III. LITERATURE REVIEW

There is a vast amount of literature on hydrodynamics of bubble columns with gas-liquid systems (primarily air-water or other pure liquids), and several good reviews are available (e.g. Van Landeghem, 1980; Ostergaard, 1980; Shah et al., 1982; Heijnen and Van't Riet, 1984). Hydrodynamic parameters in systems with pure liquids (non-foaming systems) are significantly different than in systems which have foaming capacity (e.g. hydrocarbon mixtures, industrial oils particularly at high temperature and pressure, oxygenated impurities in hydrocarbons, aqueous solutions of alcohols and organic acids, etc.) as shown in recent studies by Smith, D.N. et al. (1984b), O'Dowd et al. (1985) and Shah et al. (1985). This was illustrated in experiments by Quicker and Deckwer (1981) who found that pure hydrocarbons with the same viscosity, density and surface tension as Fischer-Tropsch (F-T) derived paraffin wax produce 2-3 times larger bubbles and about one half the gas hold-up produced with F-T wax. It follows that results obtained using liquids other than F-T waxes can not be used for design and scale-up of slurry bubble column reactors for Fischer-Tropsch synthesis. Thus, a detailed discussion of these systems will not be attempted here. Qualitative comparisons between results obtained in liquids other than F-T derived waxes and those obtained with F-T waxes are made in Sections V and VI of this report.

A summary of experimental conditions employed in hydrodynamic studies with F-T derived waxes as liquid media is given in Table III-I. The major findings from these studies can be briefly summarized as follows:

- There are virtually no experimental data obtained in large bubble columns at high gas velocities, i.e. under conditions of industrial

Table III-1. Summary of bubble-column hydrodynamic studies.

Reference	Column		Distributor			Conditions					Liquid[b]	Gas	Quantity Measured
	d_c (m)	H_s (m)	d_o (mm)	n_o	Type[a]	u_g (m/s)	w_{cat} (%)	d_{cat} (μm)	T (°C)	P (MPa)			
Calderbank et al (1963)	0.051	2.3-4.6[c]	NA	1	SN	0-0.055	0	-	265	0.1	KW	H_2/CO	ϵ_g,a
Farley and Ray (1964 a,b)	0.25	8.5[c]	NA	1	"	0.03-0.073	13	1-3	265	0.15-1.1	"	"	ϵ_g
Zaidi et al (1979)	0.04-0.10	0.6-1.0	0.075	-	SP	0-0.038	2-14	1	260-290	1.0	MP	CO,N_2	ϵ_g,d_s
Deckwer et al (1980)	"	"	"	"	"	0-0.04	0-16	5	143-270	0.4-1.1	"	N_2	ϵ_g,d_s
Quicker and Deckwer	0.095	1.35	1.1	19	PP	0.04	0	-	130-170	0.1	FT-300	N_2	ϵ_g,d_s
(1981)	"	"	0.9	1	SN	"	"	"	"	"	"	"	"
Kuo et al. (1985)	0.032,0.053	0.4-1.0	0.015-0.10	-	SP	0-0.04	"		200-230	0.1	FT200,PW	"	ϵ_g
"	"	"	0.25-1.0	1-3	PP	0-0.05	"	-	"	0.1	"	"	"
"	0.051	0.58-7.6	0.02		SP	"	"	-	138-260	0.1-0.2	FT-200	"	"
"	"	"	0.5-2	1-3	PP	0-0.12	"	-	260	"	FT-200,PW	"	"
"	0.102	6-7.6	2	1	"	0-0.065	"	-	"	"	FT-200	"	"
"	"	"	1	4	"	"	"	-	"	"	FT-200,PW	"	"
"	0.026	?	0.02	-	SP	0-0.035	15	?	177	0.1-1.15	PW	H_2,N_2	"
Sanders et al.	0.05	0.5-0.9	0.2	-	"	0-0.06	0-30	?	240	1.0	FT-300,PW	H_2/CO	"
(1986)	"	"	1.0	4	PP	?	?	NA			"		
O'Dowd et al. (1986)	0.022	NA	1	1	"	0-0.02	0	-	250,280	1.5-2.2	PW,MP	N_2	ϵ_g,d_s

[a]Distributor types: PP - Perforated Plate; SN - Single Nozzle; SP - Sintered Plate
[b]Liquid Medium: KW - Krupp Wax; MP - Molten Paraffin Wax; PW - Product Wax
[c]Expanded liquid height
NA - not available

importance. Most of the studies were done in bubble columns with diameters less than 0.10 m, and thus only the homogeneous (ideal bubbly) and slug flow regimes were observed.

- The value of Sauter mean bubble diameter of about 0.7 mm determined by photographic method in studies by Deckwer and co-workers (Zaidi et al., 1979; Deckwer et al., 1980; Quicker and Deckwer, 1981) is not in good agreement with that obtained in the Calderbank et al. (1963) study (~2.5 mm by light transmission method).
- There are large discrepancies in reported values of gas hold-ups obtained in various studies. They are caused by differences in wax compositions, distributor design and column geometry.
- Paraffin waxes have tendency to foam, whereas most of the raw reactor waxes do not foam (Kuo et al. 1985).

A detailed description of the effects of operating conditions, column geometry, distributor design and wax type on the average gas hold-up and bubble size distribution is given below.

A. Effect of Temperature

Deckwer et al. (1980) found a significant decrease in the gas hold-up with the increase in temperature from 180 to 240°C in the experiments in the small diameter column (0.041 m), whereas the hold-up was essentially independent of temperature in the larger diameter column (0.10 m). Contrary to this Quicker and Deckwer (1981), and Kuo et al. (1985) found that the hold-up increases with temperature.

In general, the liquid viscosity increases as the temperature decreases and higher liquid viscosity promotes bubble coalescence. Thus, one would expect that the hold-up would increase with temperature. The

effect of viscosity on the gas hold-up was very significant during the operation of a 0.247 m in diameter slurry bubble reactor for F-T synthesis (Farley and Ray, 1964b). During one of the runs gas hold-up dropped from 45% to 12% while the slurry viscosity increased from 2 mPa·s to over 200 mPa·s during the same period of time. This large increase in viscosity was attributed to the presence of free carbon, but it is more likely that it was caused by production of high molecular weight products (Satterfield et al., 1981).

B. Effect of Solids

The addition of solids reduces the gas hold-up (Deckwer et al., 1980; Kuo et al., 1985). This may be viewed as a viscosity effect, since the viscosity of the slurry increases with solids concentration. As stated above the hold-up is expected to decrease as the viscosity of the medium increases.

C. Effect of Pressure and Gas Type

- The system pressure in the range (0.1-1.5 MPa does not have an effect on the gas hold-up (Deckwer, et al., 1980; Kuo et al., 1985).
- Gas type (N_2 or H_2) does not have an effect on the hold-up (Kuo et al., 1985).

These results show that the density of gas has negligible effect on the gas hold-up.

D. Effect of Superficial Gas Velocity-Flow Regimes and Bubble Size Distribution

The majority of studies listed in Table III-1 were made in relatively small diameter columns-up to 0.10 m (except Farley and Ray, 1964a,b-up to 0.25 m) and low superficial gas velocities-up to 0.06 m/s (except Farley

and Ray, 1964b—up to 0.073 m/s, and Kuo et al., 1985—up to 0.12 m/s).

Deckwer and co-workers (Zaidi et al., 1979; Deckwer et al., 1980; Quicker and Deckwer, 1981) found that the bubble size distribution is rather uniform which characterizes the homogeneous (ideal bubbly) flow regime. Their experiments were restricted to velocities less than 0.04 m/s, due to foaming at higher velocities.

In Mobil's study (Kuo et al., 1985) it was found, in both short and long columns, that bubble coalescence takes place with all types of distributors (sintered metal plate and orifice) and that slugs start developing at velocities between 0.02 m/s and 0.03 m/s. Slugs or slug type bubbles were observed even in a 0.102 m diameter column. The bubbles produced by orifice plate distributors were nonuniform in size and larger than the ones obtained with sintered metal plate (SMP) distributors, but the average bubble size (Sauter bubble diameter) was not determined. Foaming was observed in experiments with a paraffin wax (tradename FT-200) and was more pronounced with SMP distributors, giving hold-ups as high as 75%, than with the orifice plate distributors.

In summary, the flow regimes observed in these studies with columns up to 0.10 m in diameter were: homogeneous (ideal bubbly), slug flow or the transition between these two flow regimes, and foaming regime.

Farley and Ray (1964a,b) conducted studies under reacting conditions in a fairly large bubble column reactor with a diameter of 0.247 m where the heterogeneous (or churn-turbulent) flow regime might be possible. However, they reported results for only one value of velocity (0.073 m/s). These results were described in the Section III-A. Farley and Ray (1964a) stated that foaming occurs at low gas velocities and that it can be

prevented by operating the reactor at gas velocities greater than about 0.06 m/s. In one of the experiments they found that foam break-up occurred when the velocity was increased from 0.03 m/s to 0.06 m/s, but the gas hold-up values were not reported.

Sauter mean bubble diameter was determined by Deckwer and co-workers by photographic method (Zaidi et al., 1979, Deckwer et al., 1980; Quicker and Deckwer, 1981) and by O'Dowd et al. (1986) by a hot wire anemometer. Zaidi et al. and Deckwer et al. found in experiments with a 75 μm SMP distributor that Sauter bubble diameter is approximately 0.7 mm and that it does not vary much with gas velocity (up to 0.04 m/s) and temperature (250-270°C). Quicker and Deckwer made measurements in a 0.095 m column equipped with a 0.9 mm nozzle and found that Sauter diameter decreases with velocity and is less than 1 mm for gas velocities greater than 0.01 m/s. Contrary to this, O'Dowd et al. found that Sauter bubble diameter increases with gas velocity from 3 mm to 3.9 mm, over the range of velocities (up to 0.02 m/s), for Mobil's reactor wax from run CT-256-4 (Run 4 wax). In experiments with a paraffin wax (P-22 wax from Fisher) somewhat smaller bubble sizes were measured (2.6-3.8 mm) but similar behavior to the Mobil wax with increasing velocity was observed.

Calderbank et al. (1963) reported values of the gas hold-up and the specific gas-liquid interfacial area for gas velocities up to 0.055 m/s. The interfacial area was determined by light transmission method. Sauter mean diameters estimated from these data are between 2 and 3 mm.

Discrepancies in results obtained in different studies may be attributed to differences in liquid medium employed, distributor types liquid static heights and experimental techniques.

E. Effect of Column Diameter

This effect was examined by Deckwer et al. (1980) and in Mobil's study (Kuo et al., 1985).

- Deckwer et al. (1980) found that the hold-up is essentially independent of column diameter (0.041 and 0.10 m columns) for temperatures greater than 250°C.
- Kuo et al. (1985) found in experiments with FT-200 wax in short columns (2.2 m in height) that the hold-up is somewhat greater in the smaller diameter column (0.032 m) than in the larger one (0.053 m ID). This was attributed to the fact that the foam is stabilized by the walls of the narrower column.
- In studies by Kuo et al. in tall columns (0.051 and 0.102 m in diameter, 9.1 m in height) with dynamically similar orifice plate distributors (same orifice hole size and same gas velocity through the orifice) have shown no effect of column diameter with FT-200 wax, but higher hold-ups (about 30-40% in the velocity range 0.015-0.065 m/s) were obtained in the larger column in experiments with reactor waxes. (Waxes produced during Runs CT-256-7 and CT-256-8.) In the latter case, the higher hold-up in the larger column might have been due to fewer and smaller slugs. However, this was not observed in experiments with FT-200 wax, where slugs are accompanied by a large number of small bubbles. In this case, the contribution of slugs to the gas hold-up is relatively less, and thus the column diameter did not have effect on the hold-up.

F. Effect of Static Liquid Height

The findings from different studies may be summarized as follows:

- No effect of liquid static height on the gas hold-up was found in studies by Deckwer et al. (1980) (H_s = 0.60 – 0.95 m; 75 μm SMP) and Kuo et al. (1985) with FT-200 in the 0.051 m column equipped with a 2 mm single hole orifice plate (H_s = 0.75-7.1 m).
- The gas hold-up increases as the static height decreases (Calderbank et al., 1963 with ball and cone distributor and H_s = 2.3 and 4.6 m; Kuo et al., 1985 with FT-200 wax, 20 μm SMP and H_s = 3.05-6.40 m).
- The gas hold-up increases with the liquid static height (Kuo et al., 1985 with FT-200 wax, 1 mm single orifice and 3 x 0.5 mm orifice plate distributors, and static heights of 0.6 m and 6.3 m).

These contradictory results indicate that there exists an interaction between the sparger design, the static liquid height and properties of the liquid medium. These factors affect the bubble coalescence and break-up which in turn determines the gas hold-up.

G. Effect of Distributor Type

This effect has been studied by Quicker and Deckwer (1981) and by workers at Mobil (Kuo et al., 1985).

Quicker and Deckwer (1981) obtained higher gas hold-ups with a single nozzle distributor than with a 19 x 1.1 mm perforated plate distributor, probably because of much higher jet velocity for the former distributor. Higher jet velocity (gas velocity through the orifice) implies higher kinetic energy of the fluid which produces finer bubbles and thus higher hold-ups. The hold-ups with the single nozzle distributor were even higher than those obtained by Deckwer et al. (1980) with the 75 μm SMP, which

contradicts results obtained in Mobil's study as well as in the present one (see Section V-B.5).

In Mobil's work it was found that:

- SMP distributors produce, in general, smaller bubbles and higher hold-ups than the orifice distributors.
- For SMP distributors, gas hold-up decreases with the increasing mean pore size which is accompanied by larger bubbles and less foam (short columns 0.032 and 0.053 m ID, 2.2 m tall).
- Distributors with small orifices (less than 0.4 mm) can give hold-ups similar to large-pore SMP distributors. Bubble size distributions, though, are different (short columns).
- Orifice-type gas distributors give similar hold-ups when the gas jet velocities through the holes are similar. However, if the orifice diameter is large enough (≥ 1 mm) lower hold-ups will result at all velocities (short columns).

H. Effect of Liquid Medium

Experiments with different waxes were conducted only in Mobil's study (Kuo et al., 1985). They found that reactor waxes give lower hold-ups than that obtained with FT-200 wax for all types of distributors (SMP and orifice plate). Also, unlike FT-200 wax most of the reactor waxes did not foam (Waxes made in runs 5, 7 and 8 did not foam, whereas the wax made during the run 4 in Mobil's pilot plant unit CT-256 produced some foam in a run with 60 μm SMP distribution at 200°C in the 0.053 m ID column). These differences in behavior of different waxes are caused to some extent by differences in their physical properties (primarily the viscosity), and

even more significantly by differences in their compositions. The presence of small amounts of surface active species is known to have a significant effect on foaming behavior and hydrodynamic parameters in gas-liquid systems. These results show that the liquid medium for hydrodynamic studies must be chosen carefully in order to obtain information useful for bubble column reactor design.