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Hydrodynamics of Fischer-Tropsch Synthesis in Slurry Bubble Column Reactors

Quarterly Technical Progress Report

for the period 1 December 1985 - 28 February 1986

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NOTICE

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I. Abstract

Measurements of the average gas holdup were made in the large glass column with three distributors: two perforated plates (19 X 1.85 mm and 19 X 1 mm) and a perforated pipe (30 X 1.5 mm) at 265°C using FT-300 paraffin wax as the liquid and nitrogen as the gas. Similar gas holdups were obtained with all three distributors.

The axial gas holdup measurements by differential pressure method in the small metal column were made at 265°C, with the 1.85 mm orifice plate and the 40 μm sintered metal plate (SMP) distributors.

Photographs of bubbles in the small glass column are presented, qualitatively illustrating the effects of orifice and SMP gas distributors, superficial gas velocity, and the column height. Also, the work on bubble size determination by image process analysis has been initiated.

II. Objective and Scope of Work

The overall objective of this contract is to determine effects of reactor geometry, distributor design, operating conditions (i.e., 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" ID and 9" ID, and 10 ft 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.

III. Summary of Progress

During this quarter additional experiments were conducted in the large glass column (22.5 cm ID, 300 cm tall - Unit AM-9G) at 265°C with three gas distributors: perforated plates with 19 holes of 1 mm and 1.85 mm in diameter, and a perforated pipe with 30 holes of 1.5 mm in diameter. The "foamy" flow regime was obtained at low superficial gas velocities (up to about 5 cm/s) in experiments conducted in the order of increasing gas flow rates. The foam break-up occurred at velocities between 3 cm/s and 5 cm/s, and at higher flow rates the gas holdup increased momotonically. The hysterisis type of behavior was observed upon decreasing the flow rate, and the largest differences in gas holdups occurred for velocities between 3 cm/s and 5 cm/s. All three distributors gave similar holdups in the range of velocities investigated (u_g=1-15 cm/s).

Modifications of differential pressure system were made on a small stainless steel column (Unit AM-2S, 5.1 cm ID, 305 cm tall), and the differential pressure cell was calibrated with water and FT-300 wax. Axial gas holdup measurements were made with N_2/FT-300 wax system at 265°C, using the 1.85 mm single orifice plate and the 40 μm sintered metal plate (SMP) distributor. The results of these measurements have not been analyzed yet.

Selected photographs of the flow field were enlarged and analyzed on a Zeiss image analyzer. A procedure for determination of bubble size distribution has been established, and preliminary results have been obtained.

In addition, photographs of bubble flow patterns are presented here, showing effects of gas distributor type, gas flow rate and column height on the bubble size distribution. The photos were taken during the gas holdup

measurements in the small glass column (Unit AM-2G, 5.1 cm ID, 305 cm tall) described in the last Quarterly Report.

IV. Detailed Description of Technical Progress

A. Task 1 - Project Work Plan

The work on this Task was completed during the first quarter of the project.

B. Task 2 - Bubble Column Reactor Design/Construction

The work on this task was completed during the fourth quarter of the project.

C. Task 3 - Process Variable Studies

1. Hydrodynamic Studies in the AM-2S Column

The axial gas holdup was determined in the AM-2S column (5.1 cm ID, 305 cm tall) by differential pressure method using a DP-cell (Validyne-Model DP 15 TL). A schematic representation of the pressure tap system was given earlier (Figure 11 of June-August, 1985 Quarterly Report) and will not be reproduced here. Additional pressure port was used at a height 190 cm above the distributor. Smaller holes (0.64 mm) were drilled at the tip of nitrogen purge lines in the column than the ones used previously (6.4 mm) to prevent the wax weeping.

The differential pressure (DP) cell was calibrated with the water at room temperature and the wax (FT-300) at 265°C. From calibration diagrams (actual height vs. DP meter reading) densities of two fluids were found to be: 1.006 (g/cm^3) for water and 0.674 (g/cm^3) for the wax. The value for water is quite accurate. The density of FT-300 wax has not been reported in the literature, but densities for similar types of waxes have been reported (e.g. Deckwer et al., 1980; Calderbank et al., 1963). These literature values are in good agreement with the value determined from the calibration diagram.

After the DP cell calibration the axial gas holdup measurements were made in the AM-2S column at 265°C with the 1.85 mm orifice plate distributor and the 40 μm SMP distributor. Plugging of some purge lines occasionally occurred during these experiments, but this was not a serious problem. The analysis of experimental data has not been completed yet, and results will be discussed in the next quarterly report.

2. Hydrodynamic Studies in the AM-9G Column

The average gas holdup measurements were made in the AM-9G glass column (22.5 cm ID, 300 cm tall) at 265°C with three gas distributors: perforated plates (PP) having 19 holes of 1.85 mm or 1 mm in diameter equally spaced in a triangular pitch, and a perforated pipe with 30 holes of 1.5 mm in diameter (a star shaped arrangement with 6 segments having 5 holes each, 60° angle between the segments). All experiments were conducted with the same batch of FT-300 wax, that was used at the end of the previous quarter (Run 1). The static liquid height in all experiments was about 180 cm.

Results obtained with the PP distributor 19 x 1.85 mm (Run 1-3) are shown in Figure 1, together with the results reported in the last quarter (Run 1-2). As the velocity increases the gas holdup rises rapidly between u_g = 1 cm/s and u_g = 3 cm/s due to formation of foam. The height of foam layer was about 35 cm at u_g = 3 cm/s, giving holdup of 24%. When the velocity was increased to 5 cm/s, the foam disappeared and the holdup dropped to 19.1%. For velocities greater than 5 cm/s the holdup increases monotonically and it reaches the value of 28.2% at u_g = 15 cm/s. During the same run when the gas velocity was decreased from 15 cm/s to 3 cm/s (solid triangles in Figure 1) lower values of holdups were obtained than in

experiments conducted in the order of increasing gas velocities. The difference in the observed holdups is larger at smaller gas velocities. This hysterisis type of behavior is caused by differences in the bubble size distribution at higher gas velocities (i.e. $u_g > 5$ cm/s), while at lower gas velocities the large differences in holdups are caused by the presence of foam layer in experiments conducted in the order of increasing gas velocities. The gas holdup at 3 cm/s is 13.5% (with about 2 cm of foam) and 24% when the foam is present (35 cm of foam). When the velocity was decreased to 2 cm/s, the height of foam layer was about 5 cm and higher gas holdup was obtained ($\varepsilon_g = 16\%$).

Results reported in the previous quarterly report (Run 1-2) are also shown in Figure 1 for comparison. The agreement between these two runs is excellent in the "foamy" regime (u_g = 1-5 cm/s in the order of increasing gas velocities), and quite satisfactory at higher gas velocities ($u_g > 5$ cm/s). The absolute difference in gas holdups observed in Runs 1-2 and 1-3 is about 2%, for superficial gas velocities between 5 cm/s and 12 cm/s, which is within experimental error of measurement. In this range of velocities the liquid level oscillates with an amplitude of about 5-7 cm, making it difficult to determine accurately the expanded liquid height.

In the run 1-4 a high startup velocity of 9 cm/s was employed, and the velocity was then increased to 12 cm/s and 15 cm/s. After that the velocity was decreased in increments of 2-3 cm/s all the way to 1 cm/s. This run is characterized by virtual absence of foam for all gas velocities employed, i.e. the "nonfoamy" regime was maintained over the entire range of gas velocities. Results obtained in this run are shown in Fig. 2, together with the data obtained in Runs 1-1 (T = 200°C) and Run 1-3 (data

for experiments, conducted in the order of decreasing velocities). The data from all three runs are well described by a single curve, which shows that the gas holdup in the "nonfoamy" flow regime is essentially independent of temperature. In the Run 1-1 the data were obtained in the order of increasing gas velocities, and the foaming was not observed. A possible explanation for this type of behavior is that at lower temperature the liquid viscosity is higher, and the latter promotes bubble coalescence which helps prevent the foam formation and growth. At 265°C (lower liquid viscosity) the foam develops at low superficial gas velocities and grows until the foam break-up ocurs as shown in Fig. 1 (Runs 1-2 and 1-3 in the order of increasing velocities). Also, the foaming can be virtually eliminated by starting experiments at higher gas velocities (Runs 1-3 and 1-4) and then decreasing the velocity to lower values. Similar type of behavior was observed in our experiments in the small glass column (AM-2G, 5.1 cm ID, 305 cm tall) as reported earlier (Quarterly Reports June - August, 1985 and September - November, 1985).

Results illustrating the effect of distributor design are shown in Fig. 3. A number of similarities can be noted as follows. The foaming occurs at low superficial gas velocities, and the foam break-up occurs between 3 and 5 cm/s. Hysterisis type of behavior, where two values of gas holdup exist for a given set of conditions, is observed when experiments are conducted in the order of decreasing velocities. The differences in gas holdups are the most significant for velocities between 3 cm/s and 5 cm/s. The gas holdups in the "nonfoamy" regime are similar for all three distributors. However, it should be noted that holdups obtained with the 19 X 1.85 mm perforated plate distributor were consistently higher than the

ones obtained with the other two distributors. In summary, the effect of distributor designs on the average gas holdup is relatively small. Of the three distributors that were evaluated, the perforated plate with 19 X 1.85 mm holes represents the best choice because it gives the highest gas holdup and it gives approximately the same pressure drop as the 30 X 1.5 mm perforated pipe distributor.

3. Summary of Visual Observations

Oscillations of the liquid level were observed with all three distributors at velocities greater than 3 cm/s. The amplitude of oscillations was in the range 3-10 cm, and it increased with velocity. Large bubbles could be seen bursting at the top of the liquid level, sometimes two or three at the same time. Slugs occupying the entire cross sectional area of the column, or rising near the wall were not observed in any of the experiments. Bubbles near the wall have a wide size distribution (0.1 - 3 cm in diameter), while the bubbles inside the column are difficult to observe particularly at higher gas flow rates. Occasionally large bubbles of 5-8 cm in diameter could be seen rising near the center, and possibly these large bubbles are causing oscillations of the liquid level at the top.

During the runs 1-3 and 1-4 the dynamic gas disengagement (DGD) technique was employed. A drop in the liquid level as a function of time was recorded on a tape with a video camera after the gas flow rate was shut down using a solenoid valve. Initially, the liquid level drops very fast (due to escape of large bubbles), which is followed by a slow decrease in height until it reaches a stationary value (i.e. the static liquid height). Towards the end a large number of tiny bubbles (about 1 mm in diameter)

could be seen rising through the entire column. These data have not been analyzed yet to obtain some quantitative information on the bubble size distribution.

D. Task 4. Correlation Development and Data Reduction

Photographs of the flow field in the AM-2G glass column (5.1 cm ID, 305 cm tall) obtained during the past two quarters were catalogued and selected ones were enlarged for bubble size distribution determination by image processing analysis. Also, photographs illustrating effects of gas velocity, distributor type and column height on bubble size were made (see section 2).

1. Image Analysis Technique for Bubble Size Determination

Selected photographs of the flow field were enlarged to 8" X 10" size, and analyzed on a Zeiss image analyzer located in the Biology Department of the University of Texas at Austin. Basic features of this system and procedures employed to obtain information on the bubble size distribution are described below.

A TV camera takes a picture of the enlarged photograph and stores it on a TV screen where it can be analyzed, and the image is stored in a computer. The image analyzer is only able to distinguish between different shades of gray, therefore, when bubbles overlap the image analyzer treats them as one image. However, the IBAS II software package system allows user to select only those bubbles which are distinct and remove all other images from the screen. Once this is done a variety of object specific parameters can be calculated.

The parameters which are most useful for characterization of the bubble size distribution are the minimum and the maximum length of the

elongated bubbles, and the diameter of the area equivalent circle. Also, distributions of the above parameters based on the number of images analyzed per photograph are obtained. From these data a Sauter mean (surface-to-volume) bubble diameter can be calculated. The Sauter diameter is needed in calculation of the specific gas-liquid interfacial area.

The data analysis has not been completed yet. Since certain bubbles are selected from each photograph, the procedure for determining bubble size distribution is somewhat subjective. In order to reduce uncertainty involved in this procedure, selected images stored in the computer will be reanalyzed and the results compared with the original analysis.

2. Photographic Analysis of Bubble-Column Hydrodynamics

During the hydrodynamic studies with the small glass column (AM-2G) performed in the last quarter photographs of the flow field were taken. Selected photographs illustrating qualitatively effects of gas distributor type, superficial gas velocity and the height along the column are presented here.

The effects of distributor type and the height above distributor are shown in Figure 4, for experiments with the FT-300 wax at 265°C and the superficial gas velocity of 1 cm/s. The bubbles produced by the 40 μm SMP distributor are smaller and more uniform than the bubbles produced by the 4 mm orifice plate. The bubble size distribution does not change with height for the SMP distributor (Figures 4a and 4b). On the other hand, the 4 mm single orifice distributor produces a wide bubble size distribution near the distributor (Figure 4c). As the height increases (Figure 4d) the bubble coalescence and break-up occur and two groups of bubbles become dominant (larger bubbles 0.4-0.6 cm in diameter, and fine bubbles less than

0.1 cm). The vertical black lines in Figures 4b and 4d represent a portion of thermocouple well (3/16 of an inch in diameter).

The effect of superficial gas velocity on bubbles produced by the 4 mm single orifice distributor is shown in Figure 5. All pictures were taken at a distance of approximately 122 cm from the distributor. At the velocity of 2 cm/s (Figure 5a) the flow may be characterized as a transition from the ideal bubbly to the churn-turbulent flow regime. Larger bubbles are about 0.4-0.6 cm in diameter, and smaller ones are less than 0.2 cm. Also, there is a number of fine bubbles less than 0.5 mm in diameter. At the velocity of 3 cm/s the density of bubbles increases, and the wide bubble size distribution is evident. At this velocity larger bubbles begin to form, but this is not clearly seen in this picture (see the lower right hand side corner of Figure 5b). At the velocity of 4 cm/s, Figure 5c, the density of bubbles increases and large bubbles become more clear (the lower right hand side corner). The flow regime at 3 cm/s and 4 cm/s may be characterized as the churn-turbulent. At 9 cm/s (Figure 5d), the large bubbles occupying nearly the entire cross sectional area of the column (slugs) can be easily observed. These slugs are surrounded by fine bubbles less than 1 mm in diameter, as well as by a few bubbles of 0.3-0.5 cm in diameter.

V. Future Work

The following activities are planned for the next quarter:

(a) Complete analysis of the data on axial gas holdup measurement obtained in the AM-2S column.

(b) Complete analysis of the data on dynamic gas disengagement technique obtained in the AM-9G column.

(c) Continue efforts to improve photography technique (e.g. use of different light sources, lenses etc.) to obtain photographs of better quality for determination of the bubble size distribution.

(d) Continue work on hydrodynamic studies in the hot flow columns.

VI. Literature References

Calderbank, P.H., Evans, F., Farley, R., Jepson, G., and Poll, A., Catalysis in Practice, Instn. Chem. Engrs., London, p. 66 (1963).

Deckwer, W.D., Louisi, Y., Zaidi, A., and Ralek, M., Ind. Eng. Chem. Proc. Des. Dev., 19, 699 (1980).

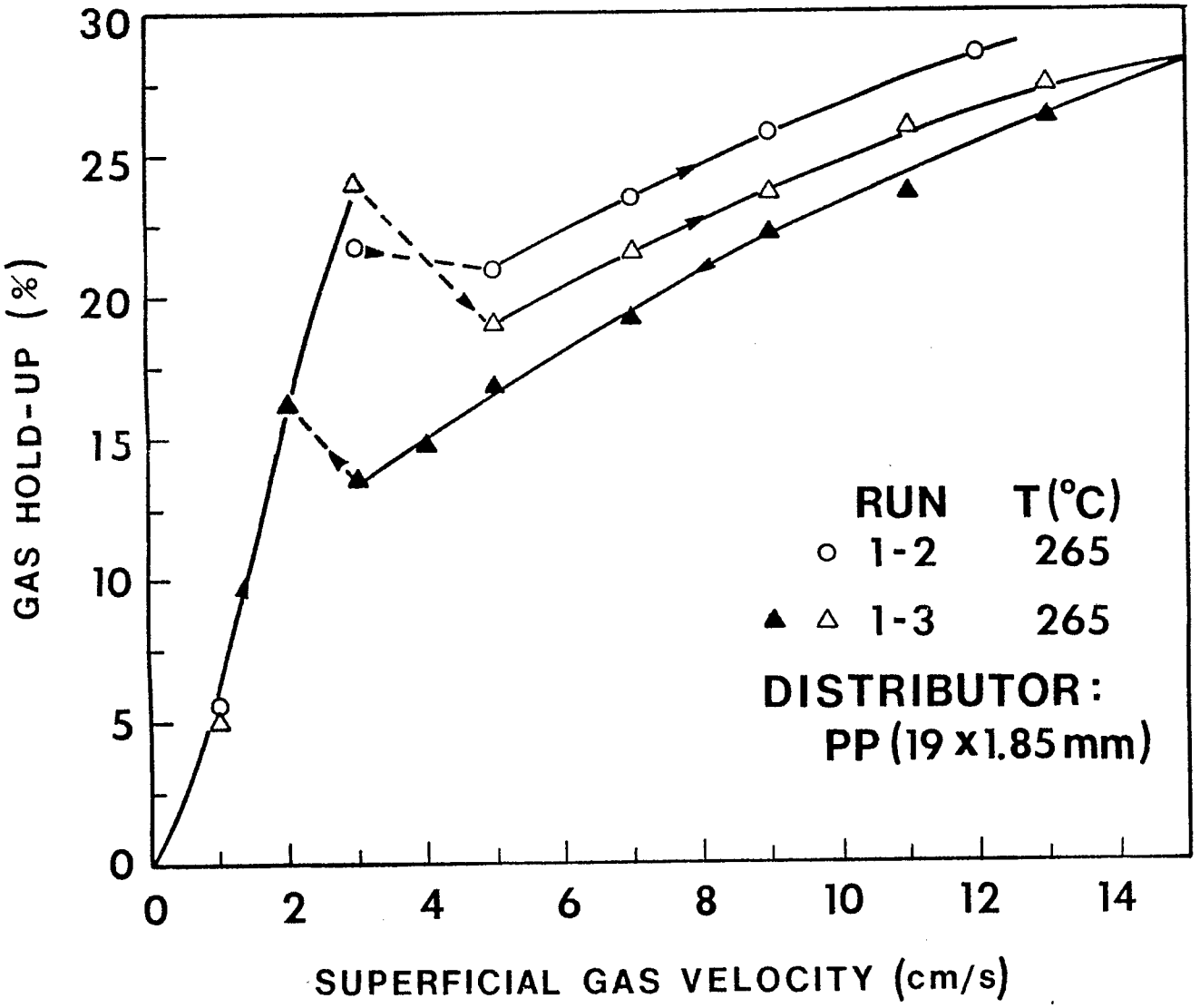


Figure 1. Effect of superficial gas velocity on gas hold-up in the AM-9G column (Open symbols: increasing gas flow rate, Solid symbols: decreasing gas flow rate).

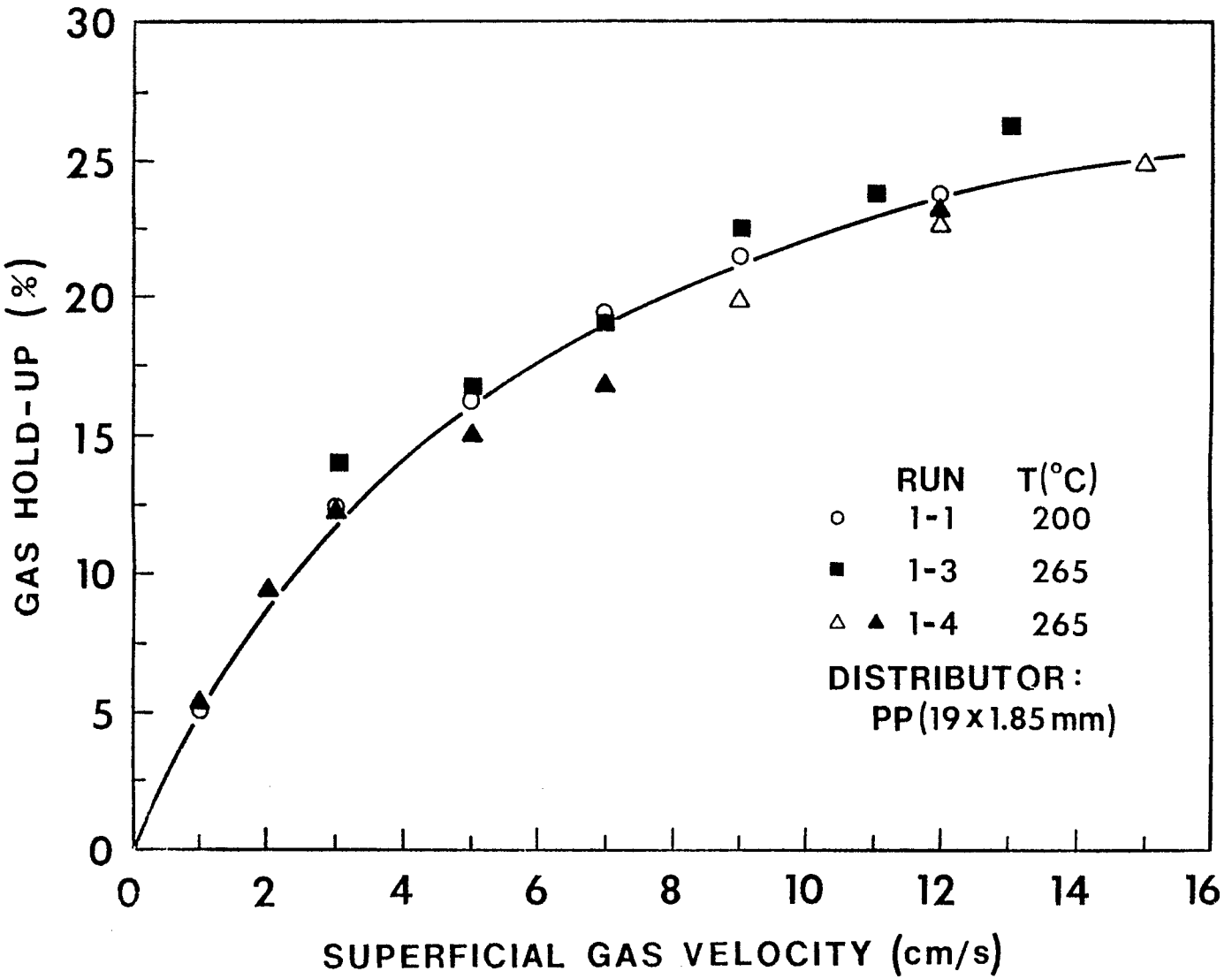


Figure 2. Effect of temperature and gas velocity on hold-up in the "nonfoamy" flow regime (AM-9G column; Open symbols: increasing gas flow rate; Solid symbols: decreasing gas flow rate).

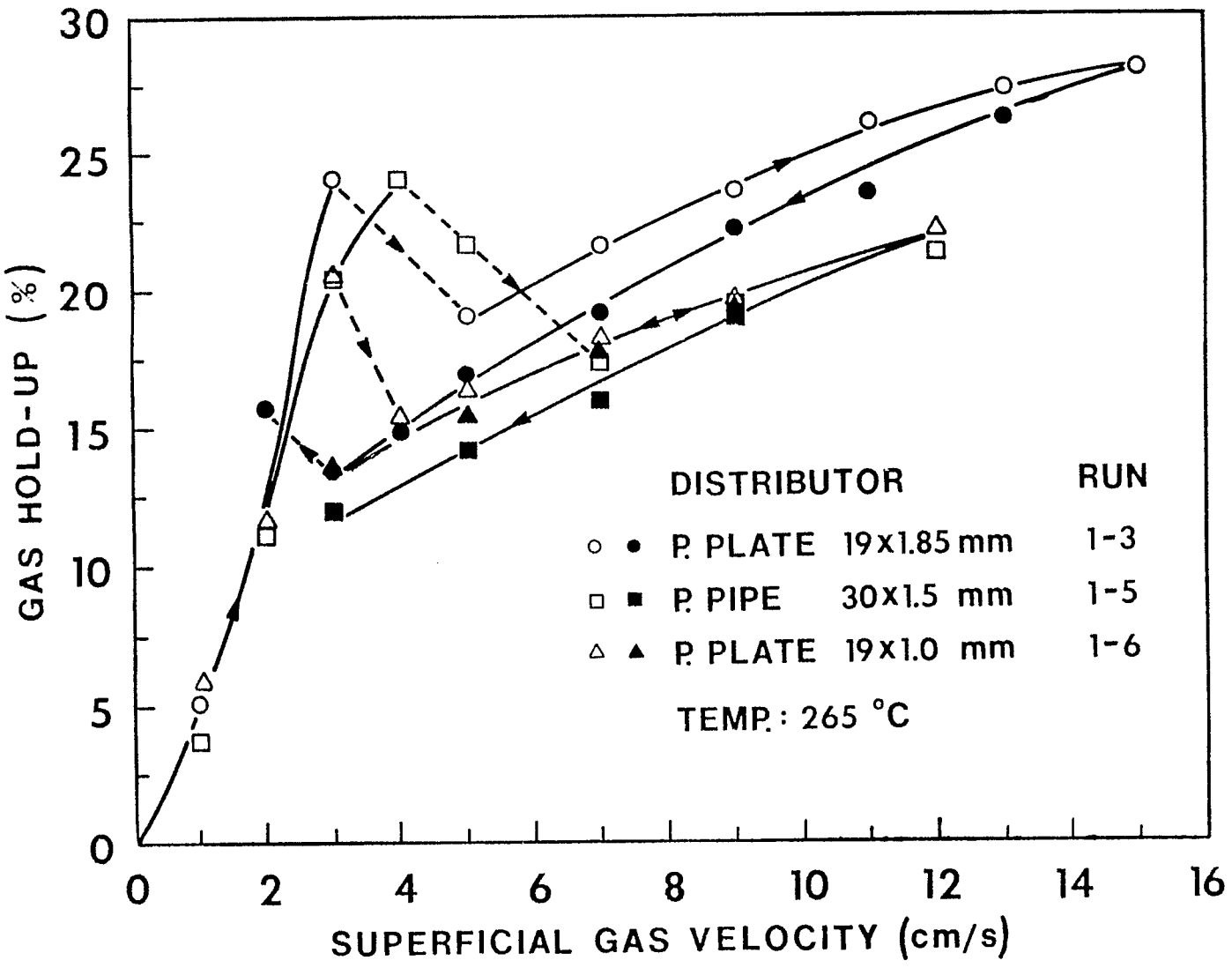
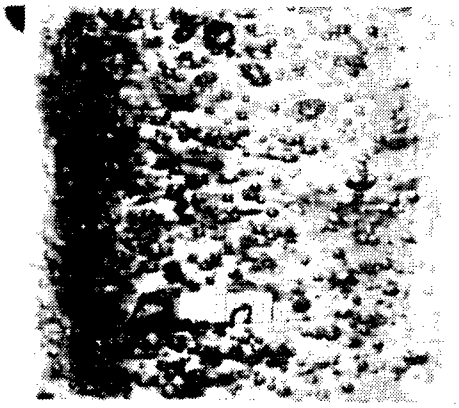


Figure 3. Effect of gas distributor type on gas hold-up in the AM-9G column (Open symbols: increasing gas flow rate; Solid symbols: decreasing gas flow rate).

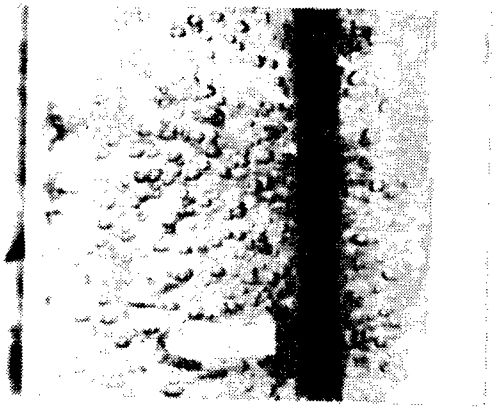
FIGURE 4

BUBBLES PRODUCED BY 40μm SMP & 4mm SINGLE ORIFICE DISTRIBUTORS

40μm SMP

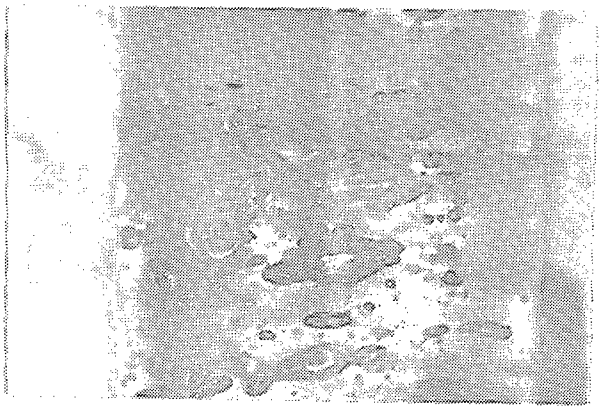


a. 45.7 cm

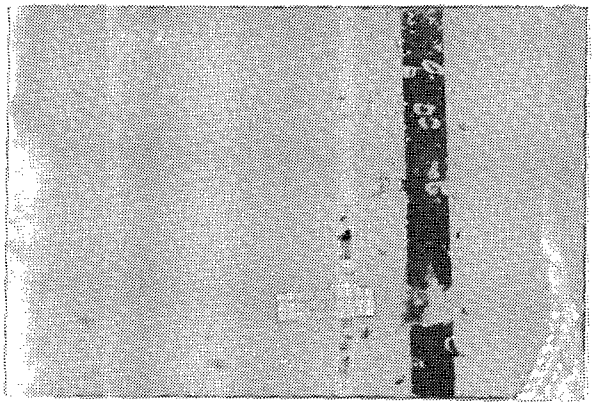


b. 213.3 cm

4 mm



c. 45.7 cm



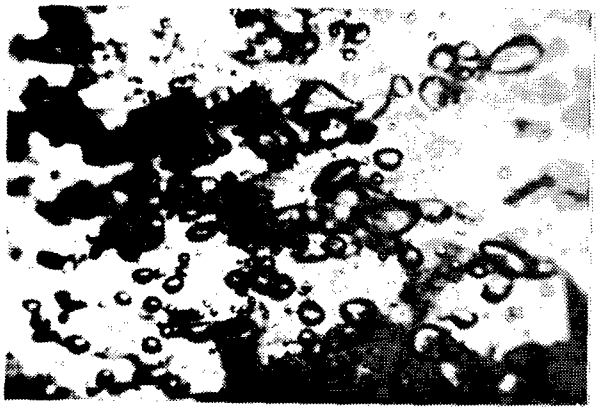
d. 213.3 cm

SCALE: ⊢——⊣ 2.54 cm

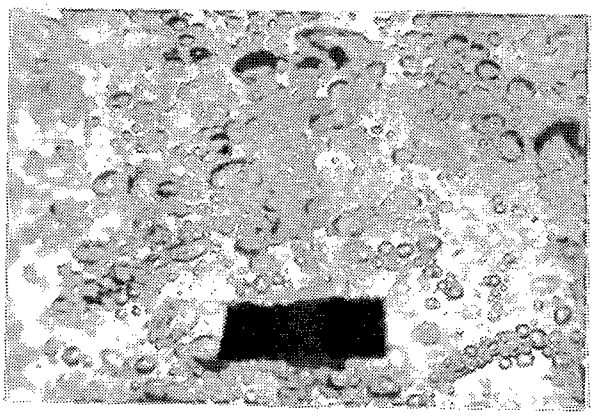
Ug: 1 cm/s ; T: 265 °C ; FT-300

FIGURE 5

BUBBLES PRODUCED BY 4mm SINGLE ORIFICE DISTRIBUTOR

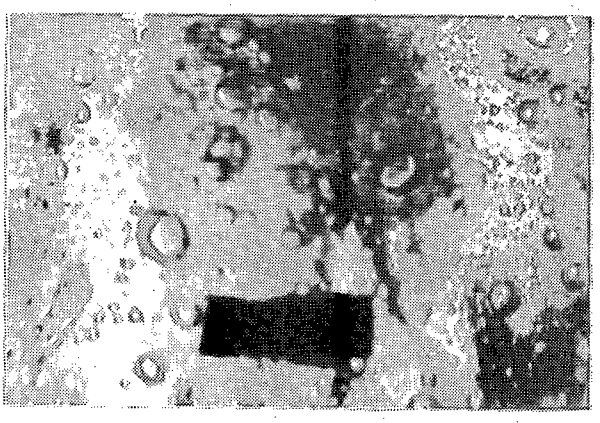


a. 2 cm/s



b. 3 cm/s

c. 4 cm/s



d. 9 cm/s

SCALE: ⊢——————⊣ 2.54 cm

HT.: 121.9 cm; T: 265 °C; FT-300