liquid/solid pairs in the 12.7 cm CFS. For silicon oxide, particle diameter is seen to have the opposite effect in an isoparaffin slurry than in an aqueous slurry.

The results for a 20% weight loading, 49 μm particle size, are plotted for the four 12.7 cm CFS solid/liquid pairs in Figure 5.4. As gas velocity increased from 1.52 to 15.24 cm/sec, gas holdup reached a limiting value of about 25%. The largest gas holdups were seen for the isoparaffin/iron oxide system. The smallest holdups were seen in the silicon oxide/water system. Isoparaffin gave a larger gas holdup because of its lower surface tension, producing smaller bubbles at the distributor, and its lower density, giving a slightly lower buoyancy force.

The 30.5 cm CFS was determined to have a lower gas holdup than the 12.7 cm CFS at the higher gas velocity. It is speculated that the bubbles, in a taller column, have a greater opportunity to coalesce. Therefore, the 30.5 cm CFS correlation was used in the computer simulation of an operating commercial Fischer-Tropsch reactor, discussed in Section II, Engineering Evaluation.

6.0 Bubble Size

Bubble size was measured because this type of information has never been obtained before for a three-phase hydrocarbon system. Also, the predicted values reported in the literature based on gas-liquid studies vary by a factor of three (Deckwer, 1981; Satterfield, 1980). Bubble size, along with gas holdup, has a considerable effect on the extent of mass transfer resistance on the overall reaction. Because of the differences in gas holdup between two- and three-phase systems, there is reason to suspect that there are also differences between two- and three-phase bubble diameters.

The objective of bubble diameter measurements was to obtain the gas-liquid interfacial area over a variety of cold flow operating

conditions. As discussed in Section 1.3, this is related to Sauter mean bubble diameter and gas holdup by

$$a = 6\,\varepsilon_G/d_{SB} \qquad (1.3.1)$$

Thus by combining a bubble diameter, d_{SB}, relationship with the gas holdup Equation 5.3.5, the above-stated objective can be realized.

6.1 Theory

A hot film double conical probe was used to measure bubble diameters in the three-phase cold flow simulator. The distribution of bubble chord lengths transected by the probe was interpreted using the cumulative gamma distribution function (CGDF):

$$CZ(\lambda) = \frac{\int_0^{\lambda} \int_{\gamma}^{\infty} x^{n-1} e^{sx}\, dx\, dy}{\int_0^{\lambda} \int_{\gamma}^{\infty} x^{n-1} e^{sx}\, dx\, dy} \qquad (6.1.1)$$

From this expression, the necessary correlations between average bubble diameter, d_B, Sauter bubble diameter, d_{SB}, and the two bubble-size distribution parameters, n and s, as shown by Hess (1982) are:

$$d_B = n/-s \qquad (6.1.2)$$

$$d_{SB} = (n + 2)/-s \qquad (6.1.3)$$

6.2 Experimental

The procedure that was used for obtaining a bubble diameter measurement in a three-phase system is shown schematically in Figure 6.2.1. For each bubble, the top of a double hot film conical probe (see Figure 6.2.2) recorded a bubble trace, Figure 6.2.3. These impulses were fed through an electrical bridge, similar to a Wheatstone bridge,

into an A-D converter and stored by the computer. The computer then determined whether both probes detected the same bubble. By measuring the difference in initial contact time between probes, the bubble rise velocity was obtained. Multiplying the time a bubble takes to pass a probe by the rise velocity yielded the actual chord length. Since the probe could be transcending any chord of the bubble, a large number of samples, 1400, must be obtained in order to obtain an accurate bubble diameter distribution to within ±10% (Azzopardi, 1979). Once 1400 bubble sizes were recorded, that information was then transferred by phone line to the mainframe computer. On the mainframe computer, a statistical analysis to convert those 1400 bubble samples into the parameter bubble size gamma distribution was performed.

The double conical probe was calibrated in the plexiglas calibration chamber.

An isometric view of the plexiglas calibration chamber is shown in Figure 6.2.4. The chamber is roughly a 12.7 cm OD cube. This shape minimized photographic aberration. The probe was inserted from the back face. The single bubble distributor could be inserted from either the bottom face or from the rear face. Pictures could be taken from either the front or top faces. A vertical reference stick denoting 1/64ths inch was placed the same distance as the probe from the camera.

6.2.1 Calibration Procedure

A GenRad Model 1531 stroboscope was used along with a Polaroid camera with adjustable shutter speed and F stop to obtain stroboscopic pictures of a stream of bubbles impinging on the double conical probe. Adjusting the strobe "froze" the bubble stream. Three to four bubbles were captured in the picture to obtain bubble rise velocities.

As the strobe frequency became an integer or half integer multiple of the bubble frequency, the action was frozen. Starting at a low strobe frequency, 300 rpm, the strobe rate was increased until freezing the action produced more bubbles in the picture than had been seen at the previous freeze frequency. The strobe was then dialed back down to that previous lower freeze point, and pictures were taken at that setting.

The shutter speed was low enough to allow two strobe flashes. Bubble rise velocities are calculated as follows:

$$j_B = SF(DX)$$

Where:

j_B = Bubble rise velocity (cm/sec)

SF = Strobe frequency (sec^{-1})

DX = Distance between bubble tops (cm)

The distance between bubble tops was measured because, for larger bubbles, bubble tops were not observed to deform.

It was necessary to place the gas sparger near enough to the probe to assure a consistent hit, about 3/4 inch. Although the bubble may not have reached a steady state rise velocity, agreement with Calderbank (1963) data was good.

The effect of the bubble probe in slowing the bubble down was greatly influenced by bubble size. The smallest bubble studied, 0.8 mm, was slowed down 20-25% upon hitting the probe. The largest bubble, 8 mm wide, experienced no reduction in velocity before and after hitting the

probe. The intermediate size, 2.2 mm bubble, had its velocity reduced roughly 10% before and after hitting the probe.

A representative bubble trace is shown in Figure 6.2.3. The beginning and end of each bubble was taken from the points at which the derivative of the trace changed sign. The larger the bubble, the clearer this transition.

6.3 Results

Bubble chord lengths, uncalibrated, were analyzed using the cumulative gamma distribution function CGDF discussed in Section 6.1. The resulting average and Sauter bubble diameters using Equations 6.1.2 and 6.1.3 and the operating conditions at which they were obtained are shown in Table 6.3.1. These uncorrected values are in a range from 0.28 to 0.44 cm. These values are slightly larger than those measured by Koppers (1961) and Calderbank (1963) in similar systems.

6.4 Discussion

The reason that the bubble diameter was slightly larger is discussed by Rowe and Masson (1981). They observed that a probe shaped similarly to the one used caused bubbles to accelerate as they were transected. Probes in general also caused bubbles to elongate making measured chord lengths appear longer than they would be in an undisturbed bubble. It was, therefore, necessary to calibrate the bubble diameter probe.

A double conical probe was calibrated in a Plexiglas calibration chamber. A GenRad Model 1531 stroboscope was used along with a Polaroid camera to obtain stroboscopic pictures of a stream of bubbles impinging on the probe. Bubble diameters in the range 0.07 to 0.21 cm were used in the calibration. The lag time, or time for the bubble to travel the probe gap distance, was well calibrated. Calibration of the

dwell time, or time the bubble spends at a given probe, proved much more elusive for a number of reasons. Intersecting different bubble chord lengths has no effect on lag time. However, it has quite an effect on dwell time. The larger bubbles in the range calibrated are nonrigid ellipsoids. While the leading edge of the bubble remains fairly rigid the trailing edge does not. Again, the effect on dwell time is considerable. Because of this difficulty, an average value was used. The corrected dwell time was assumed to equal 80% of the measured dwell time.

The calibration studies also showed that smaller bubbles are slowed down to a much greater degree than larger bubbles. This effect accounts for the mean bubble sizes being smaller at the column center on the uncorrected table than at the column wall, contrary to expectations. (The effect of the lag and dwell time calibration is shown by comparing Tables 6.4.1. and 6.3.1.)

Valuable information was obtained from the corrected bubble diameter results in Table 6.4.1. The Sauter mean bubble diameter ranges from 0.22 to 0.35 cm and the bubble velocity ranges from 26.3 to 32.7 cm/sec, both fairly narrow ranges. Larger bubbles are seen toward the column center than at the column edge as expected. The bubble sizes are in line with the predictions of Calderbank (1963) but three times those reported by Deckwer (1981). This corresponds to interfacial areas which are roughly 1/9 those of Deckwer.

Since bubble diameter varies relatively little, given a reliable correlation for gas holdup, it should be possible with a proper choice of bubble diameter to obtain a reliable correlation for interfacial area, which was the objective of the bubble diameter studies. Because of the isoparaffin's lower surface tension and observed higher gas holdup, it can be reasonably argued that bubble diameters should be smaller in isoparaffin than in water. The Calderbank (1963) correlation

suggests a Sauter diameter size of 0.23 cm for a Fischer-Tropsch type system. Entering 0.23 cm for d_{SB}

$$a = 6\ \varepsilon_G/0.23 = 26.09\ \varepsilon_G \qquad (6.4.1)$$

This relationship was used in the computer model.

7.0 Mass Transfer

The overall mass transfer coefficient, or K_La, is the product of the mass transfer rate per unit area, K_L, and the interfacial area, a. It was measured because reported values for K_La vary. This difference is primarily due again to differences in reported bubble size and gas holdup values, i.e., the interfacial area. However, even the value of K_L varies. Calderbank and Moo-Young (1961) studied the free rise of single bubbles and bubble swarms in bubble columns and obtained the following correlation for bubbles >2.5 mm:

$$K_L = 0.42(D_L^3 \rho_L g^2/\mu_L)^{1/6} \qquad (7.0.1)$$

Fair (1967a) suggested the theoretically derived Froessling equation to predict K_L in the bubbly flow regime,

$$K_L d_B/D_L = 2(1+0.276Re^{1/2}Sc^{1/3}) \qquad (7.0.2)$$

The K_La measurements are expected to serve as a check on the gas holdup and bubble diameter results.

K_La's measured in an air/water system can be related to K_La's of other systems according to Fair (1967a) by

$$(K_La)_i = (K_La)_{O_2}\left(\frac{D_{L\,i}}{D_{L\,O_2\text{-}H_2O}}\right)^{1/2} \qquad (7.0.3)$$

Where

$$D_{L_{O_2-H_2O}} = 9.65 \times 10^{-5} \text{ Ft}^2 \text{ hr}^{-1} \text{ at } 77°\text{F}$$

More importantly, as K_L was expected to be fairly constant over the range of experiments, the K_La measurements can be used to estimate the gas/liquid interfacial area.

7.1 Theory

For mass transfer of O_2 from a liquid volume, $V(1 - \varepsilon_G)$, to a gas volume, $V\varepsilon_G$, two differential mass balances can be set up, one for each phase.

$$(\varepsilon_G)dy/dt = \varepsilon_G E_{ZG} d^2y/dz^2 - Q_G dy/dz + K_La\ (C - C^*) \tag{7.1.1}$$

$$(1 - \varepsilon_G)dC/dt = (1 - \varepsilon_G)E_{ZL} d^2C/dz^2 + Q_L dC/dz - K_La\ (C - C^*) \tag{7.1.2}$$

For a batch system, $Q_L = 0$, and Equation 7.1.2 simplifies to

$$(1 - \varepsilon_G)dC/dt = (1 - \varepsilon_G)E_{ZL} d^2C/dz^2 - K_La(C - C^*) \tag{7.1.3}$$

7.2 Experimental

In the transient method to determine K_La the gas feed of air is instantaneously changed over to nitrogen. Because a large amount of nitrogen is used to strip out part per million quantities of O_2 from the liquid phase, the gas phase O_2 concentration is essentially zero. Thus, $dy/dt = 0$ in Equation 7.1.1, and $C^* = 0$ in Equation 7.1.3. With the following assumptions:

a) the liquid is well mixed,

b) the gas phase is well mixed, and

c) the response time of the dissolved O_2 electrode is fast compared to the rate of mass transfer between liquid and gas,

the first term on the right-hand side of Equation 7.1.3 equals zero, and Equation 7.1.3 can be integrated directly to yield:

$$K_L a = \frac{1 - \varepsilon_G}{t_2 - t_1} \ln \frac{C_1}{C_2} \qquad (7.2.1)$$

where C_1 and C_2 are dissolved O_2 concentrations at t_1 and t_2. The error involved in simplifying assumption c) is negligible as long as $K_L a < 0.1\ S^{-1}$ (Keitel and Onken, 1981) which was always the case. Assumptions a) and b) were justified because two O_2 probes placed at the bottom and 1/3 of the way up the column gave essentially superimposable concentration vs. time plots.

7.3 Results

Table 7.3.1 and Figure 7.3.1 show the mass transfer results. An empirical correlation of these results yielded:

$$K_L a = 0.30 \varepsilon_G^{1.06} d_p^{0.05} / W^{0.08} \qquad R^2 = 0.89 \qquad (7.3.1)$$

7.4 Discussion

Interfacial area is related to the gas holdup and mean bubble diameter by

$$a = 6\ \varepsilon_G / d_{SB} \qquad (1.3.1)$$

K_L varies little with gas holdup. Since, by Equation 7.3.1, $K_L a$ is linearly proportional to gas holdup, this implies by Equation 1.3.1 that the mean bubble diameter varies little with increasing gas

holdup. This was confirmed in the bubble diameter work. Substituting the gas holdup correlation 5.3.5 into Equation 7.3.1 also indicates that gas velocity is the primary factor in estimating $K_L a$.

The data was compared to two, two-phase correlations applied to the air/water system: Akita and Yoshida (1974),

$$K_L a = 0.6 \frac{D_L}{D^2} Sc^{0.5} Bo^{0.62} Ga^{0.31} \varepsilon_G^{1.1} \qquad (7.4.1)$$

where

D_L = O_2 liquid diffusivity, $cm^2\ sec^{-1}$

D = column diameter, cm

and Hikita et al. (1981),

$$K_L a = \frac{14.9\ g}{j_G} \left(\frac{j_G \mu_L}{\sigma}\right)^{1.76} \left(\frac{\mu_L^4\ g}{\rho_L \sigma^3}\right)^{-0.248} \left(\frac{\mu_G}{\mu_L}\right)^{0.243} \left(\frac{\mu_L}{\rho_L D_L}\right)^{-0.604} \qquad (7.4.2)$$

For the water/air system with,

ρ_L = 0.998 g/cm^3

μ_L = 0.00961 g/cm sec

μ_G = 0.000182 g/cm sec

σ = 72.3 dyne/cm

D_L = 2.22×10^{-5} cm^2/sec

D = 12.7 cm

Equations 7.4.2 and 7.4.3 simplify, respectively, to

$$K_L a = 0.323 \varepsilon_G^{1.1} \quad (7.4.3)$$

$$K_L a = 9.39 \times 10^{-3} j_g^{0.76} \quad (7.4.4)$$

The experimental data lies in the range of these two, two-phase correlations. A decrease in $K_L a$ is observed in going from 0 to 10 and from 10 to 20 wt% for both silica sizes. However, a further decrease in $K_L a$ in going from 20 to 30 wt% was detected only for the larger silica particles. Other workers observed no such effect of solids on $K_L a$ (Alper, 1980; Kars, 1979). A possible explanation for this effect would be the same as for the decrease in gas holdup with greater weight loadings observed previously (i.e., increasing slurry viscosity yielding larger bubbles with a shorter residence time and hence a smaller interfacial area).

Values of $K_L a$ for the 90–115 μm system are greater than those obtained in the 0–5 μm silica system. If K_L for the two systems is similar this points to an inverse relationship between particle size and interfacial area. Again, this could be accounted for by the slurry viscosity or bubble size effect mentioned earlier.

8.0 Liquid Dispersion

The three hydrodynamic parameters just discussed, gas holdup, bubble size, and $K_L a$, affect the extent that mass transfer controls bubble column production rates. The next two parameters, liquid dispersion and solid concentration, affect how much catalyst can be added to the system and, hence, the extent of kinetic control of the system.

Liquid dispersion also relates to how well mixed the liquid phase is and how much solid can be suspended.

The results of previous workers (Baird and Rice, 1975; Kato and Nishiwaki, 1972a; Deckwer et al., 1973; Towell and Ackerman, 1972; Hikita and Kikukawa; 1974) in measuring the extent of liquid dispersion are shown in Figure 8.0.1 for a 12 cm cold flow simulator. They all show mixing in bubble columns to be fairly good. In the 12 cm CFS at 3 cm s^{-1} (0.1 ft/sec), the liquid axial dispersion coefficient would be predicted to range from 8.4×10^{-3} to 14.9×10^{-3} $m^2 s^{-1}$, and at 15.25 cm s^{-1} (0.5 ft/sec) from 17.2 to 26.0×10^{-3} $m^2 s^{-1}$. From the relation given by Carberry (1976),

$$N = j_G L/2E_z, \qquad (8.0.1)$$

this equates to 2.5 to 1.5 CSTRs (continuous stirred tank reactors) in series at the low mass velocity and 7 to 4.5 CSTRs in series at the high gas velocity ranges.

Dispersion coefficient was found by previous workers to be a strong function of column diameter,

$$E_z \propto D^{1.3 \text{ to } 1.5} \qquad (8.0.2)$$

However, the effect of obtaining more precise dispersion data on overall space-time yields was expected to be small. This is because bubble column slurry reactors are already known to provide good mixing.

8.1 Theory

Liquid dispersion relates to how well the gas flowing through a bubble column can mix the liquid or slurry phase. Ideal mixing, also called CSTR behavior, is a theoretical limit whereby any liquid molecule can move to any other part of the column from one instant to the next. At the other extreme is PFR (plug flow reactor) behavior, whereby a

molecule will move in concert with the other neighboring molecules, entering and leaving the column at the same time.

One way to quantify where a particular reactor lies between these two theoretical extremes is with the axial liquid dispersion coefficient, E_z.

If PFR behavior existed then E_z would equal 0. If CSTR behavior existed, then E_z would equal infinity. In practice, when $E_z > 10^{-2}$ $m^2\ s^{-1}$ well-mixed behavior exists. Once E_z is known for a particular phase, it is possible to plot a sample's concentration as a function of time at a fixed point within the column. Such a plot is only a residence time distribution (RTD) curve.

The model that is used to describe the sample concentration at any time assumes a diffusion mechanism given by Fick's law:

$$\frac{\delta C}{\delta t} = E_z \frac{\delta C}{\delta Z^2} \qquad (8.1.1)$$

with the boundary conditions:

$$\left.\frac{\partial C}{\partial Z}\right)_{0,T} = \left.\frac{\partial C}{\partial Z}\right)_{L,T} = 0$$

$$C(Z_1,0) = \begin{cases} C_0, & 0 \leq Z < Z_1 \\ C_0, & Z_1 \leq Z \leq Z_2 \\ 0, & Z_2 < Z \end{cases}$$

By solving this partial differential equation, it is possible to predict how a sample, originating at the bottom of the bubble column, disperses throughout the system with time. An approximate analytical solution which describes the RTD curve generated at any point within the column is given by Ohki and Inoue (1970):

$$\frac{\partial C}{\partial t} = E_L \frac{\partial^2 C}{\partial Z^2} \qquad 1)$$

For the boundary conditions where a tracer impulse is inserted at any longitudinal location:

$$\frac{\partial C}{\partial Z}_{0,\,T} = \frac{\partial C}{\partial Z}_{L,\,T} = 0 \qquad 2),\ 3)$$

where L = extended bed height, and

$$C(Z,\,0) = \begin{cases} 0, & 0 \le Z < Z_1 \\ C_0, & Z_1 \le Z \le Z_2 \\ 0, & Z_2 < Z \end{cases} \qquad 4)$$

$$C/C_E = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L)\exp(-n^2 \pi^2 E_z t/L^2)] \qquad (8.1.2)$$

An exact solution takes the summation to infinity instead of 100. The effect on the results was negligible.

8.2 Experimental

The axial dispersion coefficient, E_z, was determined for the liquid phase by measuring the bubble column's RTD curve. To obtain an RTD curve, a tracer or an inert substance with the same properties as the phase of interest but whose concentration can be measured (in this case an NaCl solution) was used. The concentrated NaCl was injected just above the gas distributor at four locations evenly spaced around the column. Conductivity detectors, to measure the NaCl concentration, were located at four elevations in each column: at 9, 37.5, 65.5, and 113 cm for the 12.7 cm ID column and 2, 152.5, 305, and 457 cm for the 30.5 cm ID column.

Information from the four conductivity meters was digitized and read into a Tektronix microcomputer (see Figure 8.2.1). This was compared to a family of theoretical RTD curves, generated from Equation 8.1.2, for a range of liquid dispersion coefficients, as shown in Figures 8.2.2 to 8.2.5 for the 5-inch (12.7 cm) ID column.

The conductivity reading was complicated by bubble impingement on the conductivity probe (see probe in Figure 8.2.6 and RTD curve in Figure 8.2.7). A correct conductivity curve was generated by connecting the local maximum conductivity readings (see Figure 8.2.8).

8.3 Results and Discussion

Equation 8.1.2 assumes that the dispersion throughout the bubble column was constant. This may not be correct. It is possible that phase dispersion is related to energy dissipation. Energy dissipation is greatest at the gas distributor inlet. At the gas disengagement zone at the top of the column, the energy dissipation is much less. If the dispersion/dissipation relationship exists, then E_z would be height-dependent. With the four conductivity detectors, it was possible to determine whether or not this height dependence existed.

In general, one dispersion coefficient was sufficient to characterize the entire column. The results of the liquid dispersion runs were in agreement with the work of Kato and Nishiwaki (1972a).

$$Pe = \frac{13\ Fr}{1 + 6.5Fr^{0.8}} \qquad (8.3.1)$$

For the upper three port locations, the same dispersion coefficient best describes the RTD curve. For the conductivity meter located directly above the injection point, a higher dispersion coefficient better described the measured RTD curve. This was attributed to either

1) the injection not being perfect, or 2) there being a higher degree of dispersion directly above the distributor. It was not possible to distinguish between these two possibilities.

It would be feasible to test which of these two possibilities is true by changing the injection point to the top of the column. Then any imperfections in the injection would be detected by the top conductivity probe instead of the bottom probe.

However, the practical value of determining whether there is a height dependence on the dispersion coefficient is low enough to not warrant any further experimental work.

9.0 Solid Loading and Concentration Profiles

In a kinetic controlled regime, the maximum solid loading, or weight fraction, has a direct and large impact on the production rate/unit volume in a slurry reactor. The maximum solid loading is reached when solid particles just begin to settle out at the reactor bottom. Any further addition may lead to hot spots within the settled catalyst area.

Several investigators have examined how solids distribute themselves in a bubble column.

Roy et al. (1964) empirically determined the gas velocity needed to completely suspend a given amount of solid in a 5 cm ID x 1.52 m lucite column using coal and quartz slurried in water, alcohol, or oil. The degree of suspension was found to depend on physical properties as well as gas holdup, volume fraction, bubble diameter, and the contact angle between the solid and liquid.

Cova (1966) measured the solid concentration profiles of a Raney nickel catalyst with an average diameter of 15.7 μm in a 4.6 cm ID reactor, using water and acetone as the liquids. He developed a sedimentation

diffusion model, assuming solid and liquid dispersion coefficients were equal and slurry settling velocities were independent of solid concentration. The model was then applied to data for Raney nickel in 6.35 and 44.7 cm ID bubble columns, in both cocurrent and countercurrent flow.

Imafuku et al. (1968) measured the solid concentration profiles of several solids in 5, 10 and 20 cm columns using water and aqueous glycerine. The solid particles ranged from 64 to 180 μm in diameter, and included glass spheres, iron silicate, and copper powders. They measured solid dispersion coefficients, confirming Cova's assumption of equal liquid and solid dispersion coefficients, and developed an empirical correlation between the observed terminal settling velocity in a three-phase system and the calculated terminal settling velocity of a single particle in a stagnant liquid.

Kato et al. (1972b) measured solid concentration profiles, solid dispersion coefficients, and terminal settling velocities for glass spheres in water, using 6.6, 12.2 and 21.4 cm bubble columns. They developed a dimensionless, empirical correlation for the solid dispersion coefficients which agreed with their observed values to within ±20%.

Sivasubramanian et al. (1981) and Moujaes et al. (1982) measured solid concentration profiles of sand in water and ethanol/water, using 12.7 and 30.5 cm bubble columns. They developed a solids accumulation model, which correlated successfully with an actual 30.5 cm ID solvent-refined coal dissolver.

9.1 Theory

Solid concentration profiles are produced from a balance of gravitational with buoyancy and kinetic energy transfer forces. For a

single particle in a stagnant liquid, the settling velocity, V_p, is given in Bird, Stewart, and Lightfoot (1960) as:

$$u_p = \left(\frac{4}{3}\frac{g\, d_S}{f}\left(\frac{\rho_S-\rho_L}{\rho_L}\right)\right)^{1/2} \qquad (9.1.1)$$

where f, the Fanning friction factor for spheres, is a function of Reynolds number,

$$f = \begin{cases} 24/Re & Re \leq 1 & (9.1.2a) \\ 18.5/Re^{3/5} & 1 < Re < 1000 & (9.1.2b) \\ 0.44 & 1000 \leq Re < 20{,}000 & (9.1.2c) \end{cases}$$

For a slurry system with no gas phase, a single particle sees the properties of the slurry, not the liquid. Also, because the particles make up a sizable fraction of the total volume, the liquid can no longer be considered stagnant but moves upward to displace the volume of falling solid by

$$j_L = \frac{\varepsilon_S V_{ST}}{\varepsilon_L} = \frac{F_S \rho_L u_{ST}}{F_L \rho_S} \qquad (9.1.3)$$

where

$$j_L = j_{SU}/(1-\varepsilon_G) \qquad (9.1.4)$$

For $d_S \leq 50$ μm, Equations 9.1.1, 9.1.2a, and 9.1.3 give the following expression for the particle settling velocity in a slurry:

$$u_{ST,\,CALC} = g\, d_S^2\, (\rho_S-\rho_{SL})/(18\, \mu_{SL}\, (1 + F_S\rho_L/F_L\rho_S)) \qquad (9.1.5)$$

Introducing the third (gaseous) phase to the reactor changes the environment considerably. A large amount of mixing is introduced by

the gas bubbles, carrying slurry in their wakes (Levenspiel, 1972). This high degree of mixing has successfully been modeled by a one-dimensional diffusion mechanism, i.e., diffusion superimposed on the superficial slurry flow, for both the liquid (Khang & Kothari, 1980; Ohki & Inove, 1970) and the solid phases (Imafuku et al., 1968; Kato et al., 1972b), in both the continuous (positive slurry velocity) and batch (zero slurry velocity) operating modes.

From Cova (1966) and Kato et al. (1972b) (see Appendix A-9 for derivation), for continuous flow of both gas and slurry:

$$C_2 = [C_H/(j_L - u_{ST})](j_L - u_{ST}\exp[(j_L - u_{ST})(Z_2-L)/E_{ZS}]) \qquad (9.1.6)$$

For batch operation with $j_L = 0$,

$$C_2 = C_1 \exp \frac{-u_{ST}}{E_{ZS}} (Z_2-Z_1) \qquad (9.1.7)$$

The value of the solid dispersion coefficient, E_{ZS}, may be calculated from the experimental data as follows, with the assumption that E_{ZS} is independent of j_L.

The steady state concentrations from an identical batch and continuous run are measured at two or more points. Equation 9.1.7 can be written as

$$\frac{\ln C_2/C_1}{Z_1-Z_2} = \frac{\Delta \ln C}{\Delta Z} = \frac{-u_{ST}}{E_{ZS}} \qquad (9.1.8)$$

A plot of ln C vs. Z for the batch run, therefore, yields a straight line with a slope of $-u_{ST}/E_{ZS}$. Equation 9.1.6 can be rewritten as:

$$j_L/E_{ZS} = (u_{ST}/E_{ZS}) \exp(D(Z_2-L)) - (C_2/C_H)D \qquad (9.1.9)$$

where

$$D = (u_{ST}/E_{ZS} - j_L/E_{ZS}) \qquad (9.1.10)$$

The three upper slurry samples taken for each solid concentration profile, along with Equation 9.1.9, provided three independent equations, from which two parameters, j_L/E_{ZS} and C_H, were calculated. Using the batch run value of $-u_{ST}/E_{ZS}$, a least squares technique was used to estimate the two parameters. Since V_L was known, experimental values for E_{ZS} and u_{ST} were then independently determined.

With the highest slurry loadings, a small gas sidestream was also used in the slurry feed to facilitate pumping from the reservoir to the column.

For the 12.7 cm column, the gas and slurry distributor was 1.25 mm thick, with a 10% to 13% open area of 0.9 mm holes. The 30.5 cm column used different 0.3% open area, distributor plates, with 0.9, 3.2 and 12.7 mm diameter holes. The gas traveled with the slurry, separated at the column top, and passed through a demister pad, liquid trap, and rotameter before being vented. All metal parts were grounded to prevent electric arcing during experiments with the nonconducting hydrocarbon liquid.

9.2 Experimental

Gas flow was initially fed to a column approximately 2/3 full of slurry. After the gas flow rate was set, the slurry flow was started and adjusted using the calibrated volume. Flow rates were held constant during the runs, which lasted 45 to 75 minutes for the 12.7 cm column and 180 minutes for the 30.5 cm column. At the end of this time, slurry samples were taken, starting at the top of the column and working down, so as not to disturb upstream conditions. All slurry

ports were purged before taking a sample, and stopcocks were turned quickly to full open and full closed to prevent settling of slurry within the sample line.

Hydrocarbon slurries were analyzed by filtration on a tared micropore polymer funnel using a pentane wash. Water-based slurries were analyzed by oven evaporation. Control tests using slurries of known weight percent gave an absolute accuracy within 0.1% for both methods.

9.3 Results

9.3.1 Effect of Particle Size on Solid Concentration Profiles

Tables 5.3.1 and 5.3.2 list the solid concentration profiles for all of the runs. Figures 9.3.1 (a and b) and 9.3.2 (a and b) show the dominant effect that particle size has on the distribution of solids in a three-phase bubble column, without mechanical agitation. Examples in each figure were chosen to represent (as closely as possible) identical operating conditions. While a known solid weight fraction was charged to the total system, the resulting distribution of solids between reservoir and column made it difficult to match average solid weight fractions in the column precisely. In each figure, therefore, it is the profile slope, and not the actual weight fraction values, which determines how well the solid is suspended.

In every case, as expected by theory, larger particle sizes produced greater solid concentration slopes. The solid curves in Figures 9.3.1 (a and b) and 9.3.2 (a and b) were generated by solving for the values of V_{ST} and E_{ZS} in Equations 9.1.8 and 9.1.9 using the experimentally obtained concentration profiles.

9.3.2 Effect of Slurry Velocity on Solid Concentration Profiles

Figures 9.3.1a and 9.3.1b show axial solid concentration profiles for the silicon oxide system in batch and continuous mode, respectively.

Figures 9.3.2a and 9.3.2b show the same information for the iron oxide system. For both systems, concentration profiles were much more uniform in continuous mode than in batch mode. This is to be expected from Equation 9.1.6, because of the dependence shown on the difference between the solids settling velocity and the upward slurry velocity.

9.3.3 Solid/Liquid Interaction Effects

Figures 9.3.3a and 9.3.3b show the effect of different solid-liquid pairs on solid concentration profiles. In 9.3.3a and 9.3.3b, the steepest profiles were observed for the silicon oxide/isoparaffin and iron oxide/water systems. The other solid-liquid pairs, silicon oxide/water and iron oxide/isoparaffin, gave much less pronounced concentration profiles and in fact, for the continuous runs, were essentially horizontal.

9.4 Discussion

9.4.1 Solids Settling Velocity

Solids settling velocities, $u_{ST_{OBS}}$, were calculated from 84 experimental runs on the 12.7 cm column. Figure 9.4.1 plots the observed solid settling velocity ($u_{ST_{OBS}}$) as determined from Equations 9.1.1 and 9.1.3 against the theoretically derived solid settling velocity obtained from Equation 9.1.5 for all four combinations of solid-liquid pairs. A considerable spread of values is observed. This is because a small change in solid weight fraction can cause a wide change in calculated solids settling velocity when solid profiles are nearly horizontal. In spite of this spread, qualitative differences are evident in comparing the silicon oxide and iron oxide results in Figure 9.4.1. While there appears to be some agreement between the observed and theoretical iron oxide solids settling velocities, the observed silicon oxide values appear to be several times greater than expected. This difference in behavior of the

silicon oxide and iron oxide slurries cannot be accounted for by density effects. Since the ratio of the density of iron oxide and silica is ~2.14, the predicted u_{ST} for iron oxide would be ~3.8 times greater than for silica. Further work is needed to determine the critical characteristics of a solid that are important in governing its settling velocity.

9.4.2 Solid Dispersion Coefficients

Solid dispersion coefficients, E_{ZS}, were calculated from the same 84 experimental runs as the solid settling velocity results. Many of the solid concentration profiles for the 0.5-5 μm size particles were horizontal to within 0.2 weight percent. As horizontal profiles suggest an infinite dispersion coefficient, scatter for the smallest size particles was too large to be included in the analysis. For the iron oxide system, the values were in the same range as predicted by Kato et al. (1972a), although a scatter of ±100% was still too large for quantitative analysis. The silicon oxide/isoparaffin system gave better agreement with the Kato correlation, and in Figure 9.4.2 they are graphically compared. Although there is still scatter in this plot, the results seem to conform to Kato's empirical analysis, confirming the assumption of equal liquid and solid dispersion coefficients for this system.

9.4.3 Effect of Solid Concentration Profiles on Reactor Performance

If a three-phase bubble column is operated in a regime without significant diffusional limitations, and with high liquid axial dispersion and complete solid suspension, the effects of a nonuniform solid catalyst profile are expected to be minimal for the reactor space-time yield, although product selectivity may be affected in the case of the Fischer-Tropsch synthesis. However, if the reactor is operated in a regime with a significant diffusional resistance, as is likely in an ultimate commercial design, any nonuniformity in the solid catalyst suspension profile will become more important, because of the

effects of local solid loading in gas to liquid mass transfer. In tests of a 14.7 wt% slurry of reduced Fe_2O_3 catalyst, utilizing a stirred reactor with 1.4:1 CO/H_2 at 3.2 MPa, significant diffusional resistance was observed at T>250°C (Dyer et al., 1980-82; Bauer et al., 1983). Therefore, it is anticipated that nonuniformity in solid suspension will be an important consideration in the performance of a Fischer-Tropsch bubble column reactor and this will be the subject of further work.

If the catalyst is not completely suspended, reactor space-time yields could be affected without significant diffusional limitations. For the 90-106 μm silicon oxide, a considerable amount of solid settling was observed for all batch runs and, in some continuous runs, for both the 12.7 and 30.5 cm columns. Figure 9.4.3 shows this effect both with and without heat transfer internals and independent of the gas distributor hole size. As more solid was added to the system, it settled at the bottom of the reactor. The maximum solid concentration that can be supported at a given gas and liquid velocity agrees with the work of Roy et al. (1964). For >90 μm particle size, this maximum appears to provide a practical constraint to the loading of a silicon oxide supported catalyst at about 20 wt%.

9.5 Conclusions

1. The sedimentation diffusion model, when applied to the iron oxide system, gave solid settling velocities in agreement with theory. Solid dispersion coefficients were in the range predicted by the Kato correlation but showed considerable experimental scatter.

2. The sedimentation diffusion model, when applied to the silicon oxide system, gave solid settling velocities several times higher than predicted by theory. Solid dispersion coefficients, however, did mostly agree with the Kato correlation.