ABSTRACT

This report describes studies on hydrodynamics of bubble columns for Fischer-Tropsch synthesis under a DOE Contract No. DE-AC22-84PC70027.

These studies were carried out in columns of 0.051 m and 0.229 m in diameter and 3 m tall to determine effects of operating conditions (temperature and gas flow rate), distributor type (sintered metal plate and single and multi-hole perforated plates) and liquid media (paraffin and reactor waxes) on gas hold-up and bubble size distribution. In experiments with the Fischer-Tropsch (F-T) derived paraffin wax (FT-300) for temperatures between 230°C and 280°C there is a range of gas velocities (transition region) where two values of gas hold-up (i.e. two flow regimes) are possible. Higher hold-ups were accompanied by the presence of foam ("foamy" regime) whereas lower values were obtained in the absence of foam ("slug flow" in the 0.051 m column, or "churn-turbulent" flow regime in the 0.229 m column). This type of behavior has been observed for the first time in a system with molten paraffin wax as the liquid medium. Several factors which have significant effect on foaming characteristics of this syster were identified. Reactor waxes have much smaller tendency to foam and produce lower hold-ups due to the presence of larger bubbles.

Bubble size distribution and Sauter mean bubble diameters were determined by photographic method and by dynamic gas disengagement method. Significant differences in Sauter mean bubble diameters were obtained in experiments with different waxes, even though the gas hold-up values were similar.

Finally, new correlations for prediction of the gas hold-up and the specific gas-liquid interfacial area were developed on the basis of results obtained in the present study.

I. OBJECTIVE AND SCOPE OF WORK

The objective and scope of work given here are based on the original Statement of Work of the contract.

The overall objective of this contract is to determine effects of column geometry, distributor design, operating conditions (temperature and gas flow rate), and oxygenated compounds on hydrodynamics of slurry bubble column reactors for Fischer-Tropsch synthesis, using a hard paraffin 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 estimated costs and manhours expended by month for each task.

Task 2 - Bubble Column Reactor Design/Construction

Two bubble columns made of borosilicate glass of approximately 2" (0.05 m) and 9" (0.23 m) in diameter and 10 ft (3 m) tall will be designed and assembled for measurement of the gas hold-up and the bubble size distribution. After the design, 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. During this period instruments will be calibrated.

Task 3 - Process Variable Studies

The objective of this task is to determine the effect of various system variables (e.g. gas flow rate, temperature, and addition of minor amounts of oxygenated compounds) on hydrodynamic properties using the two bubble columns (2" and 9" ID) and different types of distributors. All

experiments will be conducted using nitrogen at atmospheric pressure. It is planned to determine the following hydrodynamic characteristics: gas hold-up, flow regime characterization, bubble size distribution, and the gas-liquid interfacial area.

Task 4 - Correlation Development and Data Reduction

Correlations based on our experimental data for prediction of average gas hold-up and the gas-liquid interfacial area will be developed.

II. SUMMARY

A. Background

Fischer-Tropsch (F-T) 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 commerical size units are in operation only at Sasol in South Africa. Fixed bed (Germany and Sasol) and entrained bed (Sasol) type of reactors have been used for conversion of synthesis gas into hydrocarbon products.

Slurry phase F-T 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 columns is subject to uncertainty due to the fact that important hydrodynamic parameters change with the scale. Thus the results obtained in small diameter units cannot be directly translated to a large diameter reactor. The successful reactor scale-up for the slurry phase Fischer-Tropsch process was achieved in Germany in the 50's (e.g. Kolbel et al., 1955; Kolbel and Ralek, 1980). The demonstration plant unit (1.55 m in diameter and a height of 8.6 m) was constructed by Rheinpreussen-Koppers and it operated successfully over a long period of time. This successful operation came as a result of significant development effort, the details of which have not been published. Subsequent studies were done on a smaller scale, and have not been successful in reproducing reported Kolbel's data on catalyst activity and product selectivity.

In the majority of previous studies of slurry F-T synthesis rather small bubble column reactors were employed (less than 0.10 m in diameter). According to Deckwer et al. (1980) and Shah et al. (1982), under these conditions the reactors were operating in either the homogeneous (ideal bubbly) flow regime or the slug flow regime. On the other hand, commerical size bubble column reactors are expected to operate in the heterogeneous (churn-turbulent) flow regime. The specific gas-liquid interfacial area, as well as the gas and the liquid phase mixing are different in different flow regimes. These parameters have significant effect on the secondary reactions and consequently product selectivities obtained in different flow regimes may differ significantly. Construction and operating costs for a large diameter bubble column reactor are expected to be very high. Before this is done further work is required which will provide a rational basis for the reactor design and scale-up.

The present work on hydrodynamics of bubble columns for F-T synthesis was initiated in September 1984, under DOE Contract No. DE-AC22-84PC70027. The objectives of this study were to determine the effect of bubble column diameter (0.051 m and 0.229 m), distributor type (sintered metal plate, single and multiple hole orifice plate), operating conditions (gas velocity and temperature), and oxygenated compounds on gas hold-up and bubble size distribution using molten paraffin wax as the liquid medium.

B. Results

Two glass (0.051 and 0.229 m in diameter, 3m in height) and two stainless steel columns of similar dimensions (0.051 m and 0.241 m in diameter, 3 m tall) were employed in this study. The glass columns were used for measurement of the average gas hold-up and bubble size distribution.

whereas the stainless steel columns were used for measurement of axial gas hold-up distribution. The construction work and fabrication of auxilliary vessels for all columns were completed in May 1985. The shakedown run with the small glass column was made in May 1985, and for the other three columns in June 1985. All columns were operated in a batch mode with respect to a liquid medium.

Flow regimes in the two glass columns were determined from visual observations of the flow field which were also recorded with a video camera. The homogeneous (ideal bubbly) regime, characterized by nearly uniform bubble size distribution, was observed in the small column at the gas velocity of 0.01 m/s. At velocities of 0.02 and 0.03 m/s slugs start appearing in the upper part of the column, and the flow may be characterized as a transition between the homogeneous and slug flow regimes. At higher gas velocity the slug flow regime prevails. However, even in the slug flow regime a large number of small bubbles was still present in experiments with Fischer-Tropsch derived paraffin waxes and their specific gas-liquid interfacial area is much greater than that in air-water system in the presence of slugs. Foaming, accompanied with hold-up values up to 75%, was often observed at lower gas velocities with all types of distributors (sintered metal plate - SMP, and orifice plate), and this type of operation is referred to as the "foamy" regime. Slugs were also present in this flow regime at velocities greater than 0.02 m/s. The flow regime in the larger diameter column was homogeneous at 0.01 m/s, followed by transition to "churn-turbulent" flow which was complete at the gas velocity of 0.03 m/s. During runs when foam was produced, the homogeneous flow regime was followed by the "foamy" regime in the velocity

range 0.02-0.05 m/s. At velocities greater than 0.05 m/s the "churn-turbulent" flow was the only stable flow regime.

Results of average gas hold-up measurements revealed the following:

- For temperatures between 230°C and 280°C, there is a range of gas velocities over which two values of gas hold-up are possible with FT-300 wax. The higher gas hold-ups are accompanied by the presence of foam ("foamy" regime). In the absence of foam, "slug flow" prevails in the 0.051 m ID column, whereas flow in the 0.229 m ID column is in the "churn-turbulent" regime. The start-up procedure determines which flow regime will be attained, with increasing order of gas velocities favoring the "foamy" regime. A transition from the "foamy" to the "slug flow" or "churn-turbulent" regime occurs when u_g exceeds a certain critical value, and the transition to the "foamy" regime occurs when u_g drops below a certain critical value. Since the two critical velocities are different, a hysteresis loop is created. In a system with molten paraffin wax as the liquid medium this type of behavior has been observed for the first time.
- Gas hold-up increases with temperature, and this increase is more significant in the presence of foam. As the temperature decreases the liquid viscosity increases which promotes bubble coalescence and produces lower hold-ups.
- In the absence of foam the column diameter (0.051 m and 0.229 m) had rather small effect on gas hold-up in experiments with a paraffin wax (trade name FT-300) and raw wax from Sasol's Arge reactor using 1.85 mm hole orifice distributors. However, in experiments with smaller

hole orifices (1 mm hole orifice in the 0.051 m column and 19 x 1 mm perforated plate in the 0.229 m column) with FT-300 wax higher hold-ups were obtained in the smaller column both in the presence and in the absence of foam.

- Distributor type did not have a significant effect on the gas hold-up in both columns in the absence of foaming. In the "foamy" regime the SMP distributor gave the highest hold-up values, whereas orifice distributors produced lower hold-ups. In the smaller diameter column higher hold-ups (more foam) were obtained with smaller orifices, but such effect was not observed in the 0.229 m ID column.
- The addition of small amounts (up to 10% by weight) of oxygenated species (1-octadecanol and octadecanoic acid) to FT-300 wax delayed foam break-up to higher gas velocities, but did not have a significant effect on the gas hold-up.
- Hydrodynamic behavior of four reactor waxes (Sasol's Arge wax, and three composite waxes produced during runs in Mobil's pilot plant bubble column reactor—Unit CT-256) was evaluated in the 0.051 m ID glass column. It was found that these waxes have a very small tendency to foam (only at 0.01 m/s with a 40 μm SMP) and thus do not exhibit hysterisis behavior observed with FT-300 paraffin wax. Distributor type (SMP and orifice plate) and temperature (200 and 265°C) had rather small effect on hold-up values. Hold-ups obtained with reactor waxes are similar to those obtained with FT-300 wax in the absence of foam.

Axial gas hold-up measurements were made in the two stainless steel columns with FT-300 wax, and in the 0.241 m ID column with Sasol's wax.

The hold-up profiles along the height of the column were found to be dependent on the flow regime. In the presence of foam the gas hold-ups near the top of dispersion were significantly higher than those in the lower portion of the column. In the absence of foam, the increase in hold-up with column height was only marginal. An increase in gas velocity shifts the axial gas hold-up profile upwards (towards higher values) irrespective of whether the foam was present or not.

Bubble size distribution and Sauter bubble diameter were determined by photographic method and by dynamic gas disengagement (DGD) technique. Photographs of bubbles near the wall were taken in the two glass columns, and near the center of the 0.241 m in diameter stainless steel (SS) column through a specially designed viewing port. The major findings from photographic measurements of bubble size distribution with FT-300 wax are:

- The Sauter mean bubble diameter (d_s) decreases with an increase in height above the distributor. The extent of this decrease depends on the flow regime, with more significant decreases in cases where foam is present.
- The value of d_s appears to be fairly constant with changes in superficial gas velocity in the 0.051 m ID column, however in the large columns (0.229 m ID glass and 0.241 m ID SS), it decreases marginally with an increase in superficial gas velocity.
- The 40 μm SMP distributor produced significantly smaller bubbles (d_s = 0.5-0.7 mm at 265°C) compared to the 1.85 mm orifice plate distributor (d_s = 1.2-2.2 mm under similar conditions). However, d_s in the 0.229 m and 0.241 m columns, with improvements in the technique (significantly larger bubble count), were around 0.5 mm at the wall

and around 0.8 mm near the center (for velocities greater than 0.5 m/s). The change of Sauter diameter with radial position is as expected, since large bubbles rise preferentially near the center of the column, while small bubbles concentrate near the wall.

Photographic measurements could not be made with reactor waxes due to their dark color, but the Sauter diameters for these waxes, as well as for FT-300 wax, were estimated using the DGD technique. The highlights of these investigations are:

- Column diameter and orifice hole diameter did not have a significant effect on the d_s value for FT-300 wax.
- The presence of foam had a strong effect on d_s values. At 265°C the Sauter mean diameter for FT-300 wax was approximately 0.5 mm which is the same as obtained with photographic method.
- Temperature had a significant effect on the Sauter mean bubble diameter (d_s), with values at 200°C being significantly larger than values at 265°C for all wax types, despite relatively small differences between hold-up values at the two temperatures.
- Wax type had a significant effect on d_s values, with the smallest bubbles being produced by FT-300 wax and the largest by Mobil reactor wax. The trends were similar at both 200°C and at 265°C. At 265°C Sauter mean diameters for FT-300 wax were around 0.8 mm for superficial gas velocities greater than 0.05 m/s; while those for Sasol reactor wax approached 2 mm and Mobil reactor wax gave values around 4 to 5 mm.

In general, a good agreement was obtained for Sauter bubble diameters estimated from these two methods. The important conclusion from the

present study is that similar gas hold-ups do not necessarily imply similar bubble size distributions. Significant differences in Sauter bubble diameters were obtained in experiments with different waxes at a given temperature or with a given wax at two temperatures (200 and 265°C), even though the hold-up values were similar.

Finally, based on our measurements of gas hold-ups and Sauter mean bubble diameters, correlations for prediction of the average gas hold-up and the specific gas-liquid interfacial area were developed. Since these correlations were obtained from a large data base they are expected to be useful to those engaged in design and scale-up of bubble column reactors for Fischer-Tropsch synthesis.