C. Scoping Studies Using Small Hot-Flow Bubble-Columns

Bubble-column hydrodynamics were examined using two small hot-flow columns operating at atmospheric pressure. The effects of distributor type, liquid medium, and column diameter were investigated in this study.

The major highlights of the work are:

- SMP distributors having average pore sizes of 15 and 60 micron produce very small bubbles and a great deal of foam, with holdups as high as 70 vol % at superficial gas velocities above 0.8 and 1.4 cm/s, respectively.
- For SMP distributors, gas holdup decreases with increasing pore size. This is accompanied by larger bubbles and less foam.
- Single orifice distributors produce smaller bubbles as the orifice diameter is decreased, but slugs form at higher velocities.
- Distributors with small orifices can give holdups similar to large-pore SMP distributors. Bubble size distributions, though, are different.
- Orifice-type gas distributors give similar holdups when the gas jet velocities through the holes are similar. However, if the orifice diameter is large enough, low holdups will result at all velocities.
- Reactor-wax from Run CT-256-4 gives generally higher holdups than Run CT-256-5 reactor-wax, but lower than FT-200.
- Column diameter, in the range 3.2 to 5.3 cm ID, appears to have some effect on hydrodynamics. The extent of the effect varies with the distributors.
- Pressure and diversely different gases have negligible effect on gas holdup.

C.1. Description of Two Small Hot-Flow Columns

To study the effect of distributor type on the gas holdup, two small hot-flow columns were used, 3.2 and 5.3 cm in diameter and 2.2 m height. Various types of distributors (SMP's and single orifices) can be sealed into removable joints and then clamped to the bottom of the columns, with o-rings providing tight seals. The columns are heated with strands of nichrome heating wire, with the smaller column having three such zones, and the larger column two. Both columns are mounted with glass tubes covering their entire lengths. This serves to insulate the columns, as well as provide safety. Inside, a 6.3 mm diameter thermowell containing four thermocouples runs the length of the columns to record fluid temperatures.

Nitrogen is metered by a rotameter and introduced below the distributor as the feed gas. After leaving a column, the gas is bubbled through a solvent and then passed into a wet-test meter to double-check the flow rate. The bubbles and their flow patterns are visible between the wire strands, and gas holdup is determined by visual observation of the height of the expanded liquid.

C.2. Effect of Feed-Gas Distributor Designs

C.2a. Gas Holdup Measurements

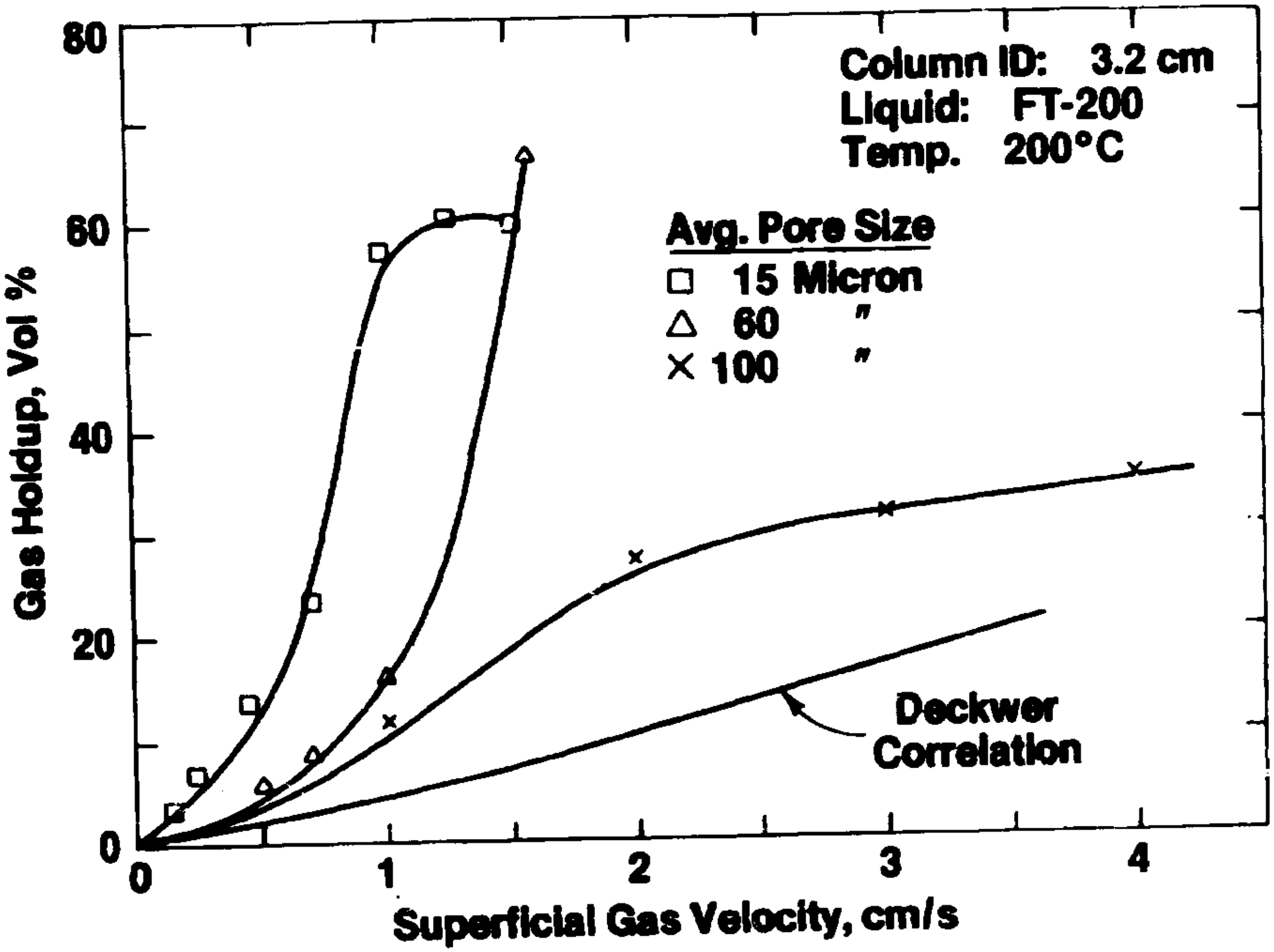
Figure VII-4 is a plot of the gas holdup observed in the 3.2 cm ID column over various SMP distributors. Also shown is the correlation proposed by Deckwer et al. (1980). The liquid medium used in our experiments was the FT-200 wax. This wax is similar in average molecular weight to that used by Deckwer et al. The static (unexpanded) liquid height varied from 50 to 100 cm, while Deckwer et al. reported using static heights of 60 to 100 cm with no significant variation in holdups.

The curves in Figure VII-4 illustrate the major difficulty we encountered: foam, or regions of very high gas holdups. Foam is undesirable since catalyst loadings per reactor volume would become very low in such systems. The regious of sharpest slope on this plot represent conditions under which the liquid begins to foam at the top, characterized by a sharply visible boundary between the swirling small bubbles below, and the rigidly held, slowly rising bubbles above.

As the gas velocity is increased, the boundary becomes less and less distinct as it moves slowly down the column, while the overall height of the suspension increases dramatically. This is because the liquid is continually being converted to high-holdup foam. This process appears to be self-propogating; that is, beyond a certain superficial gas velocity (approximately 0.8 and 1.4 cm/s for the 15 and 60 micron distributors, respectively) the foam inexorably grows until a maximum holdup is reached where the entire column is only foam. At this point, the holdups are in the 60-75 vol % range in all cases.

Figure VII-4

EFFECT OF SINTERED-PLATE PORE SIZE ON GAS HOLDUP



It should be noted that although no exact measurements of bubble size were attempted, visual observation of both foam and non-foam regimes showed the bubbles to be very small and densely packed, with little variation in size

The 100 micron SMP, however, produced significantly less foam than either of the other two distributors. In addition, the bubbles in the bulk liquid appeared to be larger and less densely packed. This produced a stable suspension at all velocities studied. In fact, at the higher velocities, large slugging bubbles could be observed coalescing near the top of the column and rising through the foam layer. This, combined with the larger average bubble size, may have helped keep the foam from propogating. It appears, then, that larger pore size SMP's produce larger average bubble sizes (leading to enhanced coalescence), less foam, and therefore, lower gas holdups.

The results obtained from single orifice distributors were decidely different (Figure VII-5). For both 0.5 and 0.32 mm orifices the holdups were substantially lower than those from the SMP distributor experiments. In addition, the bubbles varied greatly in size, with large, mushroom-cap bubbles rising quickly past smaller, swirling ones. This is in direct contrast to those observed by Quicker and Deckwer (1981a), who reported that the bubbles obtained from a 0.9 mm orifice were both small and uniform, much the same as with SMP results. In that case, however, the inside column diameter was 9.5 cm, so that nearly nine times as high a gas volumetric flow rate was needed to achieve the same superficial gas velocities as our 3.2 cm column. This provides a higher gas jet velocity through the orifice, supplying more kinetic energy for bubble breakup. This, of course, corresponds to higher orifice Weber numbers.

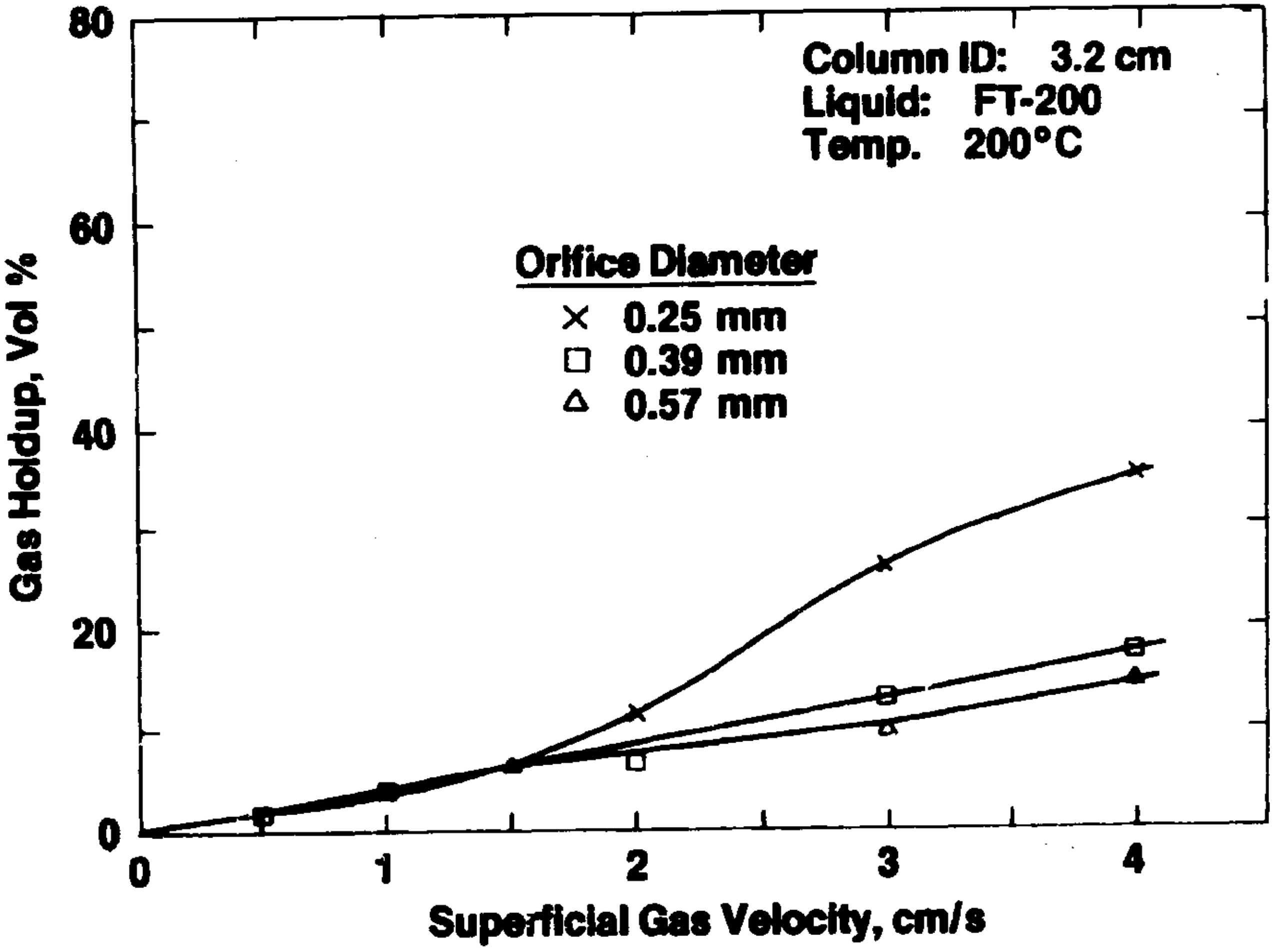
A comparison shows that for a superficial gas velocity of 3.0 cm/s, the Weber number for the 0.57 mm orifice was 143, and 0.39 mm orifice was 447, while that of Quicker and Deckwer's experiment was 3,150 (estimated). The gas holdups reported in that study were very similar to the results from the 0.25 mm orifice, also shown in Figure VII-5. In this case, the Weber number at 3.0 cm/s was 1,700. At the higher velocities, there were indeed many more small bubbles than the 0.57 and 0.39 mm orifices produced; however, large bubbles were clearly seen rising through the fine swarm. In addition, foam was observed, though not as much as produced by SMP distributors. Again, it seems that the presence of the large bubbles limits the height that the foam can reach.

At the low velocities, flow patterns were similar to those observed with the other two orifices; that is, mostly large, fast-rising bubbles. The gas jet from the orifice was only visible at the low velocities, and could be seen dissipating

Figure VII-5

EFFECT OF ORIFICE DIAMETER ON GAS HOLDUP

(SINGLE-ORIFICE DISTRIBUTOR)



immediately upon leaving the orifice. At higher velocities the jet was obscured by swirling bubbles.

In conclusion, several general trends were observed:

- For SMP distributors, the gas holdup decreases with increasing pore size. This is accompanied by larger bubble sizes and less foam, with some slugging occurring at the higher velocities.
- Single orifice distributors produce smaller bubbles as the orifice diameter is decreased, but slugs form at higher velocities, helping to break the foam.
- Distributors with small orifice can give gas holdups similar to large-pore SMP distributors, but with different bubble-size distributions. It may be that the slug-forming mechanism is different in the two cases, i.e., bubble coalescence versus unsteady jet breakup.

Studies were also carried out using reactor-wax from Run CT-256-5 in the small 5.3 cm ID hot-flow column. Four different gas distributors were used and the results are given in Figure VII-6. The gas holdup was less than 12 vol % in all cases. Also, the 60 micron SMP distributor gave about the same gas holdup as the orifice-type distributors.

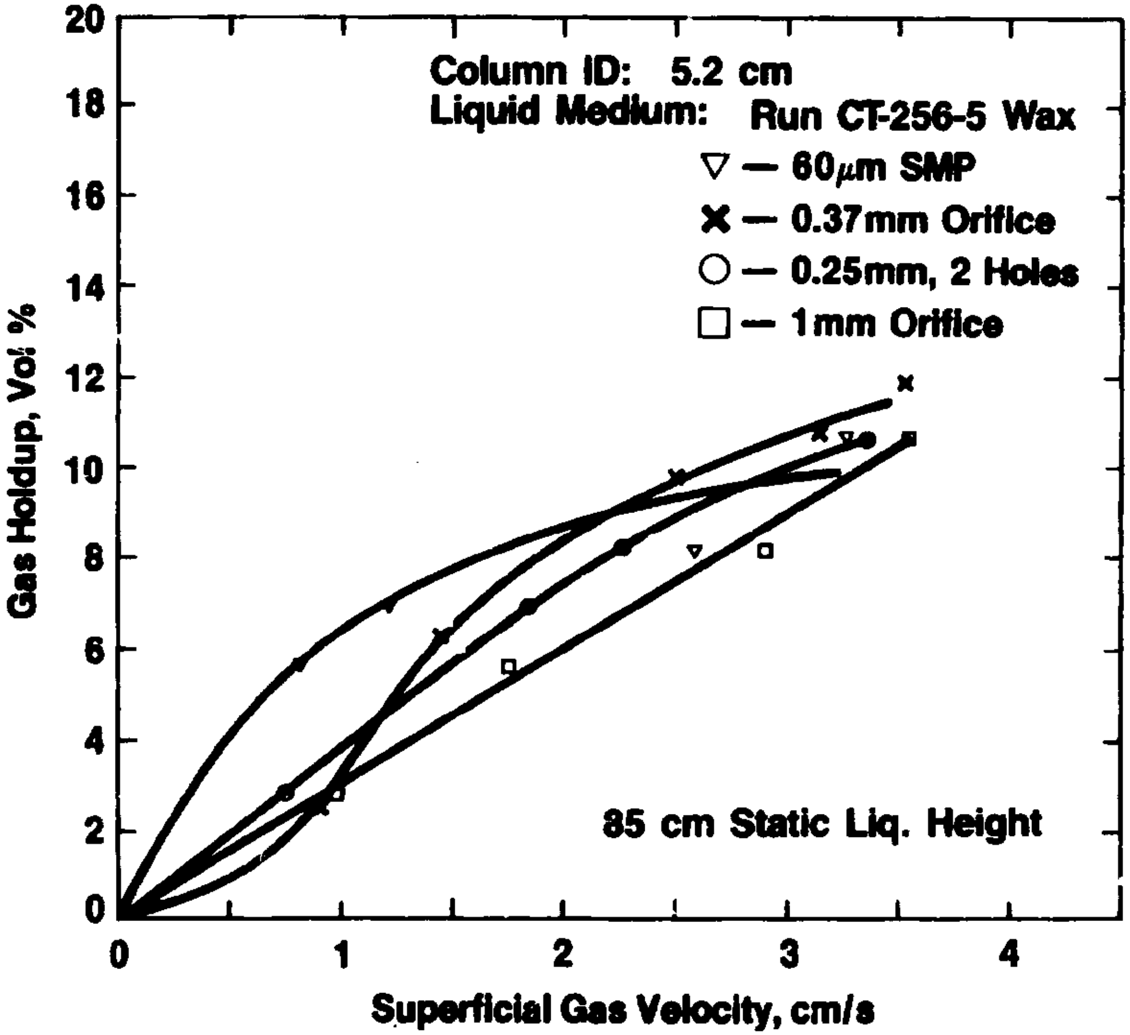
No foam was observed with any distributor This is in contrast to the behavior of the FT-200 wax, which produced substantial foam when a 60 micron SMP was used.

The results obtained with the orifice-type distributors showed the same general trends as those observed with the FT-200 wax using the same distributors. The gas holdup was found to decrease with increasing orifice diameter or decreasing Weber number. The most significant result was obtained with a 1 mm orifice distributor. The gas holdup using the 1 mm orifice distributor was only slightly lower than the 0.37 mm single orifice or the 0.25 mm dual orifice distributors. The 1 mm may be the smallest orifice applicable commercially.

Due to the dark color of the reactor-wax bubble size could not be observed. A few small bubbles could be seen near the wall on a few occasions. Also, the top of the liquid column was observed to fluctuate violently, giving some indication of large bubbles. No definite conclusions, however, can be drawn about the bubble-size.

Figure VII-6

GAS HOLDUP IN SMALL HOT-FLOW COLUMN USING REACTOR-WAX



C.2b. Photographic Analysis of Bubble-Column Hydrodynamics

During the scoping hydrodynamic studies using a small hot-flow bubble-column described previously photographs were taken to record bubble flow patterns and other hydrodynamic features. All the studies were done using the FT-200 wax since reactor-waxes from our pilot plant are too dark to permit photography.

The flow patterns from both a 100 micron SMP and a single 0.25 mm orifice gas distributor were photographed in the 3.2 cm ID column. The superficial gas velocity was varied from 1 to 4 cm/s.

The pictures reveal the following:

- The 100 micron SMP distributor produced uniform small bubbles at all velocities, with bubble density increasing as the velocity increased. Bubble size appeared to be constant.
- The 0.25 mm orifice produced a wide range of bubble sizes at all velocities, with slugs developing as the gas velocity increased. Bubble density also increased with velocity.
- Foam formation was evident when using the SMP distributor.

Figure VII-7 shows the photographs of the bubbles produced by a 0.25 mm single-orifice distributor. The static liquid height in these experiments was 99 cm. The photographs were taken 81 cm above the distributor. The horizontal lines in the pictures is the nichrome heating wire which was wrapped around the column, the spacing of them being roughly one-quarter of an inch.

At a velocity of 1 cm/s, mostly large, irregular bubbles are seen (Figure VII-7a), some coalescing as they rise up the column. Throughout the liquid are a number of very small bubbles, some of which seem to have formed in the turbulent wakes of the larger ones. This pattern continued as the velocity was increased, with the large bubbles growing to be slug-like, and the small bubbles becoming more numerous. The large bubbles are not visible, however, in Figures VII-7b or -7c.

At a velocity of 4 cm/s, the wide distribution in bubble size is clearly evident. The large bubbles formed almost immediately after leaving the distributor, and the slugging was at regular intervals (about one per second).

Figure VII-7

BUBBLES PRODUCED BY
0.25mm ORIFICE DISTRIBUTOR

a. 1 cm/s

b. 2 cm/s

c. 3 cm/s

d. 4 cm/s

Figure VII-8 shows the bubbles produced by the 100 micron SMP distributor. In this case, the bubbles produced were always of uniform size. Consequently, the bubble density increased as the velocity did.

Not clearly visible on the photographs, however, is the coalescence that took place toward the top of the expanded column at the higher velocities. This is in contrast with the results from the orifice distributor, where large bubbles persisted throughout the column. In this case, the combination of bubble density and bubble size caused the formation of larger bubbles. However, they were not as large or as regular as those produced by the orifice distributor. By comparison, earlier studies showed that a 15 micron SMP distributor produced bubbles much smaller than even those seen in the photographs (with a corresponding increase in the bubble density), yet no visible coalescence took place.

The overall gas holdups produced by both of these distributors were reported earlier (Figures VII-4 and -5); however, it is interesting that at 3.8 cm/s, the gas holdup in both cases was roughly the same (about 35 vol %). This illustrates how different bubble size distributions can lead to the same holdup under certain conditions.

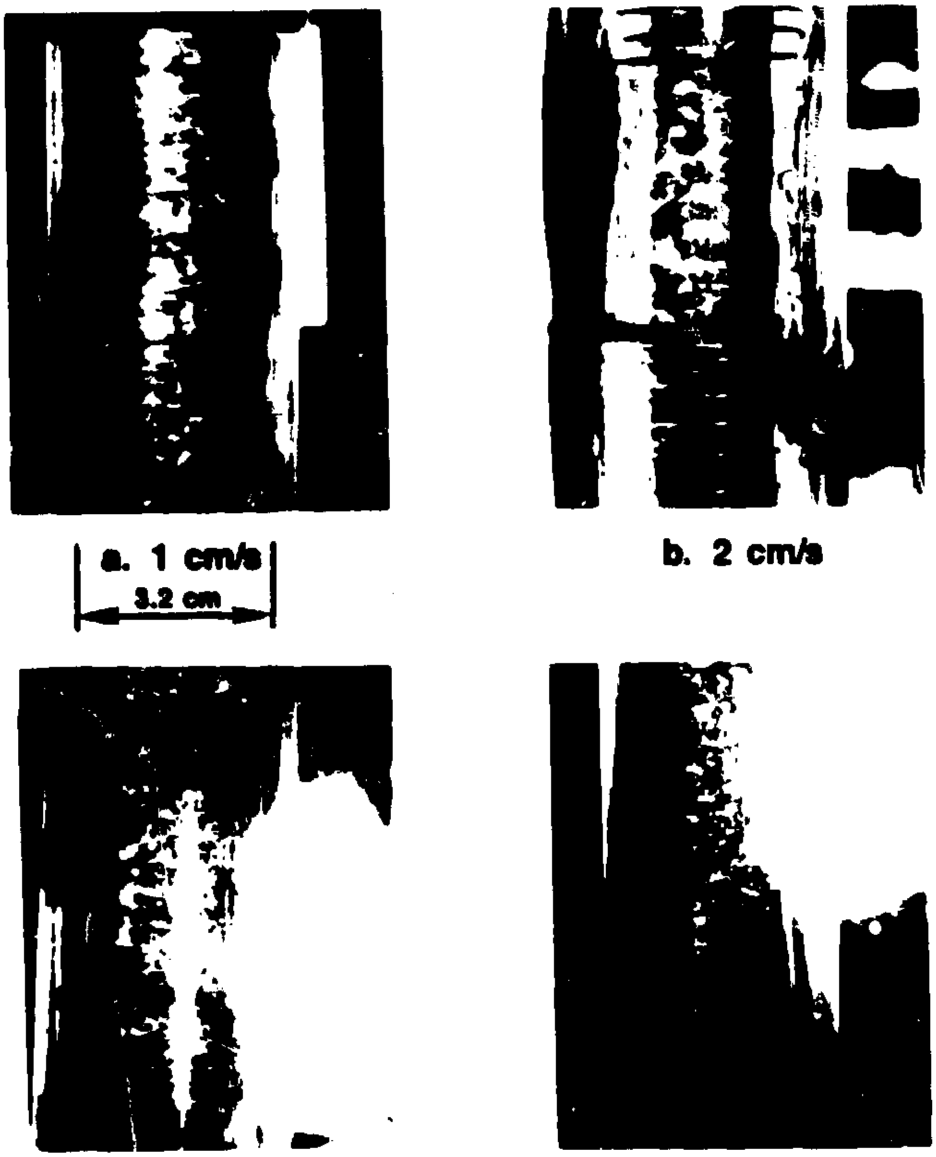
Foam formation has always been observed in our small hot-flow models when using SMP distributors. When the average bubble size is very small (like when using a 15 micron SMP distributor), the foam can occupy nearly the entire column, and produce holdups of nearly 70 vol %. The foam was also present in the studies with the 100 micron SMP distributor, but it remained as a layer at the top of the column, and holdups were not nearly as high. This may have been due to both the larger average bubble sizes, and also the coalescence which took place near the top of the bed. The larger bubbles formed there may have helped break the foam by rising quickly through it. Figure VII-9 shows the clear dividing line between the foam layer and the remainder of the bed. This picture was taken when the superficial gas velocity was 3 cm/s.

C.2c. Gas Holdup Versus Jet Velocity and Weber Number for Orifice-Type Distributors

To help determine the scaleup characteristics of orifice-type feed-gas distributors, experiments were performed using specifically designed orifice-type gas distributors. The distributors were both single and multi-hole types, designed to produce gas jets which matched in either velocity or Weber number. Run CT-256-4 reactor-wax was used as the liquid medium. Figure VII-10 shows the results of these studies.

Figure VII-8

BUBBLES PRODUCED BY 100μm SINTERED-METAL-PLATE DISTRIBUTOR



a. 1 cm/s

b. 2 cm/s

c. 3 cm/s

d. 4 cm/s

Figure VII-9

FOAM PRODUCED BY 100μm SINTERED-METAL-PLATE DISTRIBUTOR

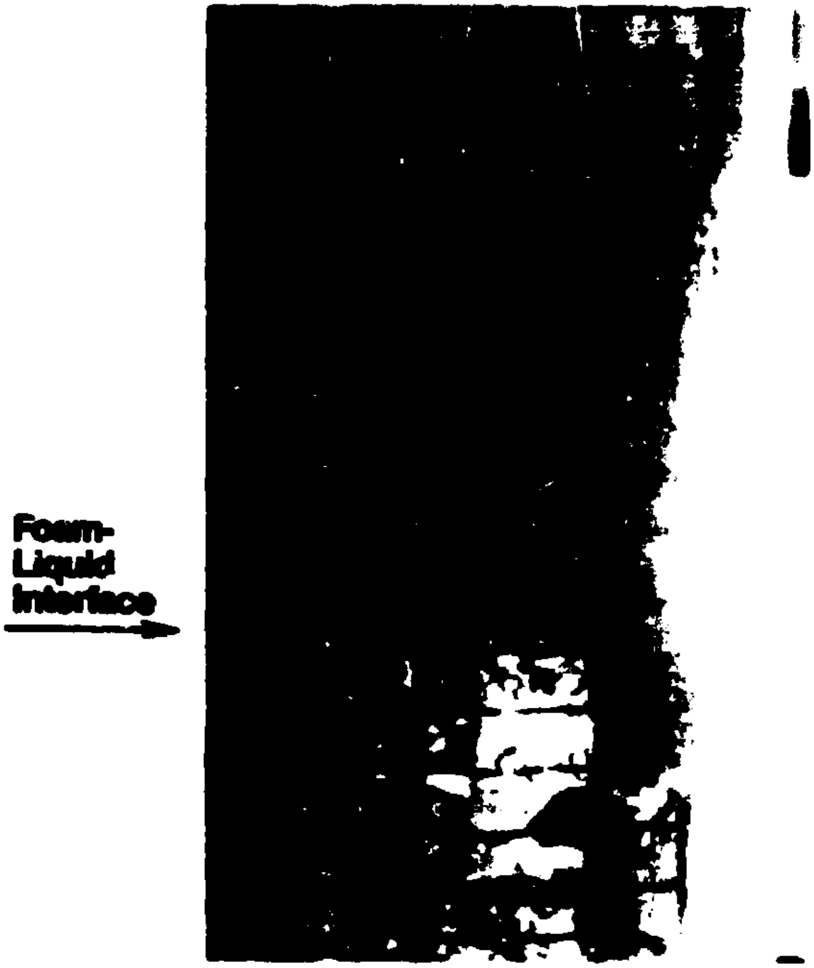
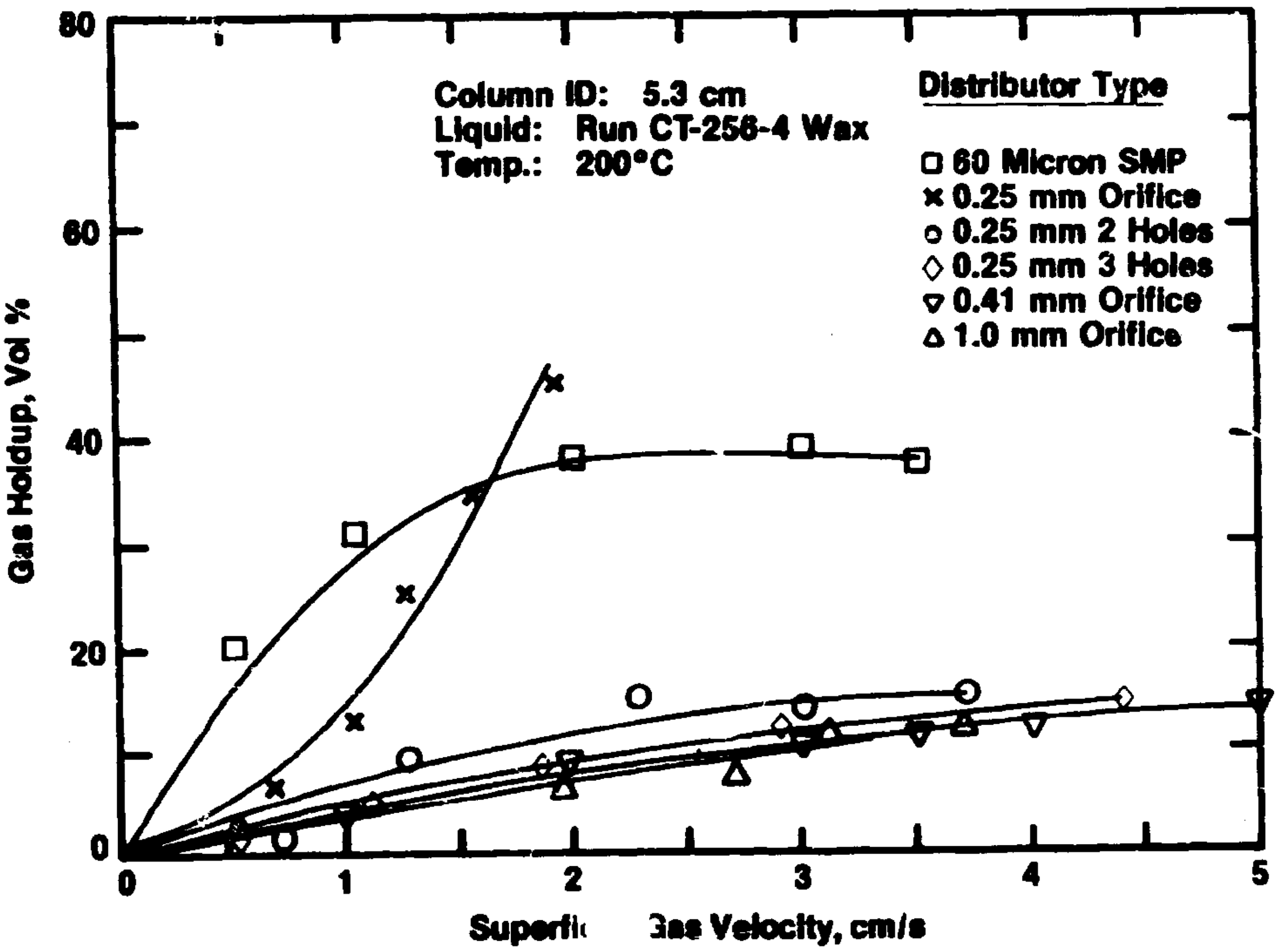


Figure VII-10

GAS HOLDUP IN SHORT HOT-FLOW COLUMN



The 0.25 mm single orifice produced a foam layer (though generally not as much as SMP's) and small bubbles (visual observation was limited by the dark color of the wax), thereby leading to the high holdup. On the other hand, the 0.41 and 1.0 mm single orifices gave nearly identical low holdups. In these cases, the top of the liquid bed could be seen undulating violently, as if large bubbles were bursting at the top. No foam was observed.

The other two gas distributors were designed to help determine whether the Weber number or gas jet velocity was more important in designing dynamically similar distributors. At the same superficial gas velocity in the column, the 0.25 mm two-hole distributor exhibits the same Weber number as the 0.41 mm single orifice, while the 0.25 mm three-hole distributor gives the same gas jet velocity as does the 0.41 mm single orifice. The results show that the gas holdup produced by the three-hole distributor was closer to that of the single orifice than was the two-hole one. This indicates that the jet velocity is more of a criterion for distributor similarity than is the Weber number (for short columns).

To further verify this, the gas holdup data were plotted against both the jet velocity (Figure VII-11) and Weber number (Figure VII-12). It is obvious that, except for the 0.25 or 1.0 mm orifices, the gas holdup data are correlated better by the jet velocity. Additionally, if the contribution of the foam from the 0.25 mm orifice distributor is subtracted from the data, the result falls to the same level as the other distributors. The data from the 1 mm orifice, however, requires a more detailed but speculative explanation. The larger the diameter of an orifice, the larger the bubbles produced by it. However, bubbles can only be as large as the maximum stable bubble size (or column diameter). Most likely, this maximum bubble size is reached for some orifice diameters less than 1 mm. Consequently, as more gas is introduced into the bubble-column to produce the same jet velocities as smaller orifices (8 times as much for a 1 mm orifice versus a 0.25 mm two-hole distributor), the bubble density will increase, leading to higher gas holdups.

In fact, if the orifice is large enough, all three liquid mediums studied thus far produce the same low holdups. This is graphically illustrated in Figure VII-13. For the FT-200 wax data, an orifice size of 0.57 mm in the 3.2 cm ID column is dynamically similar (same jet velocity) to the 1.0 mm orifice in the larger

Figure VII-11

GAS HOLDUP vs. JET VELOCITY

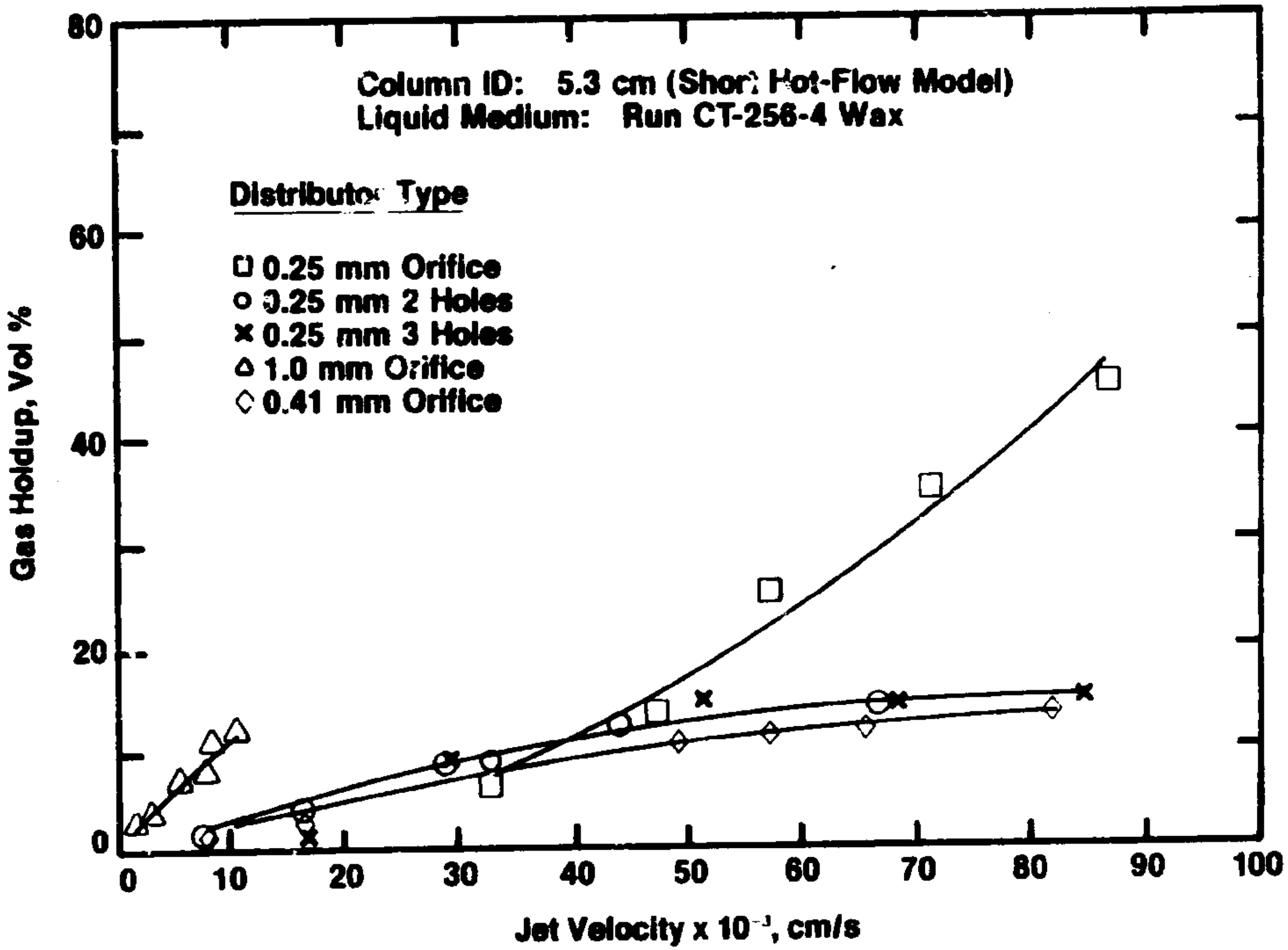


Figure VII-12

GAS HOLDUP vs. WEBER NUMBER

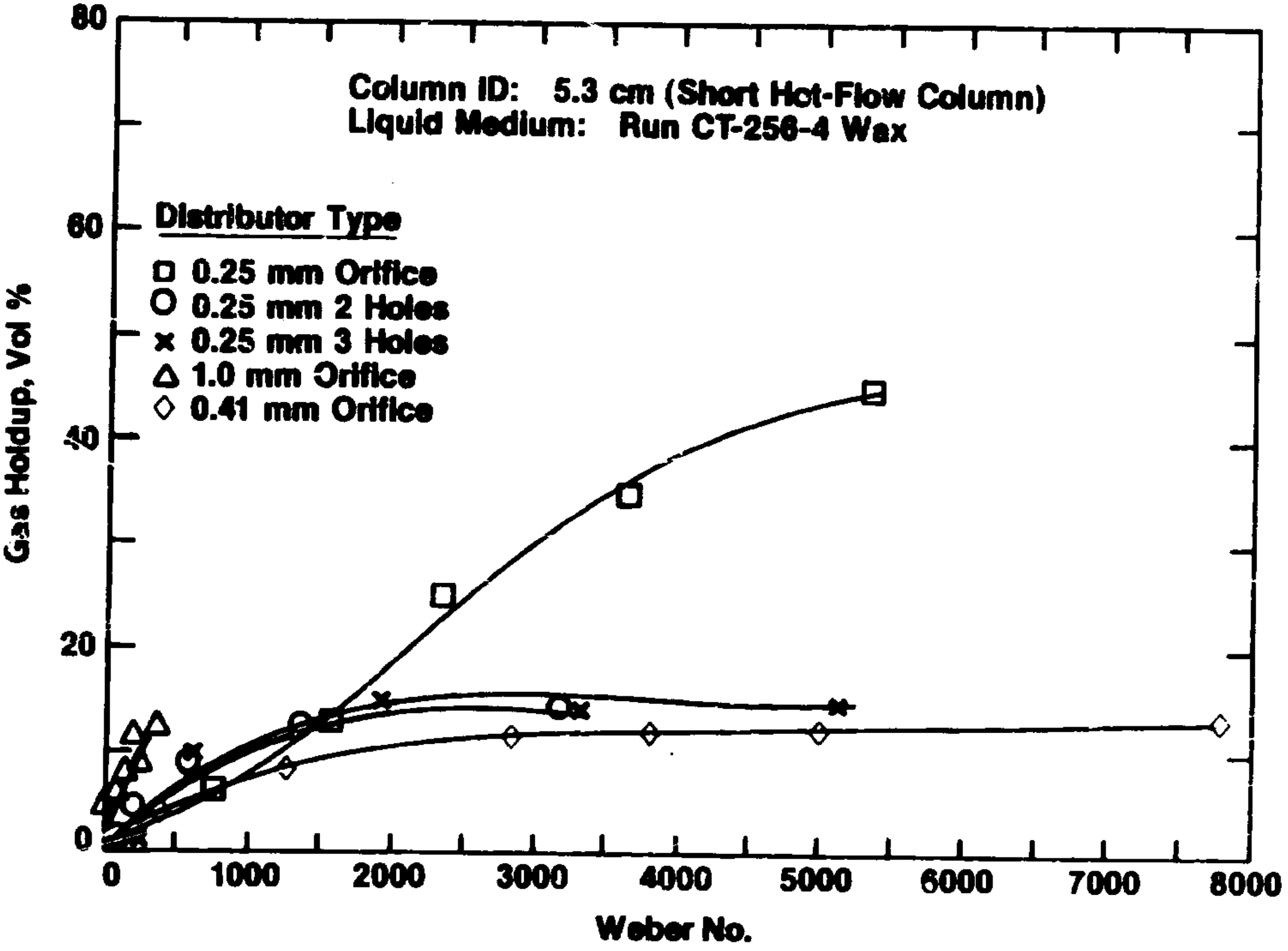
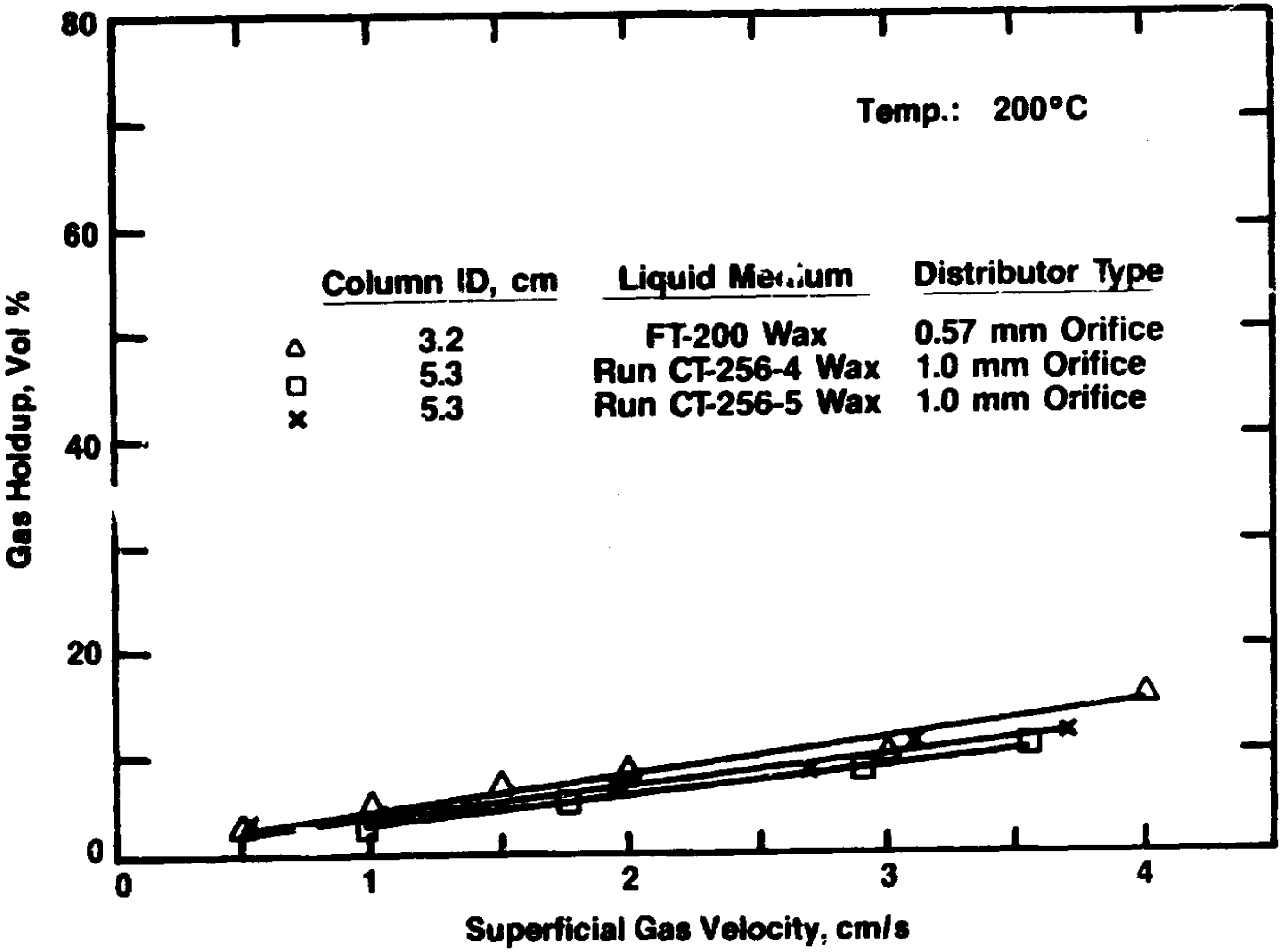

Column ID: 5.3 cm (Short Hot-Flow Column)
Liquid Medium: Run CT-256-4 Wax

Figure VII-13

GAS HOLDUP AT CONSTANT JET VELOCITY (SHORT HOT-FLOW COLUMN)



C.3. Effect of Liquid Mediums

The consequences of operating a bubble-column with a liquid which does not simulate the actual performance can be very severe. For this reason, the 5.3 cm ID glass column was used to compare the FT-200 wax which we were using to hexadecane. Hexadecane has been used by other observers in cold-flow studies, due to its similarity to wax in both surface tension and viscosity.

Using the same 15 micron SMP distributor for both liquids, gas holdups were determined for FT-200 wax at 200°C, and hexadecane at room temperature The results were vastly different, as shown in Figure VII-14. Also shown are the viscosity and surface tension comparisons. It is obvious that the two mediums behave very differently. The wax formed small, swirling bubbles and foam was present at all velocities, which contributed significantly to the gas holdup.

Hexadecane, however, formed relatively large, uniform bubbles which were much less densely packed than the FT-200 wax case. No foam was observed at any time, but at the higher velocities some coalescence was taking place toward the top of the column. The gas holdup was much lower than that in the wax, even if the effect of the foam is removed from the FT-200 wax gas holdup data (the dotted line in the figure). The removal of the effect of the foam was done by subtracting the foam height from the overall expanded bed height, and then (assuming that the foam has 70 vol % gas holdup) calculating how much liquid was remaining.

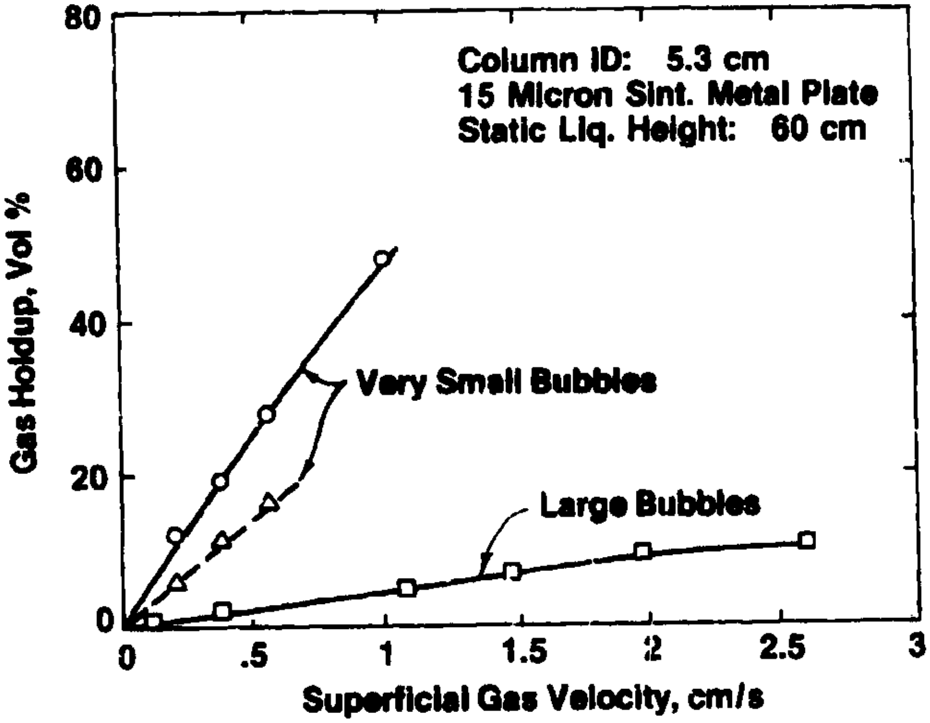
This experiment illustrates the difference that the liquid medium can make when modeling bubble-columns. This evidently makes hot-flow study a must for the F-T systems.

Figure VII-15 is a comparison of gas holdups in different liquid mediums over a 60 micron SMP distributor. The large differences in the behavior of the waxes are evident. Under these conditions, the FT-200 wax and the Run CT-256-4 reactor-wax produced a foam layer at the top of the column, while the Run CT-256-5 reactor-wax showed no evidence of such.

To try and understand why these differences occur, we compiled a table of the physical properties of the waxes used in this study. Table VII-5 shows that while the density and surface tension are relatively equal for the three mediums, the viscosity changes considerably. In fact, a trend is evident in that the holdup decreases with increasing viscosity. This is supported by literature correlations, (Shah et al., 1982), but the dependency of holdup on viscosity is not of a high enough magnitude to account for the differences we have observed. See Subsection VII.E.8. for further discussion of wax characteristics.

Figure VII-14

EFFECT OF LIQUID MEDIUM ON GAS HOLDUP



△ FT-200 Excluding Foam

	○	□
Liquid	FT-200	Hexadecane
Temp., °C	200	20
Visc., cp	2.1	3.5
Surf. Tension, Dynes/cm	26.0	27.5

Figure VII-15

EFFECT OF REACTOR-WAX TYPE ON GAS HOLDUP IN SHORT HOT-FLOW COLUMN

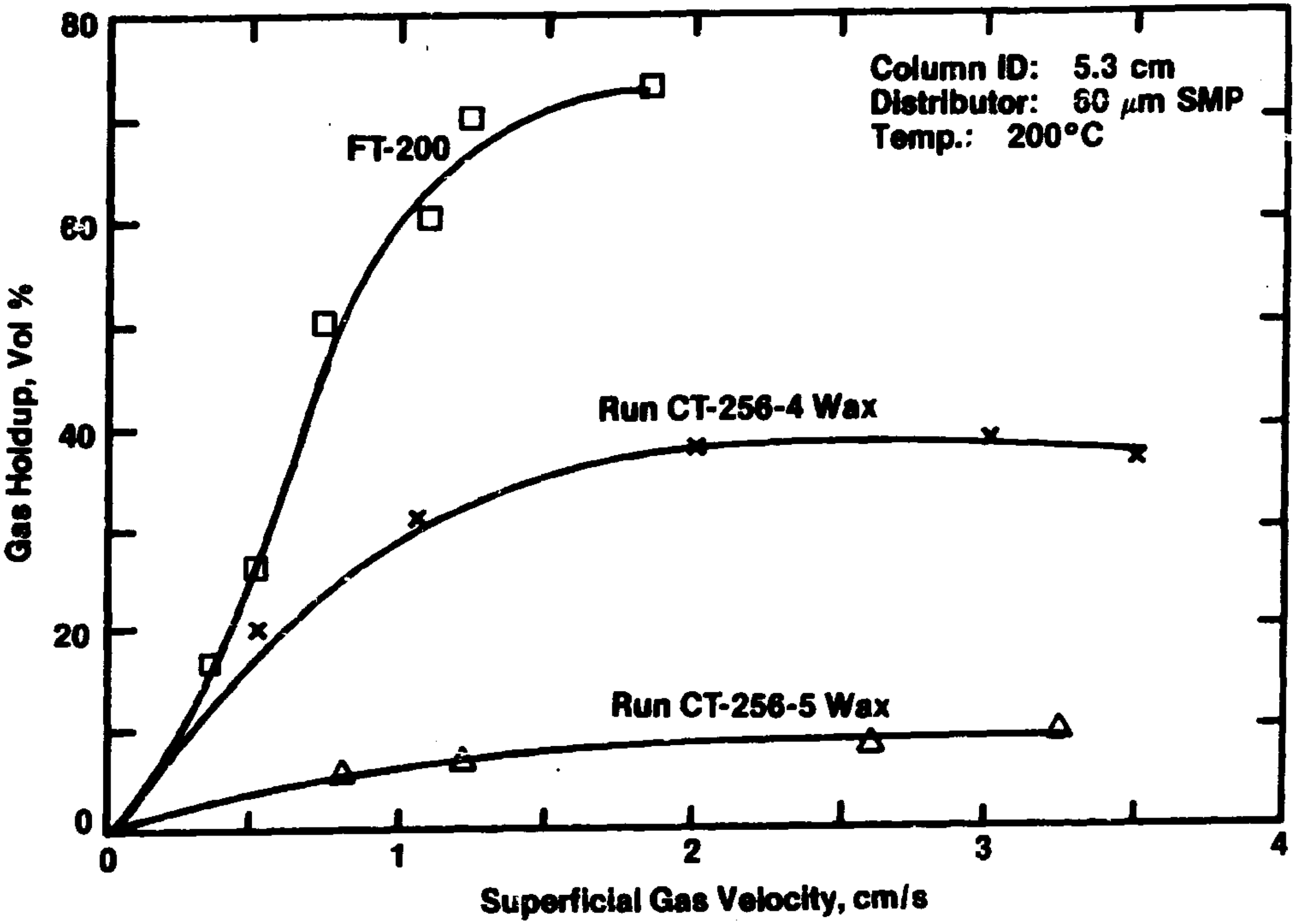


Table VII-5

Physical Properties of Bubble-Column Mediums

	FT-200 Wax	Reactor-Wax Run CT-256-4	Reactor-Wax Run CT-256-5
Density (260°C), g/cm^3	0.72	0.69	0.71
Surface Tension (260°C), Dynes/cm	24.0	26-27	28.0
Viscosity (204/149°C), cP	2.2/-	4.3/8.1	8.5/17.6

C.4. Effect of Column Diameter

To examine the influence of column diameter on hydrodynamics, SMP's as well as an orifice were used as gas distributors in the 5.3 cm ID hot-flow column. The results of the gas holdup measurements are shown in Figure VII-16. The curve for the 100 micron SMP distributor is similar to the corresponding curve for the 3.2 cm ID column (Figure VII-15). The major difference, however, was the apparent absence of slugging in the large column. This helped keep the holdups slightly larger at the higher velocities in the large column. The bubbles in the non-slugging regime seemed to be similar in average size in both cases and foam was present, though again not as much as was produced by the 60 micron SMP.

The 60 micron distributor produced a great deal of foam at gas velocities nearly one-half the rate required in the smaller column to achieve similar holdups. Flow patterns and bubble sizes appeared similar to the smaller column results, with small, swirling bubbles of essentially uniform size occupying the non-foam regions.

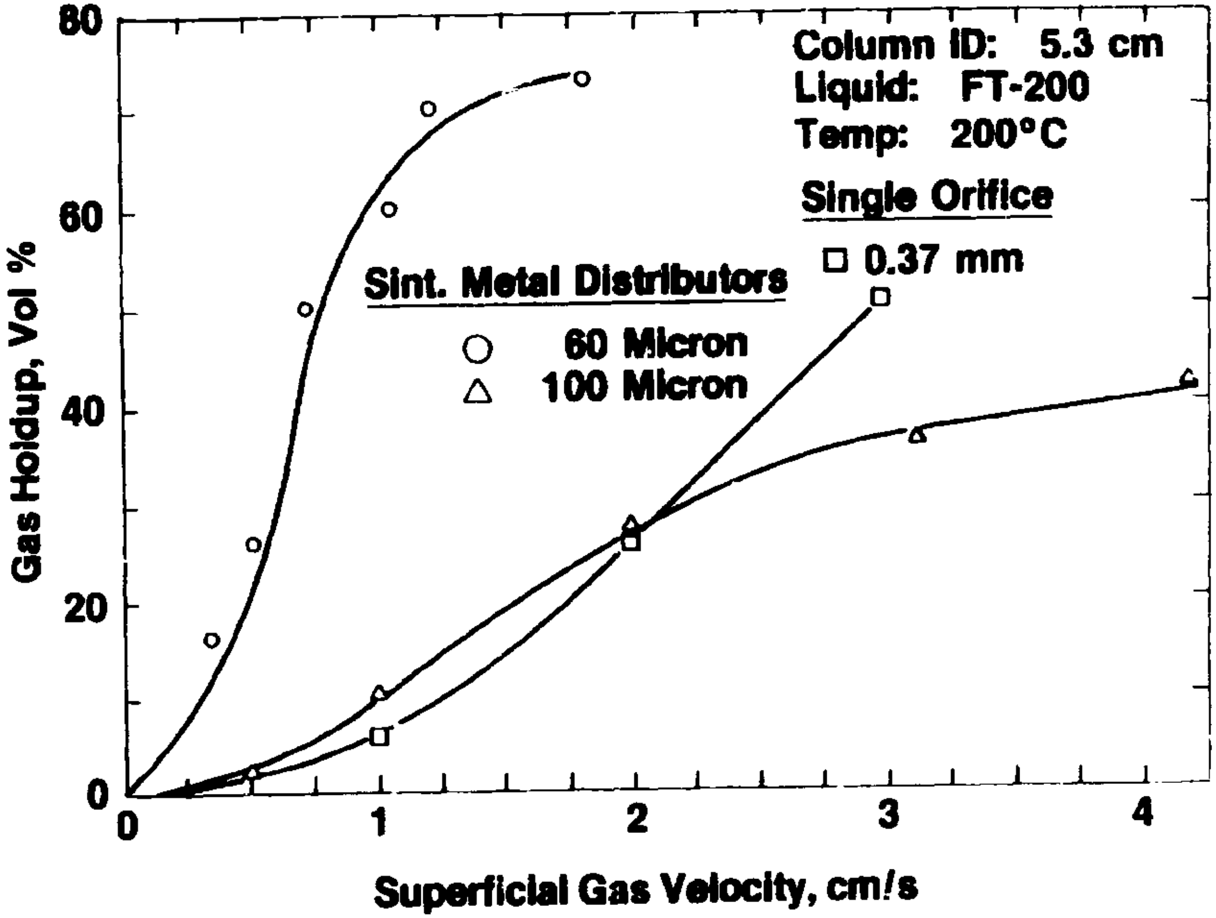
We see, then, that for SMP distributors the same general trends are present in both columns, but with the larger diameter column providing higher holdups. The magnitude of the holdup difference varies with the distributor.

In addition to SMP's, an orifice of 0.37 mm diameter was used in the larger column to obtain higher orifice Weber numbers. It was calculated that at 3.0 sm/s, the Weber number for the gas jet was 3,900, significantly higher than any orifice used in the 3.2 cm ID column. As expected, the holdup produced by this distributor (Figure VII-16) was much higher than that of any other orifice studied. Also, though the bubbles were very small in size and foam was present when this orifice was used, the holdup was still significantly lower than that of the 60 micron SMP, which produced similar size small bubbles.

It was possible, however, to observe slug-type motion at the higher velocities. This was visible as an undulation in the foam layer and an occasional rapid motion of the bubbles close to the wall. The column was otherwise containing too high a bubble density to see through. The high holdup produced by the tiny, intensely swarming bubbles was evidently reduced by the presence of large bubbles. This suggests that the column diameter was not a major factor under these circumstances.

Figure VII-16

EFFECT OF DIFFERENT GAS DISTRIBUTORS ON GAS HOLDUP (SMALL HOT-FLOW COLUMN)



It is interesting to note that the orifice distributor produces holdups significantly higher than does the 100 micron SMP distributor at superficial velocities above about 2 cm/s. This shows that two very different flow patterns can produce effectively the same holdups (uniform bubbles versus a combination of smaller and larger ones). Whether or not these two patterns would give rise to similar conversions in a reactor is unknown.

Scoping hydrodynamic studies were also carried out to determine whether dynamically similar orifice feed-gas distributors give rise to the same gas holdups in two different diameter columns.

To accomplish this, we used the data from the 3.2 cm ID hot-flow column as a base case. That data was taken with FT-200 wax and a 0.25 mm single-orifice distributor, among others. Using the 5.3 cm ID hot-flow column, we then measured the gas holdup in FT-200 wax over two other gas distributors, a 0.41 mm orifice and a 0.25 mm 3-hole. Both of these produce roughly the same gas jet velocity as the 0.25 mm orifice did in the 3.2 cm ID column, making them dynamically similar. The results are shown in Figure VII-17. The two gas distributors used in the 5.3 cm ID bubble-column produced identical holdups. The flow pattern was very violent in both cases, with very small bubbles swirling rapidly and occasional large bubbles rising through. No slugging was visible, however, as was the case with the 3.2 cm ID column.

These results lend support to the jet-velocity criterion for similarity. The 3.2 cm column, however, shows a higher holdup at superficial velocities above 2.0 cm/s, though not dramatically so. This may be attributed to the presence of foam, which was more prominent in the smaller column. It may be that the foam is stabilized by the walls of the narrower column. This difference probably would not be present in a non-foaming medium.

C.5. Effect of Pressure and Gas Type

We have installed a new DP-cell set-up on the small bubble-column reactor (Unit CT-225) as shown in Figure VII-18. This enabled the measuring of gas holdups under pressure because of the reactor design. Figure VII-18 shows a disengager at the top of the reactor. This is nothing more than an expanded section designed to prevent carryover of slurry to the downstream lines. However, it was realized that if liquid (slurry) was displaced from the 2.6 cm diameter reactor section to the 7.1 cm diameter disengager section by the introduction of gas, then the total hydraulic head recorded by the DP-cell would drop. Therefore, by knowing the change in the DP reading for given flow

Figure VII-17

EFFECT OF COLUMN DIAMETER ON GAS HOLDUP

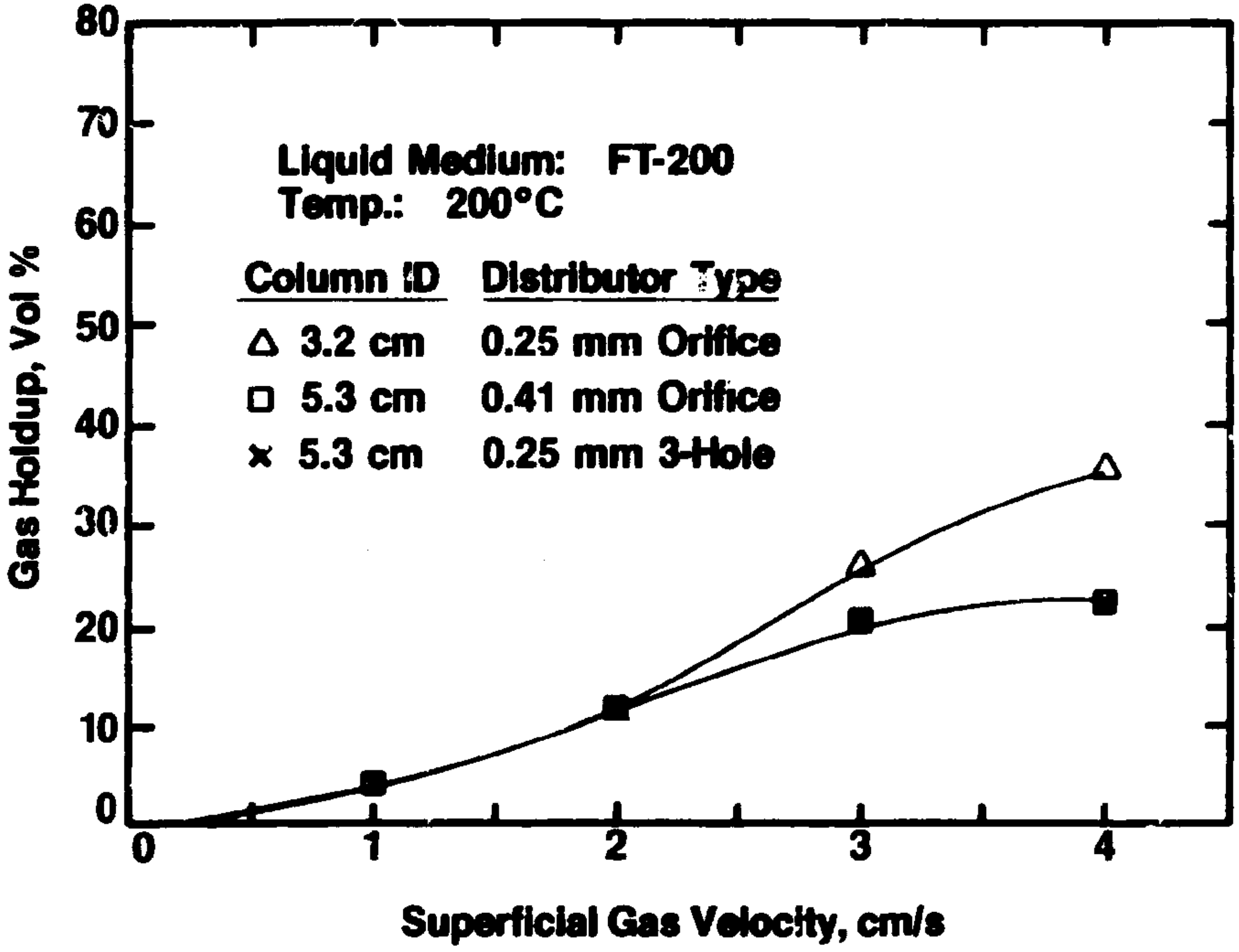
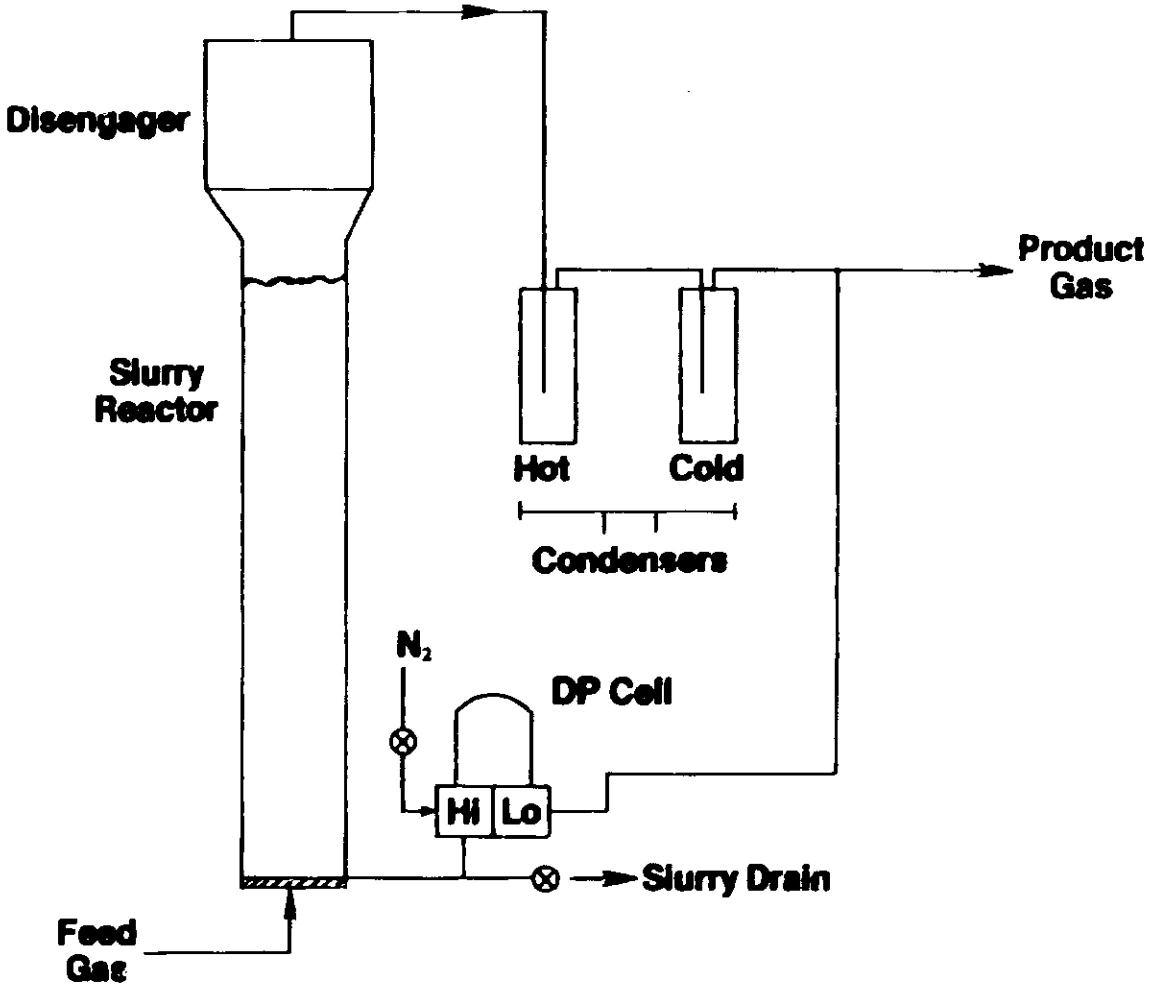


Figure VII-18

SCHEMATIC DIAGRAM OF DP-CELL ARRANGEMENT ON UNIT CT-225



rate and the cross-sectional area ratio of the two sections, the gas holdup in the narrow section could be calculated.

Each gas holdup consequently corresponds to a specific amount of liquid in that section. In effect, since the height of the lower section remains fixed, the data can be viewed as being taken at a "constant expanded height." This differs somewhat from the more straightforward technique used with the glass columns, in which static height was constant and the entire expanded bed, including foam, was measured. Nevertheless, gas holdups were measured using a slurry consisting of 15 wt % of a standard F-T catalyst in a liquid medium which combined a wax product from a previous run and Mobil base stock F-509. The temperature was held at 177°C for all experiments, and the distributor was a 20 micron SMP.

The results at different pressures using nitrogen as the feed gas are shown in Figure VII-19. Also shown is a series of points representing hydrogen, in an effort to determine whether the type of gas affects the gas holdup. It can be seen on the plot that all the data seem to fall on the same general curve. The maximum observed holdup is about 59 vol % at 1.75 cm/s superficial gas velocity. Beyond that the holdup falls off, possibly due to the onset of large bubble formation. At all velocities, however, the holdup is substantially higher than the correlation proposed by Deckwer et al. (1980). This correlation, though, is valid only for temperatures above 250°C. Below that, the authors state that the gas holdup (in a paraffin wax) goes up with decreasing temperature. However, even after correcting the correlation as recommended, the predicted holdup is still exceeded by this data.

The close agreement of the data over the wide range of pressures studied, as well as the results for hydrogen, indicate no gas density effect on the holdup and, presumably, the average bubble sizes. A comparison of Figures VII-4 and -19, meanwhile, shows that the holdups in the short hot-flow columns (which used only FT-200 wax) are higher than that in the reactor. However, note that the entire expanded bed is not seen here, and there might well exist foam which, if the reactor had no disengagement section, might add a good deal of gas holdup to that already reported.

C.6. Evaluation of an Orifice Feed-Gas Distributor in a Small Bubble-Column Reactor

For the first time, an orifice-type feed-gas distributor was used in one of our reactive bubble-columns. This type of experiment was important because SMP-type distributors are unreliable for commercial applications. They are weak structurally, and can easily become plugged with solids.

Figure VII-19

EFFECT OF PRESSURE & GAS TYPE ON GAS HOLDUP