CHAPTER I

INTRODUCTION

The oil crisis from the Organization of Petroleum Exporting Countries (OPEC) and the ongoing war in the Middle East are leading to a search for an alternative source of fuels and primary chemicals. One indirect coal liquefaction process known as Fischer-Tropsch (FT) synthesis (i.e. hydrocarbon synthesis from CO and H_2), was once used commercially to produce fuels in Germany during World War II. The only commercial scale reactors currently in use are the entrained fluidized bed (Synthol) and fixed bed tubular reactors *Arbeitsgemeinshaft Ruhrchemie/Lurgi* (ARGE) used by Sasol in South Africa.

Gas-liquid bubble columns are widely used in industry as reactors, absorbers strippers, and as fermentors. The absence of moving parts, low operating cost, and the ability to easily vary residence times make bubble columns excellent contactors and mass transfer units. Studies on the application of slurry-phase bubble columns to Fischer-Tropsch synthesis indicate that bubble columns are more advantageous than fixed bed reactors, because they can process low H_2/CO ratio synthesis gas without plugging the reactor or deactivating the catalyst due to carbon formation (Calderbank *et al.*, 1963; Kölbel and Ralek (1980); Deckwer *et al.*, 1982; Kuo, *et al.*, 1985; and Sanders *et al.*, 1986). The agitation of the slurry by rising gas bubbles provides good heat transfer to the reactor walls by minimizing temperature gradients and eliminating hot spots which may cause rapid catalyst deactivation. Moreover, bubble columns have higher flexibility, and lower construction costs than fixed bed or fluidized bed reactors.

This thesis follows the style of the *AIChE Journal*.

The rate of mass transfer in bubble column reactors depends primarily on the liquid-phase mass transfer coefficient and the gas-liquid interfacial area:

$$r_{a,i} = k_{\ell,i}\, a_g\, (C_i^* - C_{\ell,i}) \tag{1.1}$$

where: $k_{\ell,i}$ is the liquid-phase mass transfer coefficient, a_g is the specific gas-liquid interfacial area, $C_{\ell,i}$ is the concentration of component i in the liquid phase, and C_i^* is the equilibrium concentration of component i in the liquid phase. The liquid-phase mass transfer coefficient is a function of: physical properties of fluid, superficial gas velocity, and bubble diameter. The gas-liquid interfacial area for spherical bubbles is defined as:

$$a_g = 6\, \epsilon_{go}/d_s \tag{1.2}$$

where: ϵ_{go} is the gas hold-up and d_s is the Sauter mean bubble diameter. The hydrodynamic parameters, gas hold-up and Sauter mean diameter, are influenced by:

1. Dynamic factors
2. Geometrical characteristics of bubble columns
3. Physical properties of liquid

The first group, dynamic factors, consists of the gas and liquid flow rates. The bubble column diameter, type of gas distributor (e.g., orifices, perforated plates, injectors, and sintered metal plates), and liquid static height, compose the second group; while the third group is composed of the surface tension, density, and viscosity of the fluid.

CHAPTER II

LITERATURE REVIEW

A. Gas Flow in Bubble Columns

The flow of gas in bubble columns can be characterized by three primary flow regimes: The homogeneous bubbly flow regime (laminar), the slug flow regime, and the churn-turbulent flow regime. The flow regimes are largely determined by the column diameter and superficial gas velocity. In the bubbly flow regime, bubbles may be small and spherical, or larger and non spherical because of the flow of liquid around them. As the superficial gas velocity is increased slug flow is developed. Here, the gas elements are larger and occupy the column diameter. Under certain conditions (column ID > 0.1 m) slug flow transforms into the churn flow, where the flow is much more irregular and disturbed as a result of the breakdown of large gas bubbles. The dependence of flow regimes on column diameter and superficial gas velocity can roughly be estimated from the flow regime map presented by Deckwer *et al.*, 1980 (see Figure 1). Schumpe and Deckwer (1982) showed that distributor type, physical properties of the media, and gas superficial velocity have a strong influence on the transition between flow regimes (e.g., slug flow regime occurs at very low gas velocities for high viscous liquids).

B. Fischer-Tropsch Derived Waxes

Fischer-Tropsch synthesis proceeds between 230 °C to 270 °C with fine precipitated iron catalyst particles suspended in a paraffin wax. Hydrodynamic studies of bubble columns using FT derived waxes are scarce compared to non-wax

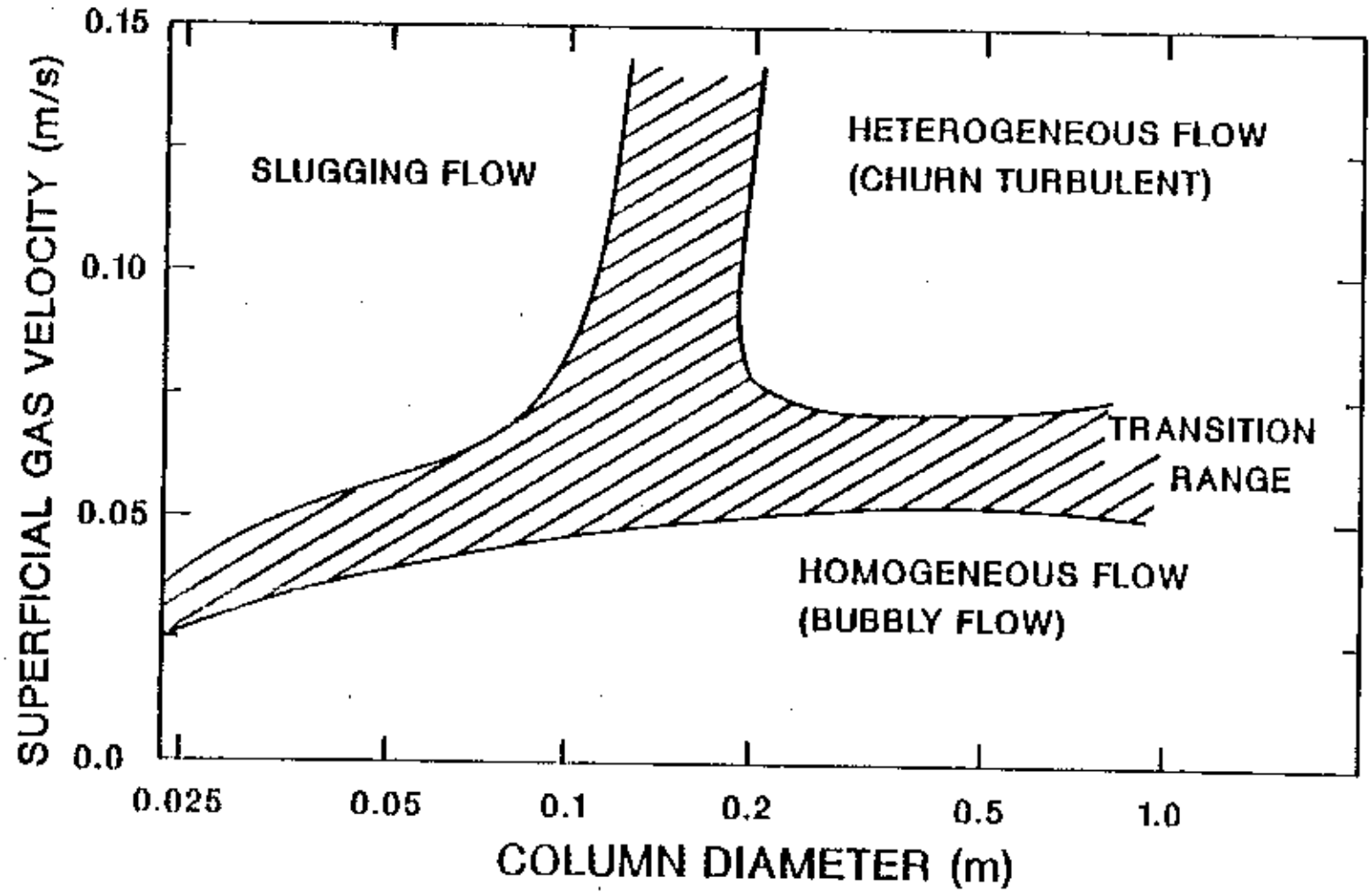

Figure 1. Bubble column flow regime map (from Deckwer *et al.* 1980)

studies. A summary of experimental conditions employed in hydrodynamic studies with FT derived waxes as liquid media is given in Table 1. The major observations from these studies can be briefly summarized as follows:

1. There are virtually no experimental data obtained in large bubble columns at high gas velocities under conditions of industrial importance. Most of the studies were performed in bubble columns with diameters less than 0.10 m, and only the homogeneous and slug flow regimes were observed.
2. Deckwer and co-workers (Zaidi *et al.*, 1979; Deckwer *et al.*, 1980; Quicker and Deckwer, 1981) obtained the value of Sauter mean bubble diameter of about 0.7 mm using photographic method. Whereas, Calderbank *et al.*, (1963) obtained Sauter mean bubble diameters of about 2.5 mm using a light transmission method.
3. There are large discrepancies in reported values of gas hold-ups obtained in various studies. These discrepancies are caused by differences in wax compositions, distributor design and column geometry.
4. Paraffin waxes have a tendency to foam, whereas most of the raw reactor waxes do not foam (Kuo *et al.*, 1985; Bukur *et al.*, 1987).

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.

1. Effect of Temperature

Deckwer *et al.* (1980) observed a significant decrease in gas hold-up with increase in temperature from 180 to 240 °C for experiments in small diameter column (0.041 m), whereas the hold-up was essentially independent of temperature

Table 1. Summary of Bubble-Column Hyhydrodynamic Studies Using Waxes.

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	250-290	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 (1981)	0.095	1.35	1.1	19	PP	0.04	0	-	130-170	0.1	FT-300	N_2	ϵ_g,d_s
	"	"	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. (1986)	0.05	0.5-0.9	0.2	-	"	0-0.06	0-30	?	240	1.0	FT-300,PW	H_2/CO	"
	"	"	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

in the larger diameter column (0.10 m). Contrary to this, Quicker and Deckwer (1981), Kuo *et al.* (1985), and Bukur *et al.*, (1987) 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, it is expected 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 FT synthesis (Farley and Ray, 1964b); whereby, in one of the runs the 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).

2. Effect of Solids

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

3. Effects of Pressure and Gas Type

Deckwer *et al.*, (1980) and Kuo *et al.*, (1985) found that the system pressure in the range 0.1 to 1.5 MPa does not have an effect on gas hold-up values. Furthermore, Kuo *et al.* observed that gas type (N_2 or H_2) does not have an effect on gas hold-up values. These results show that the density of the gas has negligible effect on the gas hold-up.

4. Effect of Superficial Gas Velocity on Flow Regimes

Most of the studies listed in Table 1 were made in relatively small diameter columns (< 0.1 m) (except Farley and Ray, 1964a, and 1964b-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). Zaidi *et al.*, 1979; Deckwer *et al.*, 1980; and Quicker and Deckwer, 1981 found that flow regime in their experiments was homogeneous (ideal bubbly), which is characterized by a uniform bubble size distribution. Their experiments were restricted to velocities less than 0.04 m/s, due to foaming at higher gas velocities. In Mobil's study (Kuo *et al.*, 1985) it was found that in both short and tall columns bubble coalescence takes place with all types of distributors (sintered metal plate and orifice) and that slugs start developing at superficial gas 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 (FT-200) and was more pronounced with SMP distributor, giving hold-ups as high as 75%.

In summary, the flow regimes observed in these studies with columns up to 0.1 m in diameter were: homogeneous , slug flow or the transition between these two flow regimes, and foaming regime.

5. Effect of Column Diameter

Deckwer *et al.* (1980); Kuo *et al.* (1985); and Bukur *et al.* (1987) have conducted extensive studies of this effect, and they have reported the following observations:

1. Deckwer *et al.* (1980) observed that for temperatures greater than 250 °C gas hold-up is independent of column diameter (0.047 m and 0.10 m ID columns)
2. Kuo *et al.* (1985) observed that for runs with FT-200 wax in short columns (2.2 m in height) the gas hold -up values were higher in the smaller ID column (0.032 m) than in the larger ID column (0.053 m). They explained this as the fact that the narrower column tends to stabilize the foam leading to higher values of gas hold-up.
3. Kuo *et al.* (1985) found that tall columns (0.051 and 0.102 m ID columns, and 9.1 m tall) equipped with similar orifice plate distributors i.e. the same orifice size and the same jet velocity through the orifice, have shown no effect of column diameter with FT-200 wax. However, runs with reactor waxes (wax produced during runs CT-256-7 and CT-256-8) produced higher gas hold-up values, about 30-40 %, for superficial gas velocities between 0.015 to 0.065 m/s in the larger column. High values of hold-up in the large column might have been due to type of flow regime, fewer and smaller slugs. This type of flow behavior was not observed in runs with FT-200, where slugs were accompanied by a large number of small bubbles. The presence of slugs lowers the gas hold-up values.
4. Bukur *et al.*, 1987 found that, in the absence of foam gas hold-up values for FT-300 wax in 0.051 m and 0.229 m ID columns equipped with similar orifice distributors were independent of the column diameter.

6. Effect of Liquid Medium

Studies with different kinds of waxes were conducted in Mobil's study (Kuo *et al.*, 1985). In general they observed that reactor waxes do not have a tendency to foam, and they give lower hold-up values than FT-200 paraffin wax for all types of distributors (SMP and orifice plates). However, a batch of reactor wax from run 4 in Mobil's pilot plant unit CT-256 produced some foam during a run with 60 μm SMP distributor at 200 °C in the 0.053 m ID column. These differences in behavior for reactor waxes may be due to differences in physical properties and their composition. The presence of small amount of impurities which act as surface active agents, may lead to substantially higher hold-ups.

7. Effect of Static Liquid Height

Results from different studies are summarized as follows:

1. Deckwer *et al.* (1980) and Kuo *et al.* (1985) found that there is no effect of liquid static height on gas hold-up values, Deckwer *et al.*, used liquid static heights from 0.6 m to 0.95 m, with a 75 μm distributor; while Kuo *et al.*, used 0.051 m ID column equipped with a 2 mm single orifice plate for static heights from 0.75 m to 7.1 m with FT-200 wax.
2. Calderbank *et al.* (1963) found that the gas hold-up value increases with a decrease in static heights in experiments with a ball and cone distributor and static heights of 2.3 and 4.6 m. Similar observations were reported by Kuo *et al.* (1985) with FT-200 wax using 20 μm SMP for liquid static heights between 2.3 and 6.4 m.
3. Kuo *et al.* (1985) observed an increase in gas hold-up with liquid static height for runs with FT-200 wax using 1 mm single orifice plate and 3 x 0.5 mm

(three holes of 0.5 mm in diameter) orifice plate distributors for liquid static heights between 0.6 and 6.3 m.

These contradictory observations indicate that there is an interaction between the distributor design, liquid static height, and properties of liquid media. These factors affect the bubble dynamics which in turn determines the gas hold-up values.

8. Effect of Distributor Type

The effect of distributor type has been studied by Quicker and Deckwer (1981) and by Kuo *et al.* (1985). The former obtained higher gas hold-up values with a single nozzle distributor than with a 19 x 1.1 mm perforated plate distributor, probably because of high Weber number for the single orifice distributor. High Weber number implies high kinetic energy of the gas which produces finer bubbles and thus higher gas hold-up values. In Mobil's work (Kuo *et al.*, 1985) it was found that:

1. In general, SMP distributors produce higher gas hold up values than the orifice plate distributors. Moreover, SMP distributors produce smaller bubbles than orifice plate distributors. Similar observations have been observed recently by Bukur *et al.* (1987) using FT-300 wax.
2. Gas hold-up values decrease with increase in pore size for SMP distributors, larger pores are accompanied by larger bubbles and less foam. This was observed for 0.032 and 0.053 m ID columns.
3. Orifice plate distributors (< 0.4 mm) can give hold-up values similar to those for large pore SMP distributors (short columns).

4. Orifice-type gas distributors give similar hold-up values when the Weber number through the holes are similar. However, large orifices (> 1 mm) result in lower gas hold up values at all superficial gas velocities.

C. Non-Wax Liquid Mediums

Extensive reviews of hydrodynamic studies in bubble columns using non-FT liquids are available in the literature (e.g., Hughmark, 1967; Mashelkar, 1970; Ostergaard, 1980; Shah *et al.*, 1982; and Heijnen and Van't Riet, 1984). A partial summary of experimental conditions employed in hydrodynamic studies with non-wax liquid mediums is presented in Table 2.

The major highlights of these studies are:

1. Schügerl, 1981 and Kelkar, 1986 observed that pure liquids and highly viscous solutions ($\mu > 0.02$ Pa.s) are strongly coalescing, whereas aqueous solutions of organic compounds (e.g., alcohol) are non-coalescing.
2. Ostergaard, 1980 found that distributor type affects gas hold-ups and bubble size only in the bubbly flow regime. Single orifices or perforated plates produce lower gas hold-up values than do sintered metal plates. Schumpe and Deckwer (1982) and Haque *et al.* (1986) observed no effect of distributor type on gas hold-up in the heterogeneous and slug flow regimes for coalescing media.
3. Ostergaard, 1980; and Shah *et al.*, 1982 found that effect of column diameter on gas hold-up is severe for column/bubble diameter ratios between 40 to 100. Godbole *et al.* (1982) and Haque *et al.* (1986), while using highly viscous non-Newtonian liquids, they observed a strong decrease in gas hold-up with an increase in column diameter. Furthermore, Haque *et al.* (1986) reported

Table 2. Summary of Bubble Column Hyhydrodynamic Studies Using Non Wax Mediums.

System	Range of Parameters	Quantity Measured	Reference
Air-Water Air-Glycol Aq. Soln. Air-Methanol O_2-Water	u_g, m/s: 0.003–0.4 u_l, m/s: 0.00–0.044 d_c, m: 0.152–0.6 H_s, m: 1.26–3.5	ϵ_g, a_g	Akita and Yoshida (1973), (1974)
Air-Water Air-Methanol Aq. Soln. ρ_l, kg/m^3: 910–1200 μ_l, Pa.s: 0.0007–0.0138 σ_l, N/m: 0.0375-0.0748	u_g, m/s: 0.042–0.38 d_c, m: 0.1–0.19 H_s, m: 0.6–1.35	ϵ_g	Hikita and Kikukawa (1974)
Air-Alcohol Aq. Soln. Air-Glucose Aq. Soln.	u_g, m/s: 0.0–0.08 u_l, m/s: 0.0 d_c, m: 0.14 Distributor: 17.5 μm SMP 180x0.5 mm PP 3 mm Nozzle	ϵ_g a_g	Schugerl et al. (1977)
Air-Alcohols Air-Halogenated Hydrogens	u_g, m/s: 0.0–0.1 d_c, m: > 0.1 H_s, m: > 1.2	ϵ_g	Bach and Pilhofer (1978)
Air-CMC Aq. Soln. (1.0–1.6 wt. %)	u_g, m/s: 0.0–0.08 u_l, m/s: 0.0 d_c, m: 0.14 Distributor: 17.5 μm SMP 180x0.5 mm PP 3 mm Nozzle	ϵ_g	Buchholz et al. (1978)
Different Gases (Air, H_2, CO_2 CH_4, N_2)–Water Air-Organic Liquids Air-Electrolyte Soln. ρ_l, kg/m^3: 790–1170 μ_l, Pa.s: 0.0009–0.0178 σ_l, N/m: 0.0229–0.0796	u_g, m/s: 0.042–0.38 d_c, m: 0.1	ϵ_g, a_g	Hikita et al. (1980)

Table 2. Continued

System	Range of Parameters	Quantity Measured	Reference
Aqueous CMC Soln. (1.0–2.0 wt. %)	u_g, m/s: 0.0–0.08 d_c, m: 0.14 H_s, m: 2.6	ϵ_g, a_g	Deckwer et al. (1980)
Air-CMC Aq. Soln. (1.0–1.7 wt. %)	u_g, m/s: 0.0–0.08 u_l, m/s: 0.013–0.015 d_c, m: 0.14 H_s, m: 3.91	ϵ_g a_g	Schugerl (1981)
Air-CMC Aq. Soln. (0.0–1.8 wt. %)	u_g, m/s: 0.0–0.18 u_l, m/s: 0.0–0.006 d_c, m: 0.102 H_s, m: 2.36 Distributor: 0.15–2.0 mm SP	ϵ_g a_g	Schumpe and Deckwer (1982)
Air-Organic Liquids Air-CMC Aq. Soln.	u_g, m/s: 0.03–0.24 u_l, m/s: 0.0 d_c, m: 0.305 H_s, m: 3.4 Distributor: 749x1.66 mm PP	ϵ_g a_g	Godbole et al. (1982), (1984)
Air-CMC Aq. Soln. (0.005–0.23 wt. %) Air-Alcohol Aq. Soln.	u_g, m/s: 0.03–0.3 u_l, m/s: 0.03–0.1 d_c, m: 0.154 H_s, m: 3.35	ϵ_g	Kelkar and Shah (1985)
Air-CMC Aq. Soln. (0.0–2.0 wt. %)	u_g, m/s: 0.01–0.24 u_l, m/s: 0.0 d_c, m: 0.1–1.0 H_s, m: 1.5–2.4 Distributor: 100x0.3 mm PP 168x1.0 mm PP 109x1.5 mm PP 109x2.0 mm PP	ϵ_g	Haque et al. (1986)

Table 2. Continued

System	Range of Parameters	Quantity Measured	Reference
Air-CMC Aq. Soln.	u_g, m/s: 0.0–0.08 u_l, m/s: 0.0 d_c, m: 0.1 H_s, m: 2.5 Distributor: 4 mm orifice	ϵ_g	Vatai and Tekic (1987)
Air-Methanol Aq. Soln. -Ethanol -i-Propanol -n-Butanol	u_g, m/s: 0.0–0.08 u_l, m/s: 0.0 d_c, m: 0.1 H_s, m: 2.5 Distributor: 4 mm orifice	ϵ_g	Posarac and Tekic (1987)

that the static height does not affect gas hold-up for H_s/d_c ratios greater than 3.

4. Schügerl. *et al.*, 1977 and Kelkar, *et al.*, 1983 report that, bubble size and gas hold-up depends on liquid properties. Bach and Pilhofer (1978), Godbole *et al.* (1984), and Haque *et al.* (1986) observed decreases in gas hold-up as liquid viscosity increased. Furthermore, they observed no effect of surface tension on gas hold-up in the heterogeneous flow regime. Schumpe and Deckwer (1982) reported that gas hold-up is independent of liquid viscosity in the slug-flow regime for 0.102 and 0.14 m ID columns.
5. Deckwer *et al.*, 1980 found that gas hold-up and bubble size correlations presented in the literature for non-wax media fail to predict gas hold-up and bubble sizes observed in bubble columns using FT derived waxes as the liquid medium, even though the physical properties of FT derived waxes are similar to the fluids used to obtain the correlations.

D. Thesis Objectives and Motivation

The objective of this thesis was to perform extensive studies on hydrodynamics of bubble column with application to Fischer-Tropsch synthesis. Experiments were carried out using different FT derived waxes; paraffin waxes (FT-200 and a limited number of experiments with FT-300 wax) and reactor waxes (Sasol and Mobil reactor waxes) in order to investigate the effect of liquid medium and bubble column parameters (geometry and operation) on gas hold-up and bubble dynamics.

Experiments conducted with paraffin waxes at 265 °C showed a foaming behavior, but no foam was observed when these experiments were conducted at 200 °C. In order to investigate the dependence of foaming behavior on physical

properties, experiments were conducted using cold mediums: pure liquids (distilled water and n-butanol), foaming mixtures (aqueous solutions of n-butanol), and non-Newtonian mixtures (aqueous solutions of n-butanol with carboxymethyl cellulose (CMC)). Cold mediums were used in this investigation because they are easy to handle (measurements of physical properties) compared to molten waxes.

Investigated parameters were extended beyond those previously studied. Finally, the effect of different parameters on gas hold-up and bubble dynamics on scale up of bubble columns was addressed.