HYDRODYNAMIC STUDIES WITH FISCHER-TROPSCH WAXES IN THREE-PHASE BUBBLE COLUMNS

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by

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INTRODUCTION

Fischer-Tropsch (FT) synthesis reaction represents an important route for indirect coal liquefaction. It was utilized on a large scale during World War II for production of motor fuels in Germany. At the present time commercial size units are in operation only at Sasol in South Africa. Fixed bed reactors (Germany and Sasol) and entrained bed (Sasol) type of reactors have been used for conversion of synthesis gas into hydrocarbon products.

In recent years, one of the processes which has received a great deal of attention is FT synthesis in the slurry phase. In this process, synthesis gas (H_2+CO) is passed through a suspension of small catalyst particles in molten wax. Some of the desirable characteristics of a slurry bubble column reactor are as follows (Kölbel and Ralek, 1980; Deckwer, 1980): (1) Uniform temperature and high rate of heat transfer; (2) high single pass conversion; (3) ability to process CO-rich syngas; (4) high selectivity (i.e., low methane production and high proportion of liquid products); (5) flexibility in operation; and (6) simple construction and low investment cost.

A number of studies have been conducted to investigate the hydrodynamics of bubble columns using molten wax as the liquid medium; however, considerable differences in results exist among these studies. Average gas holdup values from these studies (Calderbank et al., 1963; Deckwer et al., 1980; Kuo, 1985; Bukur et al., 1985, 1987a, b) may be categorized into two groups; those obtained in the presence of foam and those obtained when no foam was produced. The former show considerable variation and are dependent on the amount of foam present when measurements were made, whereas values obtained when foam was absent are well represented by a common curve. In general, gas holdups show a rather complex behavior which is, to a large extent, caused by the foaming capacity of the medium.

The objective of the present study is to investigate the hydrodynamics of the bubble column using molten waxes with solids present in varying quantities. In particular, flow regime transitions and the effect of solids on holdup, and the ability of the dispersion to suspend the solids, will be studied. The solids in the dispersion serve to simulate the catalyst particles that are present under actual reaction conditions. The effect of liquid circulation on solids suspension will also be studied. Results from measurements made using conventional techniques will be compared with results obtained using nuclear density gauges.

EXPERIMENTAL EQUIPMENT AND METHODS

Apparatus

Figure 1 shows the schematic of the bubble column apparatus. The experiments were conducted in 0.05 and 0.21 m ID by 3 m tall stainless steel columns equipped with 2 mm orifice plate and 19 X 2 mm perforated plate distributors, respectively. Gas flow rate was controlled using a mass flow meter, and the column temperature was controlled using two temperature controllers, one for the bottom half and the other for the top half of the column. A variable speed, positive displacement gear pump (Pulsafeeder, Model G12) was used to circulate the slurry in the 0.05 m ID column, and a positive displacement lobe pump (Tuthill Corporation, Chicago) was used in the 0.21 m ID column.

Prior to experiments with a given batch of wax, the mass flow meter and the pressure transducers were calibrated over the entire operating range. The pressure transducers were calibrated, while they were at their respective locations on the column wall, by filling up the column to different known heights with distilled water and recording the transducer meter readings.

The wax was charged in the storage tank and the tank was heated to bring the wax to a desired temperature. Once the solid wax melted, the stirrer was switched on to improve the heating process. For runs conducted with solids, the necessary quantity of solid particles was added to the molten wax. The slurry was heated to a temperature of 220-240°C and slurry samples were withdrawn and the slurry height in the tank measured. The column was heated up to the desired operating temperature (265°C) before the slurry (wax) was introduced. For all experiments, batch and continuous, the wax was transported to the column using a slight overpressure of nitrogen in the storage tank. For the continuous mode of operation, the pump was switched on only after the column was at least half filled with wax. This was done to prevent any solids, settled in the storage tank, from clogging the pump. Throughout the preheating period and during transportation of wax to the column, the nitrogen passed through the column at a low flow rate. Once the wax was in the column, the temperatures of the various units were allowed to stabilize before the actual run was started. For experiments conducted in the batch mode, only the column was maintained at the operating temperature using the two temperature controllers. The exit lines and expansion unit were maintained at around 200°C.

The scrubber, which is filled with a mineral spirit to recover components of wax that evaporate from the column, was maintained at about 100°C. The gas inlet line and the distributor section were maintained between 220-240°C. The lines connected to the pressure transducers and the slurry withdrawal lines were maintained at 200°C. For continuous mode of operation, all lines and vessels carrying the slurry, including the column, expansion unit, overflow line, calibration chamber, storage tank, slurry feed line, and the slurry pump, were maintained at the operating temperature. The remaining temperatures were the same as those used for the batch case. All temperatures were monitored regularly, every half hour during the preheating period (i.e., while wax was in the column and being heated up) and every hour once temperatures had stabilized.

All experiments were conducted using pre-purified nitrogen as the gas. Superficial gas velocities in the range 0.02-0.12 m/s were employed in all runs. A duration of one and a half hours was used for each gas velocity. Pressure measurements were made three times for every gas velocity (i.e., every half hour), with the first measurement made half an hour after the gas velocity was changed. Pressure fluctuations at the column wall were recorded once per gas velocity. After the last pressure measurement, slurry samples were withdrawn from the column at five different locations. The gas flow rate was then changed to the next setting. For experiments conducted in the continuous mode of operation, the superficial liquid velocity was monitored using the calibration chamber. The desired liquid flow rate was set by varying the pump speed, and liquid flow rate checks were made three times at each gas velocity.

Following the completion of a run, the slurry was withdrawn into the storage tank by using a slight vacuum in the tank (the pump was switched off for runs conducted in the continuous mode). After each run, solids and wax inventories were made to check for any losses, particularly losses in solids due to settling in the various lines and process vessels.

Phase Holdups

Figure 2 is a schematic showing the pressure ports and sample ports on the bubble column. Phase holdups for a given section of the column were determined using pressure drops across the section, and the weight fraction of solids in the sample withdrawn from the port located in that section. Average holdups for the entire dispersion were obtained using a weighted average of holdups in the individual sections. In the batch mode of operation, where sometimes the top most section was only partially full, the gas holdup, and if necessary, the weight fraction

of solids in this section were estimated by extrapolating the profiles obtained from the sections below.

Two nuclear density gauges were also used to determine phase holdups. The two radioactive sources used were Cesium-137 and Cobalt-60. These gauges are mounted on a movable assembly mechanism that is used to position the sources at the desired radial and axial positions. Prior to using these gauges calibrations were performed to determine absorption coefficients for the wax and solids. Data from the sources were acquired by a Metrabyte data acquisition system and stored on the hard-disk of a Zenith AT compatible computer.

Axial Solids Dispersion Coefficients

Several variations of the one-dimensional sedimentation dispersion model, based on different frames of reference, are available in the literature. The model presented by Cova (1966) is based on the cross-sectional area of the column; whereas, the models by Kato et al. (1982), Smith and Ruether (1985), and O'Dowd et al. (1987), are based on the cross-sectional area occupied by the slurry phase alone (i.e., area occupied by the gas phase is not included). In our analysis we have used the model presented by Smith and Ruether. Their one-dimensional axial dispersion model is given by

$$\frac{\delta}{\delta x}\left[\frac{-E_s}{L}\frac{\delta C_s}{\delta x}\right] + \frac{\delta}{\delta x}\left[\left[\frac{U_{s\ell}}{1-\epsilon_g} - \Phi_\ell U_p\right]C_s\right] = L\frac{\delta C_s}{\delta t} \qquad (1)$$

where x is the dimensionless height above the distributor (based on expanded height), E_s is the axial dispersion coefficient, C_s is the solids concentration, $U_{s\ell}$ is the average slurry flow rate, U_p is the hindered settling velocity of the particles, Φ_ℓ is the volume fraction of liquid in the slurry, and t is the time.

For batch mode of operation (i.e., $U_{s\ell}=0$) at steady state (no time derivatives), and assuming no dependency of Φ_ℓ on height, Eq. 1 reduces to

$$\frac{\delta}{\delta x}\left[\frac{-E_s}{L}\frac{\delta C_s}{\delta x}\right] - \frac{\delta}{\delta x}\left[\overline{\Phi_\ell} U_p C_s\right] = 0 \qquad (2)$$

where $\overline{\Phi_\ell}$ is the average axial liquid volume fraction in the column. Equation 2 can be integrated twice to yield:

$$C_s = C_1 + C_2 \exp\left[-L\overline{\Phi_\ell}\frac{U_p}{E_s}x\right] \qquad (3)$$

For the semi-infinite dispersion model, the boundary conditions are given by: $C_s = 0$ as x approaches infinity, and $C_s = C_s^B$ for $x = 0$, where C_s^B is the concentration of solids at the bottom of the dispersion. Application of these boundary conditions to Eq. 3 yields:

$$C_s = C_s^B \exp\left[-L\overline{\Phi_\ell}\frac{U_p}{E_s}x\right] \tag{4}$$

Solids concentration vs. axial position data can now be used to obtain estimates of $\frac{U_p}{E_s}$ and the initial feed concentration, C_s^B, using regression analysis.

For continuous liquid flow, the solution to Eq. 1 is given by:

$$C_s = \left(C_s^B + a\right)\exp\left[-(U_p\overline{\Phi_\ell} - U'_{s\ell})\frac{L}{E_s}x\right] - a \tag{5}$$

where $a = \frac{U'_{s\ell}C_s^f}{\Phi_\ell U_p - U_{s\ell}}$ and $U'_{s\ell} = \frac{U_{s\ell}}{(1-\epsilon_g)}$. The quantity C_s^f is the concentration of solids in the feed. It is assumed that no settling occurs in the feed stream (i.e., at $x<0$, $U_p = 0.0$ and $\frac{\delta C_s}{\delta x} = 0.0$). Non linear regression techniques may be used to solve Eq. 5 for U_p, E_s, and C_s^B.

For batch experiments, U_p and E_s are not separable, and in order to obtain axial dispersion coefficients, one must assume values for the hindered settling velocity of the solids. There are various correlations available in the literature for estimating hindered settling velocities (e.g., Kato et al. (1972), Smith and Ruether (1985), Zigrang and Sylvester (1981), and O'Dowd et al. (1987)). The correlations proposed by Kato et al., Smith and Ruether, and O'Dowd et al. are all of the form

$$U_p = aU_T^{\,b}U_g^{\,c}\overline{\Phi_\ell}^{\,d} \tag{6}$$

The constants in Eq. 6 are (1.33, 0.75, 0.25, 2.5) for Kato et al., (1.91, 0.8, 0.26, 3.5) for Smith and Ruether, and (1.69, 0.8, 0.23, 1.28) for O'Dowd et al. U_T is the terminal rise velocity of a single particle in an infinite liquid medium.

Various correlations have been presented in the literature for predicting axial dispersion coefficients directly. The correlation proposed by Kato et al. is:

$$Pe_p = \frac{13Fr_g(1 + 0.009Pe_pFr_g^{-0.8})}{1 + 8Fr_g^{0.85}} \tag{7}$$

For systems used in our studies, the correction factor for particle size effect in Eq. 7 was negligible. The equation presented by Smith and Ruether is:

$$Pe_p = 9.6\left[\frac{Fr_g^6}{Re_g}\right]^{0.114} + 0.019Re_p^{1.1} \tag{8}$$

and the equation presented by O'Dowd et al. for an unbaffled bubble column is:

$$Pe_p = 7.7\left[\frac{Fr_g^6}{Re_g}\right]^{0.098} + 0.019Re_p^{1.1} \qquad (9)$$

where $Pe_p = \frac{U_g D_{col}}{E_s}$, $Re_g = \frac{U_g D_{col}\rho_\ell}{\mu_\ell}$, $Fr_g = \frac{U_g}{\sqrt{gD_{col}}}$, and $Re_p = \frac{d_p \rho_\ell U_T}{\mu_\ell}$.

Wall Pressure Fluctuations

Statistical analysis of pressure fluctuations has been used in the past to determine transitions between flow regimes in both two-phase and three-phase bubble columns and fluidized beds. Various techniques may be used to determine flow regimes and flow regime transitions. The two most commonly used designs involving pressure transducers are: (1) measurement of absolute pressure fluctuations and (2) measurement of differential pressure fluctuations. For analysis of systems which operate in the slug flow regime, differential pressure fluctuations can provide more detailed information, and a more accurate measure of the transition from bubbly to slug flow, slug flow to annular flow, and annular flow to mist flow.

As discussed by Glasgow et al. (1984), the passage of a buoyant bubble can produce three distinct response characteristics: (1) sound of approach (observable if rapidly rising bubbles are present), (2) pressure field around the object, and (3) wake or vortex street behind the object. Our pressure transducers will only detect fluctuations caused by changes in the pressure field as a bubble passes the surface of the tube (i.e., low frequency oscillations). Even if our system was sensitive enough to detect fluctuations caused by the wakes of bubbles, it would be very difficult, if not impossible, to distinguish between these fluctuations and those created by the pressure field around the bubble.

Three different statistical techniques are commonly employed to determine flow regimes and flow regime transitions from pressure transducer measurements. The statistical analysis involves the use of the power spectral density function (psd), the mean square error of the pressure fluctuations (MSE), and the probability density function (pdf).

The pdf of an absolute pressure signal cannot be used as a direct measure of flow regime transitions; however, the pdf of an absolute pressure signal will broaden as turbulence increases. In other words, the variance of the pressure fluctuations in the column changes with gas and liquid velocities, and this change is reflected by an increase or decrease in the variance of the pdf. Two quantities which have found some use in determining flow regime transitions and

changes in turbulence are the mean square error (MSE) and root mean square (RMS) of the pressure fluctuations. The MSE is defined as:

$$MSE = \frac{\left[\sum(P_i - \overline{P})^2 / N\right]^{1/2}}{\overline{P}} \qquad i = 1, \ldots, N \tag{10}$$

where N is the total number of data points, P_i is the pressure corresponding to data point i, and $\overline{P}$ is the average pressure defined as:

$$\overline{P} = \frac{\sum P_i}{N} \qquad i = 1, \ldots, N$$

Fan et al. (1984) had reasonable success in using this quantity to determine flow regime transitions in a three–phase fluidized bed. Lee (1983) used the RMS, defined as :

$$RMS = (MSE)(\overline{P}) \tag{11}$$

to obtain a qualitative description of turbulence in an airlift column.

Two other statistical quantities which are sometimes used are the autocorrelation function and the power spectral density function (psd). The psd is the Fourier transform of the autocorrelation function. The autocorrelation function is the normalized autocovariance function. The autocovariance function gives an indication of how the dependence between adjacent values in a stochastic process changes with lag (u) and is defined as:

$$\gamma_{xx}(u) = E[(x(t) - \mu)(x(t+u) - \mu)] = cov[x(t), x(t+u)] \tag{12}$$

where E[y] is the expected value of y, cov is the covariance, μ is the mean of the time series, x is the measured quantity (pressures for our case), and u is the lag between observations. The autocorrelation function is given by:

$$\rho_{xx}(u) = \frac{\gamma_{xx}(u)}{\gamma_{xx}(0)} \tag{13}$$

where $\gamma_{xx}(u)$ is the autocovariance function evaluated at lag u and $\gamma_{xx}(0)$ is the autocovariance function evaluated at lag 0, or more simply, the variance of the time series. Thus, the RMS is the square root of the autocovariance function evaluated at lag 0, and the MSE is the square root of the autocovariance function evaluated at lag 0 divided by the mean of the time series (or, for our case, the mean of the pressure fluctuations).

The power spectral density is the Fourier transform of the autocorrelation function and is defined by:

$$P(f) = \int_{-\infty}^{\infty} \rho_{xx}(u)\exp(-j2\pi fu)du \qquad (14)$$

Thus, all three quantities (i.e., RMS or MSE, autocorrelation and psd) are related. For our data, we will only use the MSE and psd to show qualitatively the transitions between flow regimes for various experimental data.

Materials Used

The liquids used in this study were FT-300 wax (average molecular weight of 730) from Dura Commodities Co., New York, and reactor wax from Sasol's Arge fixed bed reactor. Physical properties of these liquids were reported elsewhere (Bukur et al., 1987b). Two types of solids were used (iron oxide and silica) in two size ranges (0-5 μm and 20-44 μm), with solids concentrations of 10, 20 and 30 wt.% in the slurry.

RESULTS AND DISCUSSION

Experiments in the 0.05 m ID Column

Phase Holdups

Average gas holdups were determined for all runs using the procedure outlined earlier. Results from the various experiments are categorized in terms of the various effects. At the end of each run wax and solid inventories were made to check for losses, due to wax evaporation or due to solids settling. Some problems were encountered with solids settling in the lines and in the zone just above the distributor; however, this did not have a significant effect on results.

Effect of liquid circulation velocity: Figure 3 shows the results from experiments conducted with FT-300 wax without solids. Foam was produced for the batch case (u_ℓ) with gas holdup values as high as 28% at a superficial gas velocity of 0.04 m/s. However, gas holdups decreased significantly for superficial gas velocities in the range 0.04-0.09 m/s when the experiment was conducted in the continuous mode of operation using a superficial liquid velocity of 0.005 m/s. A further decrease in holdup was observed when the superficial liquid velocity was increased to 0.02 m/s; however, the change was less significant.

Figure 4 shows average gas holdup values from three runs made with a slurry containing 20 wt.% of 0-5 μm iron oxide in FT-300 wax. The trends are qualitatively similar to those observed

in the run without solids, i.e., the highest holdups were observed with no liquid circulation and the lowest values were obtained at a superficial liquid velocity of 0.02 m/s. Once again the largest difference was observed when liquid velocity was increased from 0 (batch case) to 0.005 m/s.

When experiments were conducted with different solids concentrations, size, or solids type in FT-300 wax, results similar to those shown in Figure 4 were obtained. However, when experiments were conducted using Sasol reactor wax (non-foaming medium), the effect of liquid circulation velocity on average gas holdup was not significant, as shown in Figure 5. In these experiments 20 wt.% of 20-44 μm iron oxide particles were used. The greatest difference between holdup values from the two runs was at a gas velocity of 0.09 m/s, where holdup in the batch mode was 21% while that in the continuous mode was about 26%.

The above results indicate that with FT-300 wax even a small upward liquid flow (0.005 m/s) tends to lower gas holdups; however, a further increase in liquid flow does not have a significant effect on the average gas holdup values. The significant difference in holdups between the batch and continuous modes of operation is due to changes in the foaming characteristics of the medium. For the batch case, the foam accumulates at the top of the dispersion and increases the gas holdup; however, as slug flow sets in, the foam tends to dissipate and the holdup profile flattens out. In the continuous mode of operation, any foam that tends to accumulate at the top is carried back down by the circulating slurry and is dispersed. With an increase in liquid circulation, the rate of dispersion increases, decreasing the average gas holdup. The behavior of Sasol wax is significantly different from that of FT-300 wax primarily due to the absence of foam in experiments with Sasol wax.

Effect of solids concentration: Figure 6 illustrates the effect of solids concentration on gas holdup for experiments conducted in the batch mode of operation with FT-300 wax using 0-5 μm iron oxide. These results show that average gas holdups go through a maximum with the increase in solids concentration. Batch mode experiments with 20 wt.% of 0-5 μm silica and 20-44 μm silica, respectively, gave holdup values which were higher than those for FT-300 wax without solids.

Figure 7 shows results from experiments conducted with slurries containing different concentrations of 0-5 μm iron oxide particles in FT-300 wax using a liquid circulation velocity

of 0.005 m/s. These results show very little change in holdup values with increasing solids concentration; however, holdup values in the presence of solids are consistently lower than those obtained without solids, also, the lowest holdup values were obtained with the slurry containing the highest concentration of solids. The same behavior was observed with other solids types and sizes when experiments were conducted in the continuous mode of operation. No significant differences were observed between results from experiments conducted using a liquid circulation velocity of 0.005 m/s and those from runs conducted using a liquid circulation velocity of 0.02 m/s.

The above results show some interesting trends. For the batch mode of operation, the addition of solids increases the amount of foam and produces higher gas holdups; however, for continuous mode experiments, the addition of solids decreases gas holdups. This implies that the foaming tendency of the liquid medium is greatly reduced when a small upward liquid flow is used. This small liquid flow is sufficient to disperse the fine bubbles that are responsible for the foam, and only the hydrodynamics of the actual dispersion (i.e., that without the foam) determines the gas holdup. This behavior cannot be attributed to the non-coalescing nature of FT-300 wax, since similar trends were also observed with Sasol wax. The addition of solids to Sasol wax increased gas holdup in the batch mode of operation, while the introduction of liquid circulation decreased holdups and values similar to those for Sasol wax without solids were obtained. At this point it is not clear as to why holdup increases when solids are added in the batch mode of operation.

Axial Solids Distribution

The axial solids distribution profiles for all runs conducted using the 0-5 μm iron oxide and silica particles were uniform for all runs conducted in the continuous mode of operation. For batch mode experiments with these solids, the profiles show a slight gradient with higher concentrations towards the bottom of the column. For experiments conducted in the batch mode of operation with 20-44 μm iron oxide and silica particles, significant gradients in axial solids distribution profiles were observed. However, when liquid circulation was introduced, the profile became uniform and suspension of solids improved significantly, even at a liquid circulation velocity of 0.005 m/s. These results indicate that solids suspension, which does not show any noticeable improvement when gas velocity is increased, improves significantly

with the introduction of a small upward liquid flow (0.005 m/s). This is expected since the terminal settling velocity for large iron oxide particles is about 0.001 m/s and that for large silica particles is 0.0004 m/s. Both of these values are well below the liquid circulation velocity of 0.005 m/s used in this study.

The axial solids dispersion coefficients for iron oxide and silica were estimated using solids distribution profiles from batch mode experiments with these solids. As noted earlier, for batch mode experiments the terms U_p and E_s are not separable, and hindered settling velocities have to be assumed in order to estimate the dispersion coefficients.

Figure 8 shows the effect of superficial gas velocity on the quotient $\frac{U_p}{E_s}$, which was estimated by fitting solids concentration vs. normalized axial height data to Eq. 4. Figures 8a and 8b correspond to values of $\frac{U_p}{E_s}$ obtained using all solids concentration data, whereas Figures 8c and 8d show values of $\frac{U_p}{E_s}$ obtained when solids concentration data from the uppermost sampling port were omitted. This was done to eliminate effects due to the presence of foam at the top of the dispersion. Also shown in Figure 8 are the 95% confidence intervals for the $\frac{U_p}{E_s}$ estimates. Results from our work are compared with values predicted by literature correlations in Figure 9. A slight downward trend in $\frac{U_p}{E_s}$ with increasing gas velocity can be seen in this figure. This is expected since higher gas velocities would promote axial mixing of the dispersion and somewhat improve solids distribution, resulting in higher E_s values. Figure 7 also shows that results from our study are within the range of values predicted by the existing literature correlations. The effect of omitting data from the top most port is more pronounced for the run with iron oxide than for the run with silica. When the reduced data set was used for the experiment with iron oxide, $\frac{U_p}{E_s}$ values were consistently lower than values obtained when all data points were used. Whereas, for the run with silica, values for the two cases are similar. This may be due to the different amounts of foam produced with the two systems. During the run with iron oxide the amount of foam present at the top of the dispersion was significantly higher than that present during the run with silica. The higher $\frac{U_p}{E_s}$ values in the presence of foam may be indicative of the inability of foam to suspend the solids.

Figures 10 and 11 compare the measured solids concentration profile with those predicted by the semi-infinite model for the two systems. For the experiment with silica (Figure 11), there is essentially no difference between the predicted values of solids concentrations from

the two cases (i.e., using all data points and omitting the last data point). This is expected since we saw very little difference in $\frac{U_p}{E_s}$ values for the two cases (Figure 9). The semi-infinite dispersion model fits the data very well. However for iron oxide (Figure 11), there is some difference between the predicted solids concentration curves for the two cases. For the case where all points are used, there is a steeper concentration gradient predicted, possibly due to the presence of foam in the upper section.

Figure 12 shows results for axial dispersion coefficients based on the three point (closed symbols) and four point (open symbols) least square fit of the data to the semi-infinite dispersion model for both iron oxide (top) and silica (bottom). Values predicted by Eqs. 7-9 are also shown in the figure. Kato et al.'s correlation was used to estimate settling velocity for the results shown. For iron oxide, the dispersion coefficient obtained using all data points for solids concentrations were lower than the dispersion coefficients obtained when the solids concentrations corresponding to the uppermost sample port were omitted; whereas, for silica the two sets of results are similar. This is once again due to the differences in the amount of foam produced, as discussed earlier. In general, results from our study fall within the range of values predicted by the various correlations.

Flow Regime Transitions

Pressure fluctuation signals were recorded at each gas velocity using a Metrabyte data acquisition system and were analyzed on a Zenith-248 AT compatible computer. For batch mode experiments, cells 1 - 4 (Figure 2) were used, and for continuous mode experiments, cells 1 - 5 were used to record the fluctuations. Pressure signals were recorded at 50 Hz for 20 seconds (i.e., 1000 data points per set).

Flow regime transitions based on the MSE: MSE were calculated from the raw pressure signal data for all runs conducted. In general, the MSE increased with increasing gas velocity and with increasing height above the distributor, but decreased with increasing liquid velocity. Figure 13 shows the effect of slurry flow rate on MSE for the runs conducted with 20 wt.% 0-5 μm silica particles in FT-300 wax. At low gas velocities (i.e., $u_g \leq 0.06$ m/s), the MSE of the pressure fluctuations is essentially the same for all three experiments; however, at gas velocities of 0.09 and 0.12 m/s, the MSE values are significantly different. For the batch mode run, MSE is significantly higher than values from the two continuous mode runs. The

high value for the batch mode may be attributed to an increase in turbulence at the top of the dispersion due to slugs disengaging from the slurry. The decrease in MSE with increasing liquid velocity may be attributed to two factors: (1) the relative velocity between the gas and slurry decreases with increasing slurry velocity, and (2) the static height of the slurry above a given pressure port does not fluctuate as much during a continuous run as it does during a batch run. In Figure 13, there is a distinct change in the slope of the curves between gas velocities of 0.04 and 0.06 m/s. This change in slope may be attributed to a change in the flow regime from bubbly to slug flow. It appears that the transition occurs somewhere between gas velocities of 0.04 and 0.06 for all three experiments. Transition to slug flow occurred in the same range of gas velocities for the other runs conducted in this study.

Figure 14 shows the effect of gas velocity on the MSE for the run with 20 wt.% 0-5 μm silica particles. In general, the MSE increases with increasing gas velocity for all pressure transducers. It is interesting to note that MSE at port 2 is always lower than that at port 1 for gas velocities of 0.09 and 0.12 m/s. A possible explanation of this behavior is that the increase in oscillations at port 1 is due to the increase in turbulence near the distributor caused by the increase in gas velocity. The sharp changes in the slope of the MSE curve between pressure ports 2 and 3 at gas velocities of 0.06, 0.09, and 0.12 m/s indicates that slugs begin to appear in the column somewhere between the heights of 24 and 48 inches above the distributor. At gas velocities of 0.02 and 0.04 m/s, there is only a marginal change in slope between pressure ports 3 and 4, indicating the presence of large bubbles or slugs at a height of 72 inches above the distributor.

In general, based on the MSE from all experiments, the transition between bubbly and slug flow occurred somewhere between the gas velocities of 0.04 and 0.06 m/s. Also, slugs were not observed below a height of 36 inches above the distributor.

Flow regime transitions based on the psd: Pressure signals measured in our experiments required high pass filtering. Slow changes in the mean of the pressure signal, unrelated to higher frequency hydrodynamic phenomena, gave rise to a heavy low frequency bias in the psd and autocorrelation functions. To avoid this, the first difference of the time series corresponding to pressure fluctuations was used before the spectra were obtained. Results from the experiment with large iron oxide particles (20-44 μm) are discussed here, results from other experiments

were similar.

Figure 15 shows spectra of signal obtained at port 4 at different gas velocities. The psd are fairly broad at a gas velocity of 0.02 and 0.04 m/s, with frequencies ranging from 2.5 to 10 Hz. For $u_g \geq 0.06$ m/s, the dominant frequency is in the range 2.5 to 5 Hz. The shift in frequency is indicative of the onset of slug flow between gas velocities of 0.04 and 0.06 m/s. Also, the intensity of the psd increases with increasing gas velocity; a similar trend was observed with the MSE (i.e., MSE increased with an increase in gas velocity).

The effect of height above the distributor on the frequency spectra for a batch run is illustrated in Figure 16. Spectra of signals from transducers at ports 2, 3 and 4 are compared in this figure. The dominant frequency observed at port 2 is 5 Hz; whereas, the dominant frequencies observed at ports 3 and 4 is approximately 2.5 Hz. This shift from 5 Hz at the bottom of the column to 2.5 Hz at the top of the column is an indication of coalescence which may be taking place. During experiments conducted in a 0.05 m ID glass column, visual observations indicated slug frequencies in the range 2 to 3 Hz at the top of the column for $u_g \geq 0.07$ m/s, which is in agreement with dominant frequencies obtained from the spectra. At the bottom of the column, on the other hand, smaller slugs are visible which appear at a higher frequency. The results shown in Figure 16 indicate that coalescence of small slugs to form large slugs occurs between a height of 2 to 4 feet above the distributor. In the continuous mode experiments, the dominant frequency at the top of the column was in the range 2.5 to 5 Hz, implying that liquid circulation tends to retard the coalescence of small slugs.

Experiments in the 0.21 m ID Column

Average Gas Holdups From Pressure Measurements

Holdup values from two-phase experiments with Sasol wax are shown in Figure 17. Results from the three runs with the 19 X 2 mm perforated plate distributor (u_ℓ = 0, 0.005, and 0.02 m/s, respectively), and single run with the bubble-cap distributor (u_ℓ=0.005 m/s), are shown in the figure. There appears to be no effect of liquid circulation on gas holdup for Sasol wax, with similar values obtained from all three runs with the perforated plate distributor. Unlike FT-300 wax, Sasol wax does not produce foam and is coalescing in nature, therefore the introduction of liquid circulation did not promote coalescence as was the case with the FT-300 wax runs in the 0.05 m ID column. This could possibly explain the absence of any effect due to liquid

circulation. The bubble-cap distributor gave holdups that were significantly higher than those obtained with the perforated plate under similar conditions. At this point it is not clear as to why this distributor increased the gas holdup. It is possible that the wax composition changed somewhat with time on stream. The run with the bubble-cap distributor was the last run with this batch of wax, and the higher holdups could be due to aging effects. We plan to repeat this experiment with a fresh batch of Sasol wax to ascertain this behavior.

The effect of solids concentration on average gas holdup for experiments conducted in the batch mode of operation using the 0-5 μm iron oxide particles is show in Figure 18. The lowest gas holdups were obtained during the run with no solids, and consistently higher holdups were obtained in the presence of solids. There is no definitive trend in holdup behavior with the amount of solids present, and the highest gas holdups were obtained when a slurry containing 20 wt.% solids was used. At a gas velocity of 0.12 m/s, holdup values for all cases are similar. The increase in gas holdup with the addition of solids was also observed in experiments conducted in the small diameter (0.05 m ID) column (Figure 6). Figure 19 shows the effect of solids concentration on gas holdup for experiments conducted in the continuous mode of operation using a superficial liquid velocity of 0.005 m/s. Holdup values for the run without solids were similar to those for the slurry with 20 wt.% solids, while values for the slurry containing 30 wt.% solids were substantially higher. When a superficial liquid velocity of 0.02 m/s was used, holdup values from the runs with 0 and 20 wt.% solids were similar.

The effect of liquid circulation on average gas holdups in the presence of solids is shown in Figures 20 and 21. Figure 20 shows results from three runs conducted using superficial liquid velocities of 0, 0.005 and 0.02 m/s, respectively, with a slurry containing 20 wt.% of solids. The effect of liquid circulation on gas holdup is minimal, with slightly higher holdups observed when liquid circulation is introduced. Figure 21 compares gas holdups for two runs conducted using superficial liquid velocities of 0 and 0.005 m/s, respectively, with a slurry containing 30 wt.% solids. In this case the holdups increased significantly when liquid circulation was introduced. This trend is opposite of that observed with FT-300 wax in the 0.05 m ID column (Figure 4). For FT-300 wax, liquid circulation always decreased the average gas holdup. The opposite trend obtained with Sasol wax could either be attributed to differences in the foaming capacity of the two media (i.e., FT-300 wax has a tendency to foam, whereas Sasol wax is a coalescing

medium), or to differences in column diameter. However, it would be premature to attribute these differences to the effect of column diameter, until additional data from experiments with FT-300 wax in the large column become available.

The effect of distributor type on gas holdup is illustrated in Figures 22 and 23 for batch mode and continuous mode experiments, respectively. In the batch mode of operation (Figure 22), a slurry containing 20 wt.% of solids showed little effect of distributor type, and holdups from the experiment with the bubble-cap distributor were only slightly higher than those observed when the 19 X 2 mm perforated plate distributor was used. The difference between results from experiments with the two distributors was more apparent when a superficial liquid velocity of 0.005 m/s was used (Figure 23). In this case, gas holdups with the bubble-cap distributor were somewhat higher than those obtained with the perforated plate distributor.

In summary, average gas holdups increased with solids concentration (for both batch and continuous mode of operations). Liquid circulation also increases the gas holdup; however, the increase is only slight. Finally, the bubble-cap distributor gives higher gas holdups than those obtained using the perforated plate distributor.

Gas Holdups From Nuclear Density Gauges

The nuclear density gauges were used to obtain axial and radial slurry density profiles during the runs conducted in the 0.21 m ID column. Some of the results from the two-phase experiments with Sasol are presented here.

For the two-phase experiments, data from measurements with a single density gauge are sufficient to determine volume fractions of gas and liquid. Nevertheless, we acquired data with both density gauges and compared holdups from these measurements with those obtained from conventional measurements (i.e., pressure measurements). The gas holdup at a given height in the column was determined using a weighted average of the six point measurements of holdup made at different radial locations at that height. The weights used in the averaging process were proportional to the fraction of the column cross-sectional area traversed by the beam when positioned at the various radial locations (i.e., product of the beam path length through the column and the spacing between adjacent radial locations). The average gas holdup for the entire column was obtained by taking the arithmetic mean of the holdups at the different heights.

Figure 24 shows radial holdup profiles obtained at a height of 0.9 above the distributor using the nuclear density gauges at various gas velocities for the two-phase batch run with Sasol wax. Measurements were made at six radial locations at each gas velocity. For each case results from the two density gauges are presented. The two density gauges gave very similar results. The radial holdup profile is fairly uniform at a gas velocity of 0.02 m/s, which is expected since flow is in the homogeneous bubbly regime at these velocities. However, as gas velocity increases, the profile becomes slightly non-uniform with higher holdups in the center of the column. This corresponds to an increase in the number of large bubbles present in the system, which have a tendency to move along the center of the column. The trends at a height of 1.5 m above the distributor were very similar to those observed at 0.9 m above the distributor.

Figure 25 compares average gas holdup values obtained using pressure measurements with those obtained with the density gauges. There is very good agreement between the different sets of values, with values from pressure measurements being consistently lower than those from the density gauge using the Cs-137 source and comparable to those obtained with the density gauge using the Co-60 source.

SUMMARY AND CONCLUSIONS

Experimental studies were undertaken to investigate the hydrodynamics of a bubble column using the molten wax-nitrogen system. The effect of liquid circulation, and solids type, size and concentration on average gas holdup, solids suspension, and flow regime transition has been investigated. Our results show that in the batch mode of operation, FT-300 wax has a tendency to foam; however, the introduction of a small upward liquid flow (0.005 m/s) is sufficient to dissipate the foam. The addition of solids tends to increase the amount of foam, for both FT-300 wax (non-coalescing medium) and for Sasol wax (coalescing medium). Once again, liquid circulation dissipates the foam and average holdups are lower in the continuous mode of operation than in the batch mode of operation. Axial solids distribution profiles were uniform for small particles (0-5 μ) for all runs; whereas, significant gradients in axial solids distribution profiles were observed with large particles (20-44 μm) in batch mode experiments. Liquid circulation significantly improved the suspension of large solids.

Axial solids dispersion coefficients were estimated using axial solids distribution profiles

from experiments conducted with large solids in the batch mode of operation. These values are in good agreement with values predicted using literature correlations. Pressure fluctuations at different axial locations were used to obtain information on slug frequency and flow regime transitions. These measurements show that the transition from homogeneous bubbly flow to slug flow occurs somewhere between the gas velocities of 0.04 and 0.06 m/s. These measurements also show that the slugs begin to develop in the column between the heights of 24 and 48 inches above the distributor. Slug frequencies at the top of the dispersion are typically in the range 2.5 to 5 Hz, with higher frequencies observed during continuous mode experiments.

Experiments conducted in the 0.21 m ID column with Sasol wax also showed an increase in average gas holdup with solids concentration (for both batch and continuous modes of operation). Average gas holdup values showed a slight increase with liquid circulation rate. The axial solids distribution profiles were uniform for all experiments conducted with the 0-5 μm iron oxide particles, irrespective of the gas or liquid velocity used. Holdup measurements made using the nuclear density gauges in two-phase runs with Sasol wax were in good agreement with values obtained using pressure measurements. Radial gas holdup profiles were fairly uniform at low gas velocities, but showed a maximum at the center of the column at higher gas velocities. The profiles were similar at different heights along the column.

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NOTATION

a, b, c, d	constants in Eq. 6, or $a=\frac{U_{sl}C_s^f}{\Phi_g U_p - U_{sl}}$ in Eq. 5
C_1, C_2	constants of integration in Eq. 3
C_s	solids concentration, g/cm^3
C_s^B	solids concentration at the bottom of the dispersion, g/cm^3
C_s^f	solids concentration in the feed, g/cm^3
d_p	particle diameter, cm
D_{col}	column diameter, cm
E_s	axial dispersion coefficient, cm^2/s

Fr_g	Froude number $= \frac{U_g}{\sqrt{gD_{col}}}$
g	acceleration due to gravity, 981 cm/s^2
L	expanded height of the dispersion, cm
MSE	mean square error, defined by Eq. 10
N	number of data points
psd	power spectral density function, defined by Eq. 14
P	Fourier transform of the autocorrelation function, Eq. 14
$\bar{P}$	average pressure
P_i	pressure
Pe_p	particle Peclet number $= \frac{U_g D_{col}}{E_s}$
Re_g	Reynolds number $= \frac{U_g D_{col} \rho_\ell}{\mu_\ell}$
Re_p	particle Reynolds number $= \frac{U_T d_p \rho_\ell}{\mu_\ell}$
RMS	root mean square, defined by Eq. 11
t	time, s
u_g, U_g	superficial gas velocity, m/s
U_p	hindered settling velocity of particles, m/s
$u_{s\ell}$, $U_{s\ell}$	superficial slurry velocity, m/s
$U'_{s\ell}$	$= \frac{U_{s\ell}}{(1-\epsilon_g)}$ in Eq. 5, m/s
U_T	terminal rise velocity of a single particle in an infinite medium, m/s
x	dimensionless height above the distributor, cm

Greek letters

α	phase weight fraction
ϵ_g	gas phase holdup
μ	mean of the time series
μ_ℓ	liquid viscosity, N.s/m
ρ_ℓ	liquid density (g/cm^3)
ρ_{xx}	autocorrelation function
γ_{xx}	autocovariance function
Φ_ℓ	volume fraction of liquid in the slurry
$\overline{\Phi_\ell}$	average volume fraction of liquid in the slurry