## ABSTRACT

This report describes results of a study on hydrodynamics of three-phase bubble columns for Fischer-Tropsch synthesis under a DOE Contract No. DE-AC22-86PC90012.

Experiments were conducted in two stainless steel bubble columns of 0.05 m and 0.21 m in diameter and 3 m tall, at 265°C and atmospheric pressure using nitrogen gas and two types of liquid medium (hydrotreated reactor wax designated FT-300, and raw reactor wax from fixed bed reactors at SASOL). The effects of solids type (iron oxide and silica), concentration (0-30 wt%), size (0-5 μm and 20-44 μm), and slurry (liquid) velocity ( up to 0.02 m/s) on the gas holdup and axial solids concentration profiles, were investigated. Phase volume fractions were determined using conventional (differential pressure measurements together with determination of slurry concentration along the column) and novel (dual energy nuclear density gauge) experimental techniques. Bubble size distribution and the Sauter mean bubble diameter were obtained using the dynamic gas disengagement (DGD) method. Flow regime transitions in both columns were determined using statistical analysis of both pressure and density fluctuations.

Correlations for prediction of gas holdups and axial solids dispersion coefficient have been developed from experimental data obtained in this study. Data needed for calculation of the gas-liquid interfacial area (average gas holdup and Sauter mean bubble diameter) have been presented and can be used to estimate the mass transfer rate in slurry bubble column reactors. The results obtained in this study should be useful to those engaged in design and economic evaluations of slurry bubble column reactors for Fischer-Tropsch synthesis reaction.

Objective and Scope of Work

The overall objective of this contract is to determine the effects of bubble column diameter, solids loading and particle size, and operating conditions (temperature, gas and liquid flow rates) on hydrodynamics of slurry bubble columns for Fischer-Tropsch synthesis, using a molten wax as the liquid medium. To accomplish these objectives, the following specific tasks will be undertaken.

Task 1 - Project Work Plan

The objective of this task is to establish a detailed project work plan covering the entire period of performance of the contract, including a detailed program schedule, analytical procedures, and estimated costs and manhours expended by month for each task.

Task 2 - Design and Construction of the Experimental Apparatus

The existing stainless steel columns (0.05 m and 0.21 m in diameter, 3 m tall) that were constructed under our previous DOE contract (DE-AC22-84PC70027), will be modified and additions made in order to study the effect of continuous upward liquid flow. After the procurement of equipment and instrumentation, and construction of the unit is completed, a shakedown of test facilities will be made to verify achievement of planned operating conditions.

Task 3 - Measurement of Hydrodynamic Parameters by Conventional Techniques

In this task, the effects of operating conditions (liquid and gas superficial velocities), gas distributor, column diameter, and solids concentrations and particle size on hydrodynamic parameters in the stainless steel columns will be determined. All experiments will be conducted using nitrogen at atmospheric pressure. The hydrodynamic parameters that will be determined as a function of the independent variables mentioned above are: average gas hold-up, axial solids distribution, axial gas hold-

up, flow regime characterization, and qualitative information on bubble size distribution.

Task 4 - Application of a Gamma Radiation Density Gauge for Determining Hydrodynamic Parameters

The objective of this task is to determine hydrodynamic parameters for the three-phase system using a nuclear density gauge apparatus. A movable assembly mechanism and positioning racks for the two nuclear density gauges and detectors will be designed and constructed. Following the interfacing of the apparatus with an on-line microprocessor, the gauges will be calibrated using pure components (liquid wax and solid particles), and with known proportions of liquid and solid. After calibration, the following parameters will be obtained from experiments in the large stainless steel column: axial gas hold-up, axial concentration of solids, and qualitative information on flow regimes.

## EXECUTIVE SUMMARY

Slurry phase Fischer-Tropsch (FT) processing is considered a potentially economic method to convert coal derived synthesis gas into liquid fuels. Largely due to its relatively simple reactor design, improved thermal efficiency, and ability to process CO-rich synthesis gas, the slurry process has several potential advantages over conventional vapor phase processes.

The scale-up of slurry bubble column reactors is subject to uncertainty because important hydrodynamic parameters change with the scale (i..e. with the reactor diameter, and, to smaller extent, with the height). These parameters have significant effect on the synthesis gas conversion and product selectivity. Commercial size reactors are expected to operate in a churn-turbulent flow regime, and it is essential to use a bubble column with sufficiently large diameter which will allow for operation in this flow regime. A glass bubble column with 0.23 m in diameter, 3 m tall was constructed at Texas A&M University (TAMU), under DOE Contract No. DE-AC22-84PC70027, for hydrodynamic studies of Fischer-Tropsch synthesis in the absence of solids. It was demonstrated that this column operates in the churn-turbulent flow regime under typical processing conditions for slurry Fischer-Tropsch synthesis reaction. This study has provided useful information on the effects of operating conditions, gas distributor design, column geometry, and oxygenated species on gas hold-up and bubble size distribution.

Slurry FT bubble column reactors operate with solid loadings up to 30 wt%, and part of slurry is removed from the reactor and returned to it as a concentrated slurry from a wax/catalyst separation unit. These factors (i.e. the presence of solids and small continuous liquid flow) may have significant effect on hydrodynamic parameters, and need to be evaluated. Therefore, TAMU proposed to conduct a systematic study of the effect of solids, and small upward liquid flow on hydrodynamic parameter in 0.05 m and 0.21 m diameter columns, under conditions which simulate the process conditions in industrial slurry bubble column reactors for Fischer-Tropsch synthesis. The following hydrodynamic parameters were determined: the average and axial gas holdups, axial solids concentration profiles, the axial solids

dispersion coefficient, Sauter mean bubble diameter in the absence of solids, flow regimes and flow regime transitions, by utilizing both conventional and novel experimental techniques.

## SUMMARY OF RESULTS

Experiments were conducted in two stainless steel bubble columns (0.05 and 0.21 m in diameter, 3 m in height) in two modes of operation : (a) batch mode - continuous flow of gas, stationary liquid (slurry), and (b) continuous mode - both gas and liquid (slurry) in cocurrent upward flow. A total of 34 runs (28 with FT-300 wax, and 6 with SASOL reactor wax) were made in the small diameter column, whereas 35 runs (6 with FT-300 wax, and 29 with SASOL reactor wax) were made in the large diameter column. Two different types of solid particles were employed in these tests: iron oxide (0-5 μm and 20-44 μm) and silica (0-5 μm and 20-44 μm) to simulate typical catalysts and supports employed in Fischer-Tropsch synthesis. All experiments were conducted at 265°C and atmospheric pressure, using nitrogen as the gas. Experimental conditions for different runs are listed in Tables 2.4 and 2.5.

### Gas Holdups by Conventional Techniques

Axial (between two measurement ports along the column height) and average (for the entire column) holdups were calculated from differential pressure and solids concentration measurements along the column height, as described in Chapter II. The effects of slurry (liquid) flow rate, solids concentration, type and size, column diameter, distributor type, and liquid medium on the average gas holdup are summarized below.

**Effects of slurry (liquid) velocity.** The gas holdup decreased with increasing slurry (liquid) velocity for experiments conducted with FT-300 wax (with and without solids) in the both columns. The decrease in holdup was most pronounced at gas velocities which favor the formation of foam, since a slight upward liquid (slurry) flow rate is sufficient to dissipate the foam layer. In the absence of foam, the effect of slurry flow rate on gas holdup is negligible.

SASOL reactor wax does not have tendency to foam, and the slurry velocity did not have significant effect on the gas holdup. The trends observed in our study are consistent with results reported in literature with other systems.

**Effects of Solids Concentration.** The addition of solids increased gas holdup in experiments conducted in the batch mode of operation with both FT-300 wax and SASOL reactor wax. This may be attributed either to reduction in bubble size with addition of small particles or to poor wettability of particles in the region of high gas holdups (upper portion of the column).

In continuous mode of operation addition of solids to FT-300 wax causes a slight decrease in the gas holdup; whereas, addition of solids to SASOL wax causes a slight increase in the gas holdup. This difference in the behavior of the two wax types might be due to differences in the wettability of the particles with respect to each wax type.

**Effects of Solids Type and Size.** In general, this effect was found to be insignificant, i.e. neither the particle size nor the solids type have marked effect on the gas holdup. However, in the presence of large axial concentration gradients of solids the holdup decreased with increase in particle size (e.g. experiments with large iron oxide particles in the batch mode of operation). In the latter case, the solids accumulate near the distributor increasing the apparent viscosity of the slurry which results in larger bubbles and thus lower gas holdups.

**Effect of Column Diameter.** From the limited data it appears that column diameter does not have significant effect on gas holdup when the foam is not present in the system.

**Effect of Distributor Type.** Two type of gas spargers were used for experiments in the 0.21 m ID column; (a) a perforated plate (19 holes of 2 mm in diameter), and (b) bubble cap distributor (7 caps, each with 3 holes of 2 mm in diameter). For both waxes, gas holdups in experiments with the bubble cap distributor were slightly higher than those obtained with the perforated plate distributor.

**Effect of Liquid Medium.** In the batch mode of operation and at low gas velocities gas holdups

obtained with the FT-300 wax were substantially higher than those obtained with the SASOL reactor wax, primarily due to foaming tendency of the former. However, in the absence of foam the holdups were similar.

**Gas Holdup Correlation**

Data from both our three-phase (present work) and two-phase studies (DOE Contract No. DE-AC22-84PC70027) were combined and the following general correlation was developed for prediction of gas holdups in Fischer-Tropsch slurry bubble column reactors in the absence of foam.

$$\varepsilon_g = 0.24\ (Fr_g^{0.28}\ Bo^{0.14})$$

where: $Fr_g = (u_g^2 / gd_c)$; $Bo = (d_c^2\ \rho_{sL} g/\sigma_L)$ ; $d_c$ = column diameter; $g$ = gravity constant; $u_g$ = superficial gas velocity; $\rho_{sL}$ = density of slurry; $\sigma_L$ = surface tension of the liquid medium.

The mean square error based on 514 data points was $7 \times 10^{-4}$, and approximately 94% of experimental data were within $\pm$ 30% of the predicted values by the above correlation.

**Axial Solids Concentration Distributions**

Axial solids concentration profiles were obtained during experiments conducted in both the 0.05 m and 0.21 m ID columns with 0 - 5 μm and 20 - 44 μm iron oxide and silica particles. Solids concentrations of 10, 20, and 30 wt% were employed throughout these studies. The small (0 - 5 μm) iron oxide and silica particles were completely suspended in both columns in the batch and continuous modes of operation. However, significant concentration gradients were observed with large (20 -44 μm) particles, in the small diameter column during batch experiments. In the large diameter column, the solids concentration gradient was smaller. The solids distribution became uniform with the introduction of upward slurry velocity (0.005 or 0.02 m/s), since the slurry velocity was greater than the terminal settling velocity of the largest particles. Axial solids dispersion coefficients were estimated from axial solids concentration profiles obtained in experiments conducted with large solids in both the batch mode and continuous mode

(the latter in the large diameter column only) of operation. The axial solids dispersion coefficients in the large diameter column were significantly greater than those obtained in the small diameter column. The following correlation for prediction of the particle Peclet number was obtained.

$$Pe_p = 8.4 \left[ \frac{Fr_g^6}{Re_g} \right]^{0.107}$$

where: $Re_g = u_g d_c \rho_L / \mu_L$ ; $Pe_p = u_g d_c / E_s$; $\mu_L$ = viscosity of liquid; $E_s$ = axial dispersion coefficient for solids. The above correlation was developed from data obtained with both large iron oxide and silica particles using both SASOL wax and FT-300 wax.

**Nuclear Density Gauge Measurements**

A dual energy gamma-ray densitometer was designed and constructed for the purpose of obtaining phase (i.e. gas, liquid, and solid) fractions in the large diameter column. The sources and detectors were placed on a movable platform so that measurements could be made at various axial and radial locations. Cesium-137 and Cobalt-60 radioactive sources were used. For the (Cesium-137) - (Cobalt-60) system, slight errors in various parameters (e.g. the distance through the column) cause significant errors in the measured phase fractions. This is due to similarities in the absorption coefficients for the various phases associated with the two sources. However, when a three-phase system was treated as a two-phase (slurry/gas) system, the measured volume fractions of gas and slurry were comparable to those obtained using conventional (i.e. DP cells) technique.

**Bubble Size Measurements**

Sauter mean bubble diameters were measured using the dynamic gas disengagement (DGD) technique. The DGD technique is based on the fact that the volumetric flow rate at which the liquid level decreases once the gas flow is shut-off is equal to the volumetric flow rate at which the bubbles exit the dispersion. In the past, the DGD measurements were made in clear columns, and the rate at which the

liquid level (or dispersion) dropped was recorded via a VCR/camera system. In this study, we utilized pressure measurements to determine the rate of disengagement. Pressure measurements not only remove some of the subjectivity associated with VCR/camera measurements, but also enable one to determine the effect of axial position on the bubble size distribution. Sauter mean bubble diameters for FT-300 wax were quantitatively similar in both the 0.05 m and 0.21 m ID bubble columns for the range of gas velocities employed in this study. The Sauter mean bubble diameter ranged from approximately 0.9 mm at a gas velocity of 0.02 m/s to a value of 1.4 mm at a gas velocity of 0.12 m/s. Sauter mean bubble diameters for the experiment conducted with SASOL wax (increasing gas velocities, 0.21 m ID column) were similar to those obtained with FT-300 wax. However, for the experiment conducted using a decreasing order of gas velocities, the Sauter mean bubble diameters were slightly higher (e.g., $d_s$=1.7 mm at a gas velocity of 0.12 m/s). For the experiment conducted with SASOL wax in the 0.05 m ID column, the Sauter mean bubble diameters ranged from 1.4 mm ($u_g$=0.02 m/s) to 2.2 mm ($u_g$=0.09 m/s).

**Flow Regime Transitions**

Statistical analysis of wall pressure and nuclear density gauge fluctuations was used to determine flow regime transitions in both columns. For experiments in the small diameter column, the transition from the bubbly to the slug flow regime occurred between gas velocities of 0.04 and 0.06 m/s, regardless of solids concentration or slurry velocity (up to 0.02 m/s). Likewise, in the large diameter column, the transition from the homogeneous bubbling regime to the churn-turbulent regime occurred between gas velocities of 0.04 and 0.06 m/s. In the small diameter column, slugs start forming at a height of 0.6 m above the distributor. The flow regime transitions obtained in this study are in agreement with those predicted using correlations presented by Taitel et al. (1981) and the flow regime map presented by Deckwer et al. (1980).

## RECOMMENDATIONS FOR FUTURE WORK

On the basis of results obtained in this study the following recommendations are made:

- Continue work on development of nuclear densitometry for measurement of volume fractions and bubble rise velocities in three-phase systems.
- Continue work on refinements (theoretical and experimental) of the dynamic gas disengagement (DGD) method for determination of bubble size distribution. In particular, experiments should be conducted in which the bubble size distribution is measured by various techniques (e.g., photography, probes, DGD), and applicability of the DGD method should be extended to three-phase systems.

Future work in the area of hydrodynamic studies of Fischer-Tropsch slurry bubble column reactors should be directed towards measurement of additional parameters needed for design and scale-up slurry bubble column reactors, such as:

- Volumetric mass transfer coefficient ($k_L a$);
- Axial dispersion coefficients for the gas and the liquid phase by tracer studies;
- Heat transfer coefficient between the slurry and the immersed heat exchanger surfaces.

These measurements should be conducted under conditions similar to those that are planned for use in slurry bubble column reactors for Fischer-Tropsch synthesis (i.e., at reaction temperatures and pressures, and with wax as the liquid medium). Experiments should be conducted in a bubble column with sufficiently large column diameter to ensure operation in the churn-turbulent flow regime.