispersion of small bubbles, a few large bubbles appear that rise through the column in a churn-like motion (21). In slim reactor columns, the size of these bubbles can even reach the diameter of the column, the gas flow in this situation being characterized by slugs (Figure 4-3c).

One approach to characterizing these various flow regimes in two-phase bubble column reactors as a function of superficial gas velocity and reactor diameter has been presented by Deckwer (Figure 4-3) (21), who claims that it is applicable to three-phase systems for sufficiently small catalyst loads ( $<16$  wt%) and particle sizes ( $d_p < 50 \mu\text{m}$ ). The transition range in Figure 4-3 (the shaded area) is believed to also depend on the dispersion height, the gas distributor, the liquid velocity, and the physiochemical properties of the three phases involved, and actually conceals all that is really unknown. Figure 4-3 also shows the operational ranges (represented by vertical lines and dots) of the slurry-phase studies summarized in Table 4-6. It is seen that most studies apparently pertain to the homogeneous flow regime. Apparently, because "excessive foaming" and "gas bubble slugging" were reported by Mobil workers (29) in a 5.2-cm diameter column at gas velocities above 0.4, respectively 1.5 cm/sec (asterisk in Figure 4-3), hence revoking the general reliability of Deckwer's representation.

Kölbel (4) tried to characterize the flow regimes as a function of the solid content of the slurry phase,  $C_s$ , as shown in Figure 4-4 and Table 4-6. No mention was made of the reactor geometry, gas distributor, or solvent medium

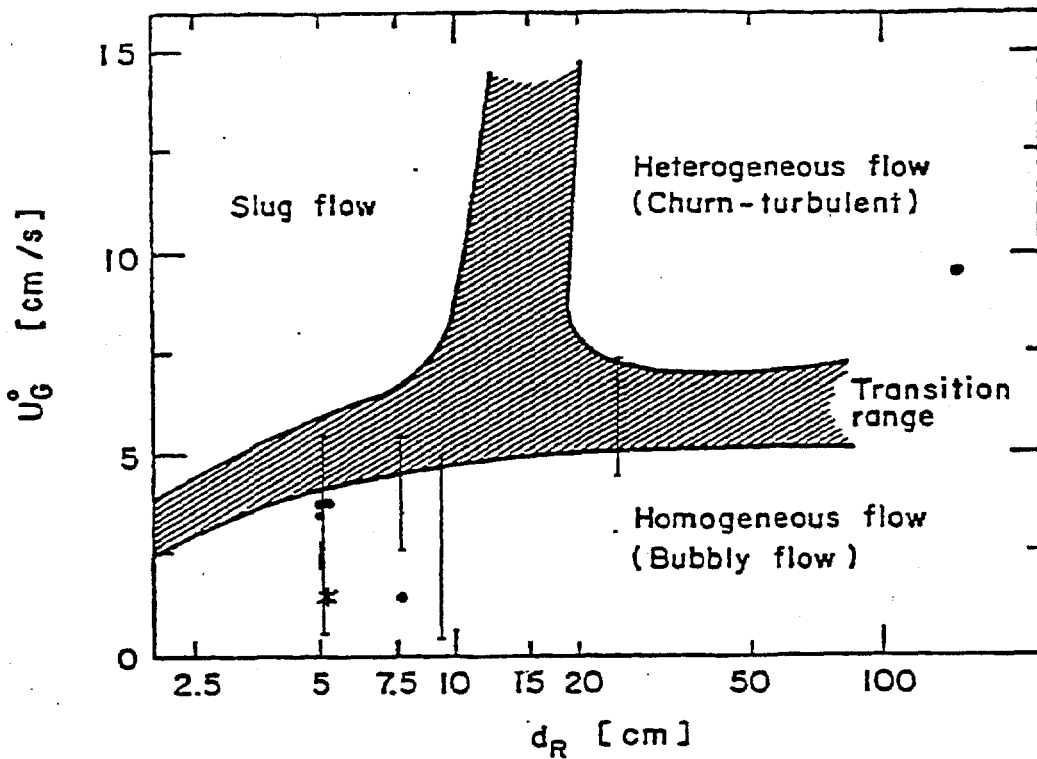
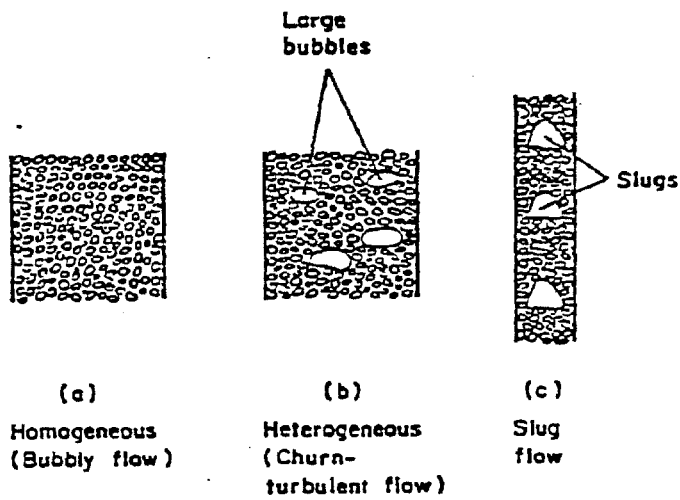


Figure 4-3. Assumed Dependency of Flow Regimes on Superficial Gas Velocity and Reactor Diameter ( $d_p < 50 \mu\text{m}$ , catalyst load  $< 16 \text{ wt}\%$ )

Reference: (21)

Table 4-6

## Reactor Dimensions, Superficial Velocity, and Catalyst Concentration and Size

Authors	$L_R$ [cm]	$d_R$ [cm]	$L_R/d_R$ [ ]	$U_G^*$ [cm/sec]	cat. load [wt. %]	$d_p$ [ $\mu$ m]
Kölbel et al. (1956)	860	155	5.55	9.5	28.4*	30
Quicker et al. (1981)	135	9.5	14.21	0.5-5	0	/
Hall et al. (1952)	120	5	24	2.2-2.9	22.2-55.6	75
Forley and Roy (1964)	853.4	24.8	34.4	4.5-7.4	~8*	1-3
Schlesinger et al. (1951)	304.8	7.6	40	2.7-5.5	25-30.8	61
Schlesinger et al. (1954)	304.8	7.6	40	1.5	21.1	?
Forney et al. (1974)	304.8	7.6	40	2.7	42.1*	61
Mitra and Roy (1963)	213.4	5.1	42	1.5-2.2	16-18	?
Mitra and Roy (1963)	304.8	5.1	60	0.9-2.2	16-18	?
Kölbel et al. (1956)	300	5	60	3.5	11.2*	?
Calderbank et al. (1963)	457.2	5.1	90	0.6-5.5	1.5-4.4*	?
Kunugi and Sakai (1968)	550	5	110	3.8	4.8	?
Sakai and Kunugi (1974)	600	5	120	3.8	10.1	?
Mobil (1982)	730	5.2	140.4	3.9	14.3	?

\*Calculated assuming  $\epsilon_g = 0.053 U_G^{1.1}$  and/or  $\rho_L = 0.85$  g/ml

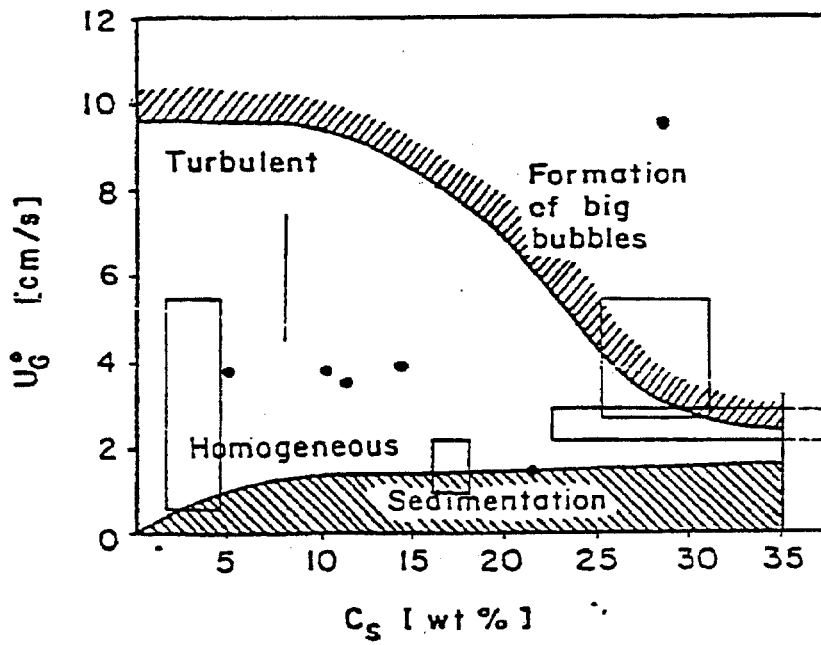


Figure 4-4. Operational Range Diagram for a Bubble-column Reactor with Suspended Solid Matter ( $d_p = 30 \mu\text{m}$ ,  $\rho_s = 2 \text{ g/cc}$ ,  $\rho_L = 1 \text{ g/cc}$ )

Reference: (4)

used, but if their terminology is properly understood, the upper region of "big bubble formation" probably coincides with Deckwer's heterogeneous flow regime. What is important is that the homogeneous flow regime, considered to be the region between the shaded areas, narrows with increasing solid concentration. The minimal superficial gas velocity required for catalyst fluidization, on the other hand, does not seem to change much when the solid concentration is varied. The minimal fluidization velocity, however, most likely depends on the densities of solvent and solid, because, as British researchers found, the gas velocity of 2.75 cm/sec was insufficient to maintain effective fluidization at a solid load of ~5.3 wt% (23). From Figures 4-3 and 4-4 it is concluded that some of the Fischer-Tropsch studies reported in Table 4-6 most likely pertain to the churn-turbulent flow regime. If it is true that industrial applications imply operation at churn-turbulent conditions (since high  $U_G$  and  $d_p$  values are desired for high capacity), it is important to realize that most correlations for important design parameters have only been derived for bubbly flow conditions.

A complicating factor in the proper assessment of the flow regime that prevails under given operating conditions in a bubble-column reactor is that the hydrodynamic behavior also appears to depend upon the axial position inside the reactor. Kölbl (4) states that in bubble columns of sufficient size, three reactor sections of different flow pattern can be distinguished. In the lower, or "inflow," region of the column, a quite perturbed flow regime exists, as created by the dispersion action of the gas distributor. As the distance from the sparger increases, the state of flow develops into an equilibrium between bubble coalescence and break-up. This is determined by the operating conditions and the physicochemical properties of the phases involved. Finally, in the upper section of the column, a zone of increasing gas content is formed as a result of the decreasing hydrostatic head of the liquid phase. Analogous observations have also been reported by other investigators (23).

The occurrence of these distinct flow regions, together with the existence of different flow regimes, emphasizes how difficult it is to correctly predict the hydrodynamic behavior of bubble-column reactors through the use of mathematical models.

#### 4.4.2 Degree of Phase Mixing

Even if the hydrodynamic behavior of the reactor system would be properly understood, reliability in predicting large-scale operation still depends on the completeness of the mathematical model used. For this model to be complete, it is essential that it incorporates those design parameters that determine the flow mechanics of the three phases present. Major design parameters include the axial dispersion coefficients, because they determine the degree of phase mixing in the reactor system and substantially impact the predicted performance. Bukur (34) emphasizes that the degree of mixing in the liquid phase continually depends on the magnitude of the axial mixing parameter:

$$N_L = D_L \epsilon_L / U_G^\circ L_S \quad (4.18)$$

in which the axial dispersion coefficient for the liquid phase,  $D_L$ , may be estimated from (21,35):

$$D_L = 3.676 U_G^{0.32} d_R^{1.34} \quad (4.19)$$

to yield

$$N_L = (3.676 U_G^{0.32} d_R^{1.34} \epsilon_L) / (U_G^\circ L_S) \quad (4.20)$$

From this equation it can be conceived how dramatic the impact of the  $L_S/d_R$  ratio can be on the liquid (and related solid-phase) mixing. The considerable range of the  $L_S/d_R$  ratios used in Fischer-Tropsch investigations, as reflected by the considerable range of  $L_R/d_R$  values in Table 4-6, therefore, partially accounts for the observed divergences in reactor performance and product composition.

Reliable correlations for axial dispersion coefficients are few: only one correlation has been published for the gas-phase dispersion coefficient (36), while the solid-phase dispersion coefficient is usually taken to be infinite (uniform distribution of the solids) or at least equal to the dispersion coefficient of the liquid phase (4,37). Perhaps because of this limited availability, mathematical models are often simplified by assuming the type of

flow (plug flow, perfect mixing) prevailing in the gas and liquid phase. However, though general agreement exists on the plug flow behavior of the gas phase in bubble columns, controversy still exists regarding the degree of back-mixing in both the liquid and solid phases. That considerable deviation in predicted performance may result from different flow behavior assumptions for the liquid phase is illustrated in Figure 4-5 for several catalyst activities (38). These observations, which have been confirmed by other investigators (13,34,39), dramatically emphasize the need for reliable dispersion correlations and the necessity for incorporating them in the mathematical models, for instance through the use of a sedimentation diffusion model (39).

#### 4.4.3 Other Important Design Parameters and Physicochemical Properties

Apart from the inevitable shortcomings of the kinetic models, remaining uncertainties in scale-up arise mainly from the limited availability, applicability, and/or reliability of correlations about some other essential parameters, such as gas holdup, diffusivity, solubility, and mass transfer coefficients ( $k_L a$ ). Correlations pertaining to these parameters, about which some excellent discussions are available in the literature (19,21,40-43), often apply only to the specific range of operational conditions (including reactor geometry, gas distributor, physicochemical properties of the phases, solid concentration and size, and temperature) for which they were derived. One should be aware of this limited applicability, because considerable inaccuracy may result upon extrapolation to other conditions. Figure 4-6 illustrates this for several gas holdup correlations and values obtained at different operating conditions in bubble columns. An obvious recommendation is that important design parameters should always be determined specifically for the reaction system studied. Scale-up of bench-scale or pilot-plant operation for design purposes, which is always based on extrapolations, however still remains hazardous.

The limited reliability of other parameter correlations is probably most revealing in the case of diffusion coefficient estimates. As mentioned earlier, knowledge of the diffusion coefficients is important, because they also determine the mass transfer in the reactor system and hence the phase concentrations of the

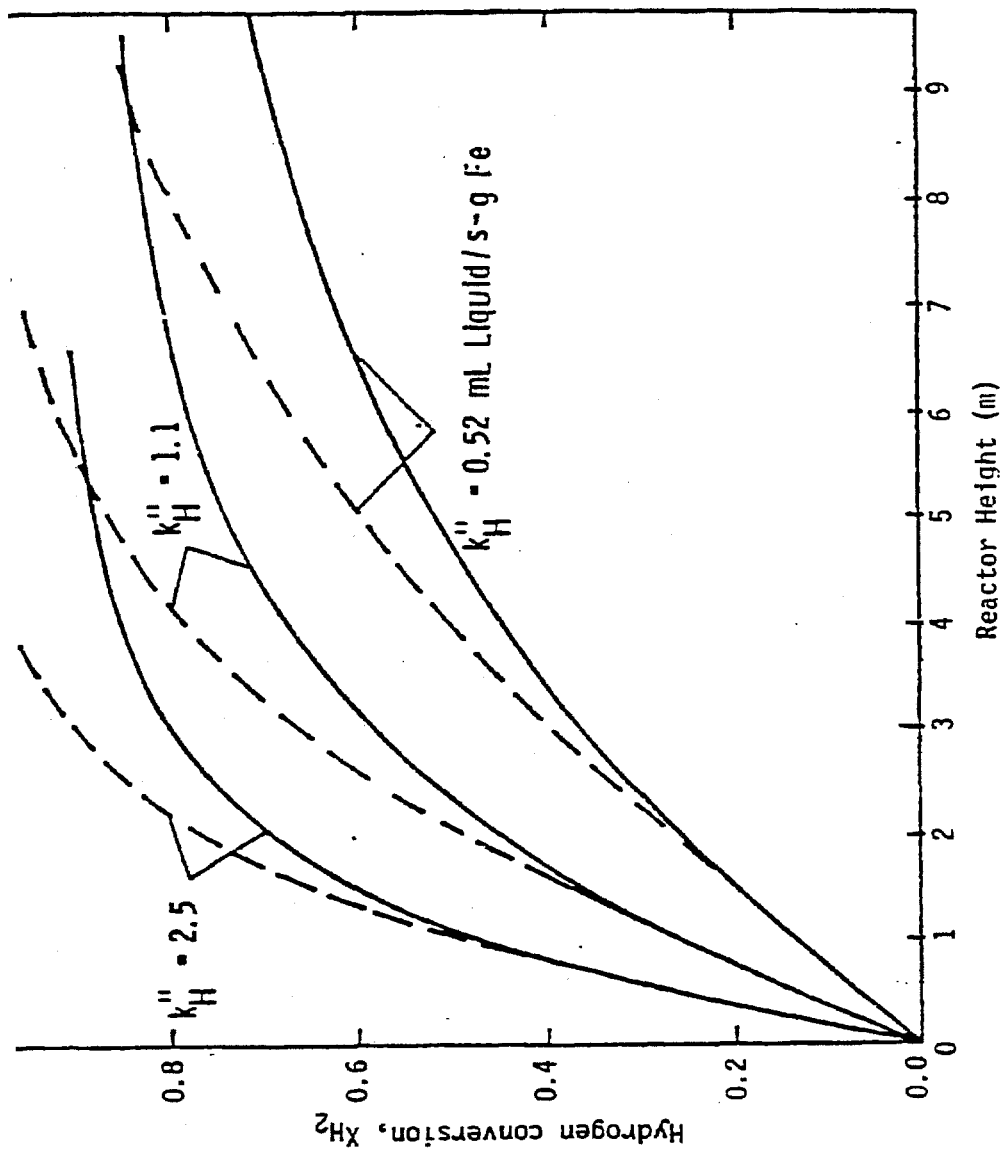


Figure 4-5. Effect of Liquid-phase Mixing and Catalyst Activity on Hydrogen Conversion. ---: perfect mixing; - - -: plug flow;  $k_H''$  = kinetic rate constant (parameter).

Reference: (30)



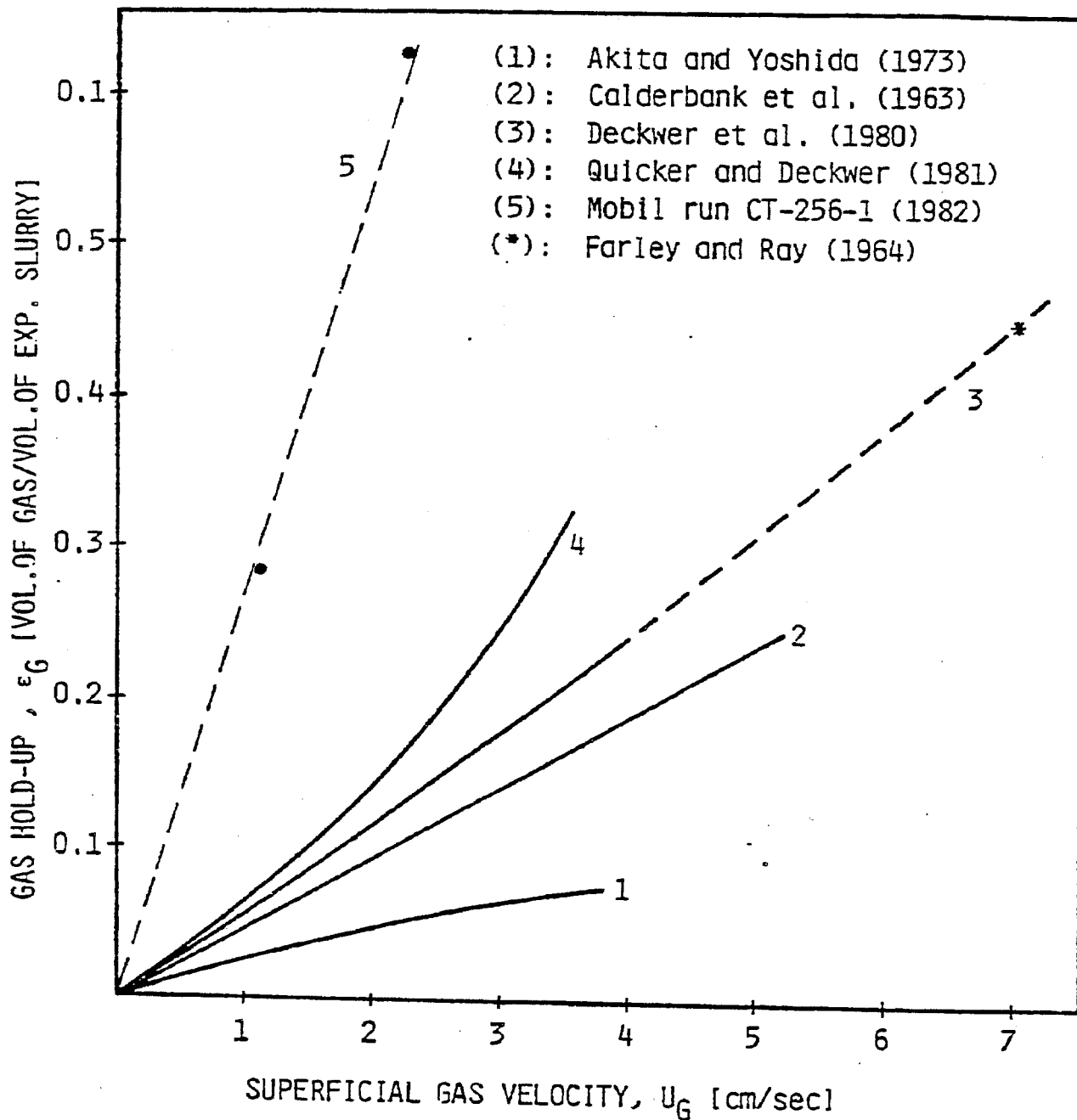


Figure 4-6. Gas Holdup as a Function of the Superficial Gas Velocity

reactants. The reliability of the correlations for these diffusion coefficients is questionable, because the two diffusivity correlations usually recommended (21,22)—the Sovova equation (45) and the Wilke-Chang correlation (46)—predict values that, under typical Fischer-Tropsch conditions, may differ as much as 120% (13). Obviously, this also affects diffusivity-dependent parameters such as the gas-liquid mass transfer coefficient,  $k_L$  (21).

The limited availability of data is especially crucial when estimating solubilities, though essential in determining the liquid-phase concentrations of hydrogen and carbon monoxide. Solubility coefficients for hydrogen and carbon monoxide are, still, most often estimated from the data of Peter and Weinert (47) in molten paraffin (Figure 4-7). The composition of the "wax" media used in slurry-phase reactors, which is too often improperly defined, may however, differ considerably, depending upon the operating conditions and time on-stream (product formation) (13,15,25). How this probable composition change affects the gas solubilities has, to our knowledge, never been investigated.

A final consideration pertains to some other physicochemical properties (density, viscosity, and surface tension) of the phases involved, which directly or indirectly affect most of the design parameters. Better agreement between different correlations for some design parameters might be obtained by using the "effective" physicochemical properties of the (aerated) slurry, as has been successfully applied by Deckwer (21) to correlate the heat transfer coefficient to one unique relationship.

#### 4.5 CONCLUSIONS

The slurry-phase bubble-column reactor appears to be an attractive reactor technology alternative to conventional Fischer-Tropsch processing because of its favorable economics and ability to solve the major problems associated with Fischer-Tropsch synthesis, such as temperature control and low  $H_2/CO$  feed ratios. Its ability to handle low  $H_2$ -to- $CO$  feed ratios, a property believed to generally apply to three-phase systems with sufficient liquid mixing, depends on the water-gas shift activity of the catalyst used, the high degree of back-mixing

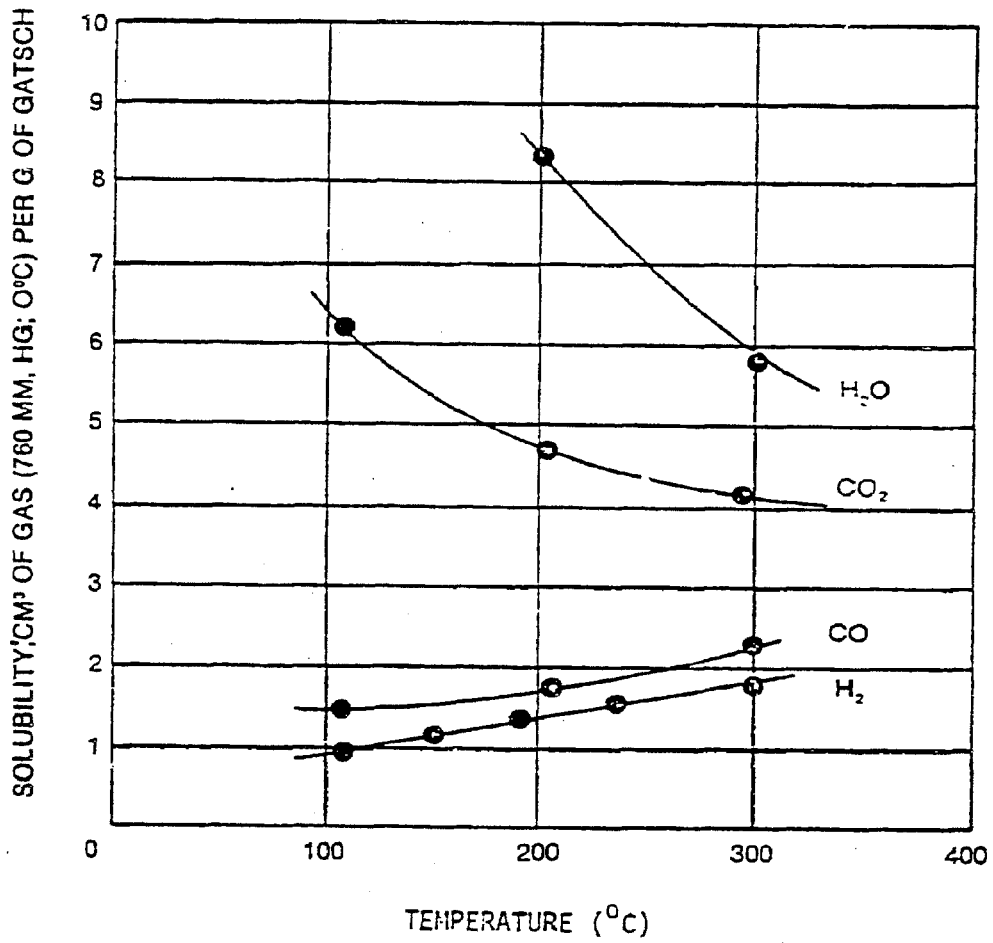


Figure 4-7. Solubility of Various Gases in Paraffin Gatsch (Mixture) at 10 atm

Reference: (47)

usually prevailing in the liquid phase, and the substantial differences in diffusivities of the reactant gases in wax media. Similar considerations are believed to hold for slurry-phase alcohol synthesis.

However, a better understanding of the reactor hydrodynamics is still required to establish sound scale-up and design rules. The flow regimes, although dependent upon dispersion height, gas sparger design, catalyst size, and liquid medium, have not been sufficiently studied in terms of their dependency on these parameters. There is still considerable disagreement concerning the degree of mixing in both liquid and solid phases, which can only be avoided by incorporating the proper contributions of axial dispersion in the mathematical model used. The incorporation of these dispersion contributions, which accounts for the dramatic impact of the reactor geometry ( $L_S/d_R$  ratio) on the reactor performance and product selectivity, requires the knowledge of reliable correlations for the axial dispersion coefficients. This knowledge appears deficient, as, for instance, no correlation exists for the dispersion coefficient of the solids. A limited availability, reliability, and/or applicability also appear for correlations about some essential design parameters (gas holdup, mass transfer coefficients) and physical properties (diffusivity, solubility) of the liquid media used. The best recommendation that can be given is that these essential parameters should always be specifically determined for the reaction system used. Finally an elucidation of the synthesis mechanism and related kinetics can only contribute to more accurate model predictions and to a better understanding of the factors that influence the  $H_2/CO$  usage ratio.

The bench unit size used for F-T investigation in slurry-phase is not of major importance, as long as one knows how to interpret the performance data in terms of intrinsic kinetics. To know how to interpret the data, it is necessary to collect more information about the hydrodynamic behavior and design parameters for the bench reactor under specific consideration. The degree of mixing of the three phases will depend on the reactor geometry and physical properties of the phases involved. For high conversions, high L/D ratios are required as they increase plug flow behavior, but a drawback might be decreased temperature control of the reactor. Clearly, investigation depends on the goals of the laboratory experiments, such as high yields or kinetic data.

#### 4.6 List of Symbols

$a$	specific gas-liquid interfacial area [ $\text{cm}^2/\text{cm}^3_R$ ]
$C_S$	solids concentration [wt% of slurry]
$d_p$	catalyst particle size [ $\mu\text{m}$ ]
$d_R$	reactor diameter [cm]
$D_L$	axial dispersion coefficient for the liquid phase [ $\text{cm}^2/\text{s}$ ]
$\epsilon_g$	gas holdup
$\epsilon_L$	liquid holdup
$E$	$\text{H}_2/\text{CO}$ ratio at reactor outlet
$g$	gravitational acceleration [ $\text{cm}/\text{sec}^2$ ]
$I$	$\text{H}_2/\text{CO}$ feed ratio
$K_H$	first-order kinetic rate constant [ $\text{cm}^3_L/\text{s.g Fe}$ ]
$K_L$	liquid-side mass transfer coefficient [cm/s]
$K_{La}$	volumetric gas-liquid mass transfer coefficient [ $\text{s}^{-1}$ ]
$\xi$	dimensionless axial distance in reactor
$L_S$	expanded height of slurry [cm]
$L_R$	reactor height [cm]
$N_L$	axial mixing parameter, given by Equation (4.18)
$\Delta p$	pressure drop [ $10^{-1}$ Pa]
$\theta_{G,i}$	dimensionless gas-phase concentration of component $i$
$\theta_{L,i}$	dimensionless liquid-phase concentration of component $i$
$\rho_L$	density of the liquid phase [ $\text{g}/\text{cm}^3$ ]
$\tau_G$	gas space time [s] (referring to reactor volume)
$\tau_L$	liquid space time [s] (referring to reactor volume)
$U$	$\text{H}_2/\text{CO}$ usage ratio [moles $\text{H}_2$ consumed/moles $\text{CO}$ consumed]
$U_G$	superficial gas velocity [cm/s]
$U_G^\circ$	superficial gas velocity at reactor inlet [cm/s]
$X_{\text{CO}}$	carbon monoxide conversion
$X_{\text{H}_2}$	hydrogen conversion
$X_{\text{CO}+\text{H}_2}$	syngas conversion