TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS. QUARTERLY REPORT, 1 JANUARY 1984-31 MARCH 1984

MOBIL RESEARCH AND DEVELOPMENT CORP.
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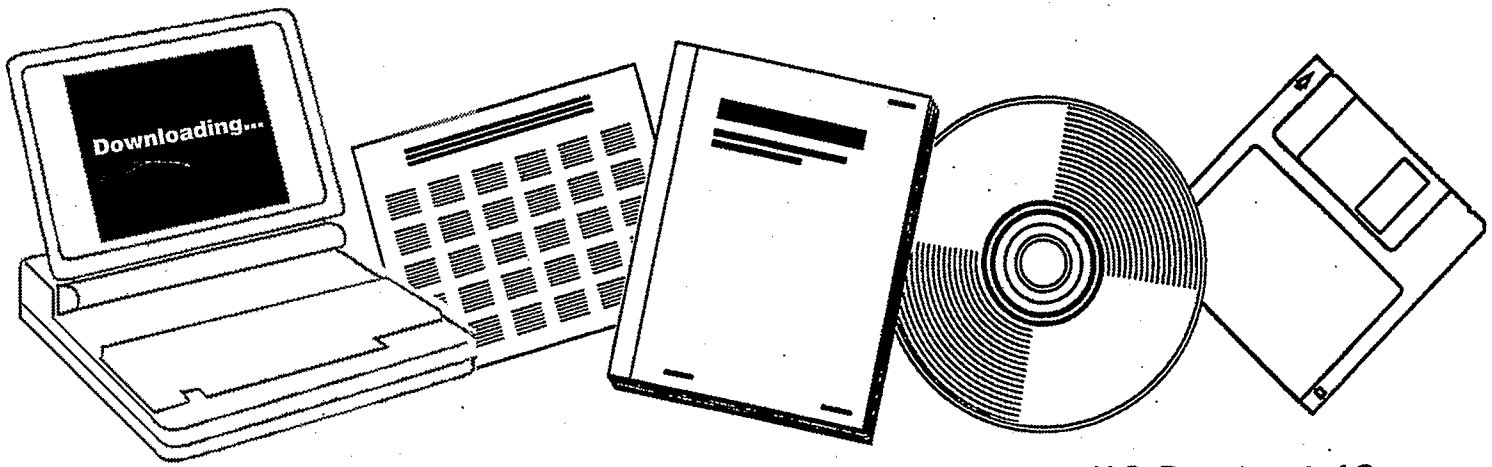

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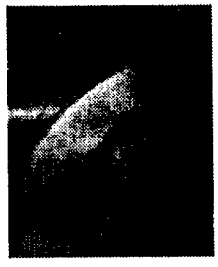

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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS

QUARTERLY REPORT FOR THE PERIOD
1 JANUARY - 31 MARCH, 1984

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TABLE OF CONTENTS

I. Abstract

This Quarter has seen the shakedown and startup of both the two-stage pilot plant and the tall hot-flow non-reacting bubble-column (5.1 cm ID x 9.1 m height). Evaluation of a new Fischer-Tropsch catalyst was initiated in the pilot plant, while the hot-flow model was used to study the effects of distributor type, temperature, pressure, and static liquid height on gas holdup.

Scoping hydrodynamic studies were done, using the short hot-flow bubble-column, and a short run was performed using a small bubble-column reactor (Unit CT-225) to determine the effect of pretreatment on the new F-T catalyst. During the run, a single orifice was successfully used as a gas distributor for the first time.

II. Objective and Scope of Work

The general objective of this work is to develop a slurry Fischer-Tropsch/ZSM-5 process for converting low H_2/CO system, into maximum yield of transportation fuels. To accomplish this objective, the following tasks wil be undertaken.

Task 1 - Process Studies in Two-Stage Bench-Scale Unit

Operation of the bench-scale unit will be directed toward production of hydrocarbons containing less than 8 wt % of methane plus ethane with high throughput, high conversion, and good catalyst stability. Together with Task 2, high quality liquid fuels, particularly the distillate, will be maximized. At least two tests shall be conducted using at least two different catalysts. One of these catalysts may be provided by DOE's alternate catalyst development projects.

Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

The methods for upgrading the reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated. These methods should include conventional refinery processes, such as Fluidized Catalytic Cracking, Hydrocracking, Catalytic Selective Cracking, Thermal Cracking, and Hydrodewaxing. Proprietary mathematical models and open literature information will be used to the extent possible for these process evaluations.

Means for separating the reactor-wax from the catalyst fines, if such a separation is needed prior to reactor-wax upgrading, shall be investigated.

Task 3 - Product Evaluation

The quality of the hydrocarbon liquid products from the two-stage unit and the reactor-wax upgrading processes shall be evaluated. Gasoline octane and distillate cetane quality, as well as pour points should also be determined.

Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic Studies

The effect of different feed-gas distributor designs on the slurry Fischer-Tropsch reactor performance will be investigated. Tests will be conducted in the BSU slurry reactor, or other bubble-column reactors, to provide guidance for subsequent runs in Task 1 as well as for design and operation of the non-reacting models. For hydrodynamic studies, the design, construction, and operation of hot, non-reacting models. For hydrodynamic studies, the design, construction, and operation of hot, non-reacting bubble-column models will be required.

Task 5 - Development of Conceptual Process Schemes

A conceptual process scheme to maximize gasoline and distillate yield using a combined system of slurry Fischer-Tropsch/ZSM-5 reactor plus reactor-wax upgrading will be developed. Scoping costs of the plant will be estimated.

III. Summary of Progress to Date

Following modifications, the two-stage bench-scale unit was shaken down and then started up in an effort to evaluate a new Fischer-Tropsch catalyst ($Fe/Cu/K_2CO_3$), designated as I-D. A separate pretreatment step was performed, and the pretreatment time was only two hours. Initial results from the run (Run CT-256-6) indicate that the catalyst activity is equivalent to that of previously studied F-T catalysts.

Before this run, the effect of pretreatment on the catalyst was determined by a short run in a small bubble-column reactor. There, the rapid pretreatment was also observed, as well as the excellent activity. For this run, a single 0.375 mm orifice was used as a gas distributor, the first time we have ever attempted this. No detrimental effects could be found.

Scoping hydrodynamic studies continued, using the small (5.3 cm ID x 1.9 m tall) hot-flow bubble-column. Among other things, it was found that different orifice-type distributors give rise to similar gas holdups when the jet velocity through the holes is the same. That is, the jet velocity correlated the holdup data well, except for a large orifice (1 mm), which showed higher holdup at low jet velocities than did the others studied.

These effects were further examined using the new tall hot-flow bubble-column (Unit CT-284). The 5.1 cm ID column of the unit was shaken down using hexadecane as a liquid medium, and then hydrodynamic studies were carried out using FT-200[1]. Three gas distributors were investigated: a 20 μm sintered-metal-plate (SMP), a 1 mm single orifice, and a 0.5 mm three-hole orifice. Important results from the study include:

- Increasing static liquid height decreases gas holdup over an SMP, and increases holdup over an orifice-type distributor.
- Orifice-type distributors which have similar jet velocities and Weber numbers give rise to similar holdups.
- Gas holdup increases with temperature, and is unaffected by pressure up to the maximum operating pressure of the column.

Lastly, a correlation for pressure drop across orifice-type gas distributors was chosen from the literature. It has been useful in selecting gas distributors for our studies and will be used to evaluate commercial designs.

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[1] A F-T paraffin wax, probably from SASOL, with an average molecular weight of 600.

IV. Detailed Description of Technical Progress

A. Task 1 - Process Studies In Two-Stage Bench-Scale Unit

1. Supporting Studies

As reported in the last Quarterly Report, Catalyst I-D was evaluated in a 5.7 cm ID x 1.9 m tall bubble-column reactor (Unit CT-225). The catalyst was activated without a separate pretreatment step, and showed low methane + ethane yield throughout the run. A second short evaluation has since been done; to study the effect of pretreatment on start-of-cycle performance.

The run, designated as CT-225-113, lasted only one day, but the main objectives were accomplished, as the catalyst pretreated rapidly and produced excellent conversion and low methane + ethane selectivity. The pretreatment conditions were:

Temperature, °C	280
Pressure, MPa	1.14
H_2/CO Feed Ratio, Molar	0.67
Space Velocity, NL/gFe-hr	3.0
Catalyst Loading, Wt %	20
Duration, hrs	4.0

The pretreatment was stopped when the molar gas contraction reached 50 Vol %, which represents about a 75 mol % H_2+CO conversion (see Figure 1).

Following the pretreatment, synthesis operation was started at the same conditions which were used in Run CT-225-112: 250°C, 2.17 MPa, 0.67 H_2/CO feed ratio, and 4.5 NL/gFe-hr. Figure 2 shows the conversion and methane + ethane selectivity for the run. At these conditions, the initial H_2+CO conversion of 53 mol % is comparable to other F-T catalysts we have studied.

The catalyst continued to activate over the first fourteen hours on-stream, while the methane + ethane selectivity dropped to 2.0 wt % of hydrocarbons. The reactor-wax produced during the run was allowed to build up in the reactor, since wax removal might have resulted in some catalyst loss, as happened in Run CT-225-112.

These results, combined with the previous study, indicate that the catalyst I-D is a flexible catalyst which can produce low methane + ethane yields, and may also activate fully after in-situ additions without a separate pretreatment step.

This run also marked the first time that an orifice-type feed-gas distributor was used in a reacting bubble-column. The details of this are reported in Section IV.D.1.

2. Modifications and Shakedown of the Two-Stage Bench-Scale Unit

The Two-Stage BSU was modified for improved operation. The major modifications are:

- Improved on-line reactor-wax separation hardware
- Improved DP-cell set-up for bubble-column hydrodynamic measurements
- Hardware for steam co-feeding to the Fischer-Tropsch reactor

The improved on-line reactor-wax separation hardware is described in the Mobil Proprietary Appendix of this report. The purgeless DP-cell and steam co-feed systems were described in the previous Quarterly Report (Oct.-Dec., 1983).

Following modifications and a one-year idle period, the Two-Stage BSU was shaken down. The major items are:

- Cold- and hot-pressure tested section by section with N_2 and H_2 at 2.86 MPa and fixed leaks.
- Calibrated Glycol System.
- Calibrated NDIR CO and CO_2 monitors.
- Tested new on-line reactor-wax separation and purgeless DP-system first with Mobil F-509[1] and then with the end-of-run CT-256-5 slurry.
- Tested and calibrated the on-line gas chromatograph system

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[1]A proprietary high molecular weight paraffinic base stock

3. Run CT-256-6 - Startup

The major objective of Run CT-256-6 was to evaluate a new F-T catalyst ($Fe/Cu/K_2CO_3$, designated as I-D) for low methane + ethane mode operation.

Run CT-256-6 was successfully started on March 21, 1984. Catalyst activity was equivalent to that of catalysts previously tested (I-B, I-C). At the end of this reporting period (ten days on stream), the catalyst was still performing satisfactorily.

Detailed description of the F-T catalyst loading and pretreatment are given here. However, only a brief description of the synthesis operation of this run is reported. The details of the synthesis operation and a summary of its performance data will be given after the completion of the run.

a. Fischer-Tropsch Slurry Catalyst Loading and Pretreatment

Catalyst loading and pretreatment similar to those of Run CT-256-4 were used in this run. 1,863 g of F-T catalyst I-D, along with 1,327 g of Mobil F-509 and 6,046 g of spent reactor-wax (from Runs CT-256-4 and 5) were loaded. The initial catalyst loading was 20.2 wt %.

The F-T catalyst pretreatment conditions were:

H_2+CO Flow Rate, Nm^3/hr	2.57
H_2/CO Feed Ratio, molar	0.7
Superficial Feed-Gas Vel., cm/s	6
Space Velocity, NL/gFe-hr	2.0
Temperature °C	280
Pressure, MPa	1.14

The pretreatment operation was ended after two hours, when the gas volume contraction reached 49.4 vol % and the CO conversion reached 74 mol %. Figure 3 shows the product gas volume contraction and CO conversion during pretreatment.

b. Brief Description of First-Stage Fischer-Tropsch Reactor Synthesis Operation

In switching from pretreatment to synthesis operation, the slurry reactor temperature was lowered to 250°C. The conversion declined after the temperature drop, and then gradually increased, reaching 74 mole % H_2+CO conversion at 72 HOS. This activity is equivalent to that of other F-T catalysts previously tested in the Two-Stage BSU.

The synthesis operation continued at 250°C and 1.14 MPa for most of the first 10 days. During this period the H_2+CO conversion was 65-77 mol%, while the methane + ethane selectivity was a low 1.7-2.3 wt % of hydrocarbons produced (70-80 wt % reactor-wax yield).

The range of synthesis conditions of the first stage Fischer-Tropsch reactor were:

H_2+CO Flow Rate, Nm^3/hr	1.37-3.43
H_2/CO Feed Ratio, Molar	0.7
Superficial Feed-Gas Vel, cm/s	3-4
Space Velocity, NL/gFe-hr	1.49-4.02
Temperature, °C	250
Pressure, MPa	1.14-2.17
H_2+CO Conversion, Mol %	42-77
Methane + Ethane Yield, Wt %	1.7-2.3
Reactor-Wax Yield, Wt %	70-80

At 1.1 DOS an upset occured due to a leak in the new catalyst-wax separation system. As a result, about 26% of the catalyst was lost. It is planned to make up this loss by adding fresh catalyst to the reactor at a later time.

The second-stage reactor was not operated during the first ten days of this run. This was due to a leak at the bottom of the fixed-bed, which required unloading of the catalyst and replacing the flange gaskets.

4. Future Work

- Continue Run CT-256-6 to establish stability of low methane + ethane mode operation.
- Test an orifice-type feed-gas distributor in the bubble-column reactor.

B. Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

1. Testing of a High-Gradient Magnetic Separator (HGMS) for Cleaning Reactor-Wax

Proprietary work using a high-gradient magnetic separator to obtain solids-free reactor-wax is described in the Mobil Proprietary Appendix.

2. Hydrocracking and Hydrodewaxing Studies for Fischer-Tropsch Reactor-Wax Upgrading

Preliminary results from proprietary hydrocracking and hydrodewaxing studies to upgrade reactor-wax are described in the Mobil Proprietary Appendix.

3. Future Work

- Continue scoping studies for F-T reactor-wax upgrading using conventional refinery processes.

C. Task 3 - Product Evaluation

1. Reactor-wax Analysis by Gel Permeation Chromatography (GPC)

We have evaluated a high temperature Gel Permeation Chromatography (GPC) method for reactor-wax molecular weight distribution analysis. Two samples were submitted to a consulting analytical laboratory (Springborn Labs, Enfield, CT) for high temperature GPC which employed a standard column packing optimized for general polymer analysis. After reviewing the GPC data, we concluded that in order to obtain a correct F-T wax molecular weight distribution, further optimization of the GPC column packings is required to improve the resolution. This would reqire column packings with smaller pore distribution. Since it is expensive to modify the column packings, we do not plan to pursue this method any further at this time.

2. Product Analyses

Necessary product analyses to support other tasks were carried out.

3. Future Work

- Evaluate Field-Ionization-Mass-Spectrometry (FIMS) for F-T reactor-wax analysis.
- Improve existing GC analysis with the addition of internal standards and cold-on-column injection port.
- Continue providing product analyses to support other tasks.

D. Task 4 - Slurry Fischer-Tropsch Bubble-Column Hydrodynamic Studies

1. Scoping Hydrodynamic Studies

a. Evaluation of an Orifice 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 is important because SMP-type distributors are unreliable for commercial applications. They are weak structurally, and can easily become plugged with solids. Therefore, a 0.375 mm diameter single-orifice distributor was installed in the small bubble-column reactor (Unit CT-225) prior to Run 113, which was described in Section IV.A.1.

As was seen, the conversion and methane + ethane selectivity were excellent during the run, illustrating the applicability of such distributors. The pressure drop across the orifice was constant during the run (at constant superficial gas velocity) and no slurry came through the opening.

The size and shape of the bubbles produced by the orifice is not known, but the gas holdup during the run was similar to holdups produced by a 20 μm SMP using the same wax medium without catalyst.

This is in contrast to the results of our hot-flow bubble-column work, which to date have shown that orifice-type gas distributors generally give lower gas holdups than SMP's. It may be that the small diameter of this reactor causes higher holdups, as indicated by literature reviews. Nevertheless, it appears from this study that the overall Fischer-Tropsch reaction may be more kinetically controlled than mass-transfer limited. Of course, experiments in the two-stage pilot plant and larger systems are called for to verify this.

b. Studies Using a Small Hot-Flow Bubble-Column

Scoping hydrodynamic studies were carried out using Run CT-256-4 reactor-wax in a 5.3 cm ID x 1.9 m tall hot-flow glass bubble-column. Single and multiple orifice distributors as well as a 60 μm SMP were used. The highlights of the study are:

- Reactor-wax from Run CT-256-4 gives generally higher holdups than Run CT-256-5 reactor-wax, but lower than FT-200, an F-T derived paraffinic wax used in previous studies.
- Foaming was observed for the first time in a medium other than FT-200.
- 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.

Figure 4 is a comparison of gas holdups in different liquid mediums over a 60 μm SMP gas distributor. The large differences in the behavior of the waxes is evident. Under these conditions, the FT-200 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 (Sept.-Dec. 1983 Quarterly Report.

To try and understand why these differences occur, we compiled a table of the physical properties of the waxes used in this study. (This was also published in the Sept.-Oct. 1983 Quarterly Report.) Table 1 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.

It should be pointed out that a new analytical technique showed that the molar average carbon number of the Runs CT-256-4 and 5 reactor-wax are higher than reported here. It may be that the composition of the waxes plays a role in determining their hydrodynamic behavior.

To help determine the scaleup characteristics of 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 (a dimensionless number relating kinetic to surface energies). Run CT-256-4 reactor-wax was used as the liquid medium. Figure 5 shows the results of these studies.

The 0.25 mm single orifice produced a foam layer 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 diameter 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 a constant 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 through each hole as does the 0.41 mm single orifice. The results show that the 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 6) and Weber number (Figure 7). 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 vs. 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 8. The holdup data for the Run CT-256-5 reactor-wax is taken from the Sept.-Dec. Quarterly Report, and the FT-200 data is from the June-Sept. Quarterly Report. For the latter, 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 column. The sharp contrast between this and Figure 4 demonstrates the overlap of liquid medium/distributor type studies.

c. Gas Holdup Studies Using Run CT-256-5 Slurry in BSU Bubble-Column

Gas holdup in the bubble-column reactor of the two-stage pilot plant was measured by visual observation (at the 610 cm viewport), using nitrogen as the feed gas and end-of-run CT-256-5 slurry. The gas holdup was only 8.6 vol % at 199°C, 101 kPa, 12 wt % catalyst loading, and 4 cm/s superficial gas velocity. This is the lowest gas holdup ever observed at such a velocity in the BSU bubble-column, and is in agreement with results from scoping studies using the short hot-flow bubble-columns.

Increasing the pressure to 1.48 MPa while maintaining the same superficial gas velocity and temperature had no effect on the gas holdup. This is in agreement with results from scoping studies using our small bubble-column reactor reported in June-Sept. 1983 Quarterly Report.

2. Construction and Shakedown of Two Tall Hot-Flow, Non-Reacting Bubble-Columns

The construction of two 5.1 cm and 10.2 cm ID x 9.1 m tall hot-flow non-reacting bubble-columns (Unit CT-284) was completed in the first week of January, 1984. The shakedown of the unit, which was completed in one month, included:

- checking of all piping and valves
- calibration of equipment
- training of operators
- testing of equipment

All shakedown tasks were carried out smoothly as planned. The specific tasks carried out for both columns are listed below:

- Calibrated N_2-purge rotameters for DP-cell.
- Calibrated gas meters and feed N_2 mass-flow meters.
- Cleaned and flushed both columns, cold condenser-scrubbers, all slurry sample lines and drop-out pots.
- Pressure-tested the entire system with 308 kPa N_2 at ambient temperature; repaired all leaks.
- Checked all steam tracings for proper operation.
- Tested all temperature indicators and controllers.
- Hot-pressure-tested the entire system (5.1 cm ID column only) with 308 kPa N_2 at 121°C.
- Tested the slurry loading tank operation using n-hexadecane at ambient temperature.

Later, during normal operation, the column was tested at the design temperature of 260°C with 287 kPa N_2.

The 5.1 cm ID column was put into operation first. A shakedown run was carried out using hexadecane as a liquid medium at ambient temperature (23°C) and 204°C. The static liquid height was 653-735 cm. Figure 9 gives the gas holdups as a function of average superficial gas velocity, u_g. The gas

distributor used was a 20 μm SMP. The effect of temperature can be clearly seen: gas holdups increase substantially as the liquid temperature is increased. Since the viscosity of hexadecane decreases with increase in temperature, based on the literature correlations (Shah et al., 1982), gas holdups are expected to increase with increase in temperature.

The bubble flow-patterns revealed large bubbles and constant slugging at 23°C and at superficial gas velocities larger than 0.7 cm/s. The slugging was always accompanied by smaller bubbles in the wake of slugs forming foam in the top zone. In contrast, at higher temperatures foam was negligible and slugging occurred only at u_g greater than 3.8 cm/s. Also, the bubble sizes appear to be smaller. These gas holdup data confirm our previous results in small hot-flow bubble-columns: even though the viscosity and surface tension of n-hexadecane are similar to F-T wax (FT-200), larger bubble sizes and lower gas holdups are obtained with n-hexadecane.

3. Hydrodynamic Studies Using a Tall Hot-Flow Bubble-Column

Hydrodynamic studies using the 5.1 cm ID x 9.1 m tall hot-flow bubble-column have been carried out. The liquid medium used in all studies so far was a F-T derived paraffinic wax FT-200. Since FT-200 wax is clear, it enables us to observe and photograph the bubble flow patterns. The reactor-wax from the two-stage pilot plant is dark in color and will be studied later at the end of the program.

Three gas distributors have been evaluated: a 20 μm SMP, a 1 mm single orifice, and a 0.5 mm three-hole distributor. The 20 μm SMP is similar to the one used in the two-stage bench-scale unit (Unit CT-256). A 1 mm orifice distributor was studied since it is probably the smallest commercially applicable orifice distributor. The 0.5 mm three-hole distributor is dynamically similar (i.e., similar jet velocity and Weber number at the same superficial gas velocity) to the 1 mm orifice. The comparison of these distributors is presented here. We have also studied the effect of temperature, pressure and static height.

a. Effect of Gas Distributor Designs

Figure 10 is a plot of the gas holdups observed using the three gas distributors. The static liquid height was 627-640 cm for both orifice distributors. In the case of the 20 μm SMP distributor the static height had to be decreased from 640 to 305 cm (as marked in the figure) to allow for the high gas holdups resulting from the SMP distributor.

As seen in the figure, the hydrodynamic behavior of the two orifice type distributors is very similar. The gas holdups with the SMP distributor, however, are substantially higher (almost twice as much) than those with the orifice distributors. As reported earlier in the short bubble-column results, substantial foaming was observed with the SMP distributor. Also, the bubbles formed at the distributor are uniformly small and they stay uniform throughout the column. Because of these very small bubbles, stable foam is formed in the upper zone, giving very high gas holdups. As the superficial velocity is increased, the foam region increases, and the boundary between the foam and small bubbles becomes less distinct. At superficial velocities greater than 2 cm/s, slugging at constant frequency was observed. The slug size and frequency increased with increasing superficial gas velocity. This slugging phenomenon was not observed earlier in the short column. Even when slugging is observed, the bubbles in the bottom 150 cm zone were small and densely packed. Many small swirling bubbles were observed in the wake of the slugs.

The bubble-size distribution with the orifice-type distributors was wider than with the SMP. The large bubbles formed in the lower zone tended to break up in the upper zone forming uniformly small bubbles. However, even the small bubbles in the top zone were larger than those observed with the SMP. Consequently, the foam height was extremely small (about 5-8 cm) compared to 20-38 cm with the SMP distributors. Also, with the orifice distributors, the larger bubbles in the bottom zone created more violent bubble movement than that observed with uniformly small bubbles produced with the SMP distributor. This violent bubble movement should be beneficial to gas-liquid mass transfer.

The slugging was observed at lower superficial gas velocities (>1.5 cm/s) than those of the SMP distributors. Once again very small bubbles were observed in the wake of the slugs. As with the SMP distributor, the slug size and frequency increased with increasing superficial gas velocity. Data from literature indicate that the gas holdup is expected to level off with slugging. In this case, however, the formation of very small bubbles due to slugs tend to increase the gas holdup with increasing gas velocity.

Figure 11 compares the gas holdups obtained with the two orifice type gas distributors. As reported in the last Quarterly Report, one of the criteria used to design an orifice-type distributor for making small gas bubbles is that the Weber number is larger than 2. The 1 mm orifice and 0.5 mm three-hole distributors were chosen to match the Weber numbers at the same superficial velocity. Due to the equipment limitations, we could not make a 0.58 mm three-hole distributor which would have had exactly the same We at the same u_g. Thus, the Weber number for 0.5 mm three-hole distributor is 12% higher than that for the 1 mm single-hole distributor. Also, the jet velocities

for these two distributors are very similar (within 25%) at the same superficial velocity. The hydrodynamic behavior of the two distributors are, also, extremely similar (Figure 11). This indicates that the two distributors with similar jet velocities and similar Weber numbers give similar hydrodynamics. This is further illustrated in Figures 12 and 13 where the gas holdups are plotted as a function of Weber numbers and jet velocities, respectively.

b. Effect of Static Liquid Height

Figure 14 shows the effect of static liquid height on the gas holdup in the case of the 20 μm SMP distributor. In the 5.1 cm ID x 9.1 m tall hot-flow bubble-column the liquid height was varied from 305 to 640 cm. As described earlier, the static liquid height had to be lowered to allow for the high gas holdups which occurred at the high superficial gas velocities.

It can be seen from the figure that when the static liquid height is lowered substantially (i.e., 640 to 305 cm) the gas holdup goes up. Also, substantially higher holdups are observed at 61 cm static height in the short column (5.3 cm ID). This observation is consistent with the literature results. Such an effect of static height is observed because of the existence of a high holup zone at the top due to slow disengagement of bubbles from the liquid. When the static liquid height is lowered, the upper high holdup zone (the height of which stays about the same) contributes more to the overall holdup. Higher overall holdups are, hence, observed for lower static height. It is not clear why the increase in gas holdup was not that significant when the static height was lowered from 640 to 483 cm.

Figure 15 shows the static liquid height effect with the 1 mm single-hole distributor. Once again, as with the SMP case, no significant effect on gas holdup can be seen when the static height was lowered from 627 to 452 cm.

In contrast to the SMP distributor, the gas holdup decreased when the static liquid height was lowered to 58 cm. This is mainly due to different bubble-size distributions observed with the two distributors. In the case of an orifice distributor the lower zone is occupied by many large bubbles. The lower zone is hence a low holdup zone. The large bubbles tend to break up as they rise upward, giving uniformly small bubbles in the upper zone. Thus, a shorter bed height does not permit the large bubbles to break up, preventing the formation of a high holdup zone. The overall holdup at a low static liquid height is hence lower than that with a high static liquid height.

The behavior of the 0.5 mm three-hole distributor was similar to that of the 1 mm single-hole distributor.

c. Effect of Pressure

The effect of pressure on the gas holdup was insignificant with all three distributors. Since the hydraulic height of the liquid column was high, the relative pressure variation from bottom to top of the column was substantial (35-49 kPa). It was, therefore, necessary to observe the effect of such pressure variation on the gas holdup. Even though the absolute pressure was varied over a limited range, (101-184 kPa), a percentage change from top to bottom of 17-50% was achieved. As seen from Figures 16 and 17, no significant effect on gas holdup was observed.

d. Effect of Temperature

In one experiment with the 20 μm SMP, gas holdup data was taken at 138°C and 260°C to determine the effect of temperature. As shown in Figure 18 the gas holdup increased substantially when the temperature was increased from 138°C to 260°. This is consistent with the results from the literature, i.e., the lower the viscosity of the liquid medium, the higher the gas holdup. The bubbles are also larger at lower temperature. Although slugging started at about the same superficial gas velocity of 2 cm/s, substantially larger bubbles (2-3 cm) were observed at all velocities at the lower temperature, 138°C.

4. Pressure Drop Across Orifice-Type Gas Distributors

The pressure drop across gas distributors is an important consideration for both pilot-plant studies and evaluations of commercial designs. For this reason, a correlation from the literature was used to predict the pressure drops across orifice-type distributors used in our hydrodynamic studies. While the predicted values nearly always underestimate the experimental results obtained in the current study, the use of the correlation has enabled us to avoid potential problems with either excessive or too low a pressure drop.

The working equation for weight rate of discharge through an orifice, adopted by the ASME Research Committee on Fluid Meters is (Perry, 1973):

$$w = CYA \quad [2g_c \ (\Delta P) \ \rho_1/(1-\beta^4)]^{1/2} \qquad (1)$$

In our studies with small orifices, the value of β can be assumed negligible, and the value of C is held constant at 0.61. Equations for the expansion factor (Y) as a function of the downstream to upstream pressure ratio (r) can be theoretically derived for either adiabatic or isothermal flow. However, neither gives satisfactory results as the flow becomes supercritical (r less than about 0.53 for most gases). For this reason, a correlation by Cunningham (1951) was used.

In his paper, Cunningham experimentally measured the value of the gas expansion factor through various orifices for both sub- and super-critical flows. All the data was taken with air at room temperature, which differs from our case of hot (>204°C) gases expanding into a somewhat hotter liquid medium. Pipe-taps were used for the DP-measurements. The author recommended that for high pressure ratios (r>0.77) the expansion factor is represented well by an ASME-proposed relation:

$$Y = 1-[0.333 + 1.145\ (\beta^2 + 0.7\ \beta^5 + 12\ \beta^{13})]\ (1-r)/\gamma \quad (2)$$

At low pressure ratios (r<0.77) however, the author presents the following:

$$Y = Y_{0.77} - .364\ (.77-r) \quad (3)$$

where $Y_{0.77}$ is the value of Y from Equation (2) at r = 0.77.

Comparison of the correlation with actual data from our bubble-columns is shown in Table 2. The pressure drop reported here is the difference between the feed-gas pressure and the downstream pressure. It is seen that the equation over-predicts the pressure drops from the hot-flow bubble-column, and under-predicts the values from the small bubble-column reactor (Unit CT-225). However, this is about the best agreement we have been able to obtain, and use of the equation helps to prevent unusually high or low pressure drops.

Using this correlation, we have prepared a graph (Fig. 19) showing expected pressure drops across various orifices in the bench-scale unit bubble-column reactor. The values were calculated for reactor conditions of 2.51 MPa, 260°C, and 0.7 H_2/CO ratio feed-gas. The plot will help us select orifice-type distributors for the upcoming run.

5. Future Work

- Continue scoping hydrodynamic studies using small hot-flow bubble-columns.

- Continue hydrodynamic studies using the tall 5.1 cm ID hot-flow bubble-column.
- Shake down the tall 10.2 cm ID hot-flow bubble-column and then conduct hydrodynamic studies.
- Continue evaluation of a series of CSTR as an alternative to the bubble-column reactors.

V. Nomenclature

A	Orifice cross-sectional area, (cm^2)
C	Discharge coefficient
d_o	Orifice diameter, (mm)
P	Pressure, (Pa)
u	Superficial gas velocity, (cm/s)
r	Pressure ratio, downstream/upstream
u_o	Gas orifice velocity, (cm/s)
Y	Expansion factor

Greek Letters

β	Ratio of orifice to tube diameter
ρ	Density, (g/cm^3)
γ	Ratio of specific heats
σ	Surface tension, (dyne/cm)

Dimensionless Numbers

We	Weber number, (orifice), $u_o^2 d_o \rho_g / \sigma$

Acronyms

ASME	American Association of Mechanical Engineers
BC	Bubble-Column
BSU	Bench-Scale Unit
DOE	Department of Energy
DOS	Days on Stream
DP	Differential Pressure
FIMS	Field-Ionization-Mass-Spectrometry
F-T	Fischer-Tropsch
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
HGMS	High-Gradient-Magnetic-Separator
HOS	Hours on Stream
NDIR	Non-Dispersed Infra-Red
SMP	Sintered-Metal-Plate

Superscripts

i	At reactor inlet

Subscripts

g	Gas

VI. References

Cunningham, R. G. , Trans. ASME, 73, 625 (1951).

Dry, M. E., and Hoogendoorn, J. C., Cat. Rev-Sci. Eng., 23, 265 (1981).

Perry, J. H., "Chemical Engineers Handbook", McGraw-Hill New York, Fifth Edition, pp. 5-11 - 5-13 (1973).

Shah, Y. T., Kelkar, B. G., Godbole, S. P., and Deckwer, W. D., AIChE Journal, 28, 353 (1982).

Table 1

Physical Properties of Bubble-Column Mediums

	Bubble-Column Mediums		
	FT-200	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	27.8(1)	26.4	27.9
Viscosity (204/149°C), cp	2.1/-	3.0/5.3	7.2/14.6

(1)At 204°C

Figure 1

PRETREATMENT OF FISCHER-TROPSCH CATALYST I-D (RUN CT-225-113)

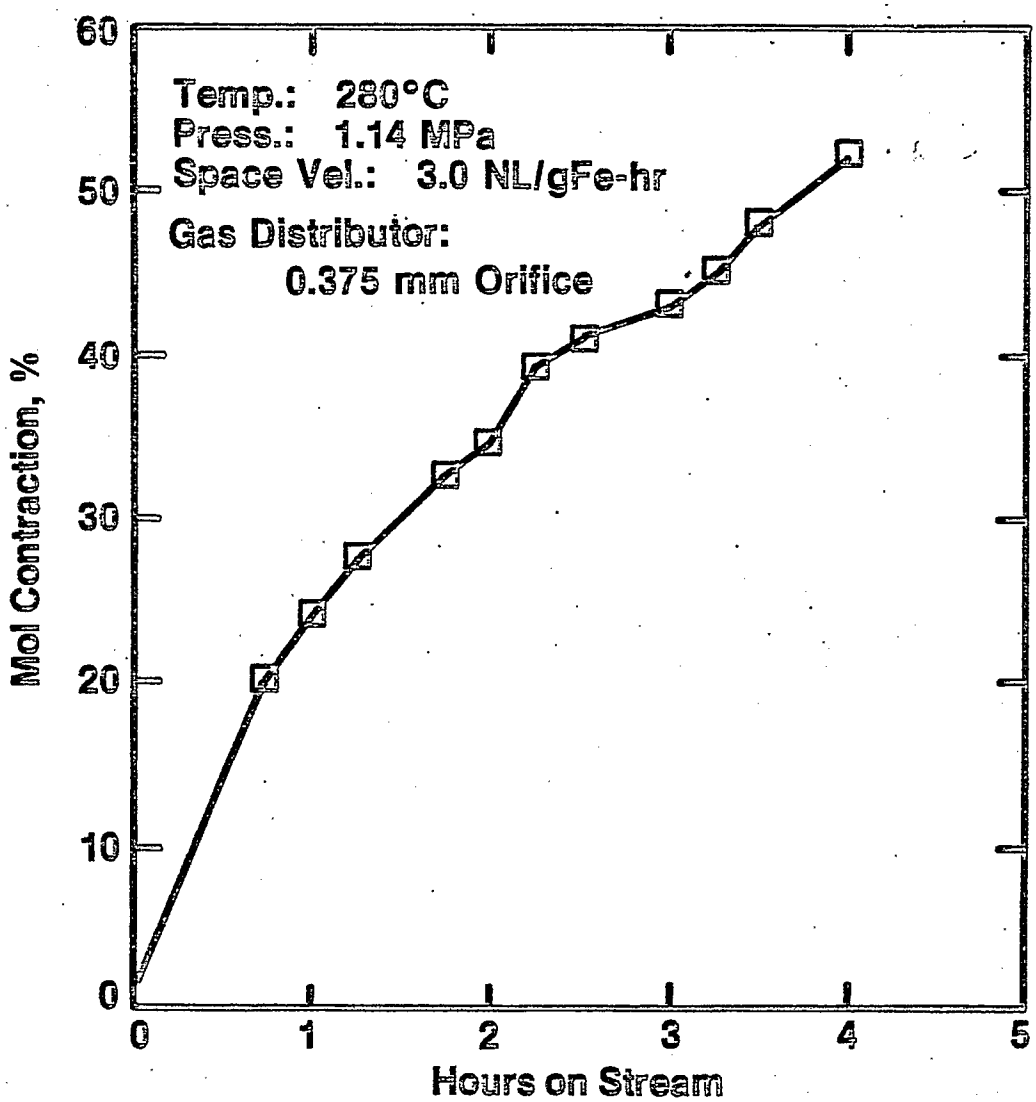


Figure 2

SYNTHESIS GAS CONVERSION AND METHANE AND ETHANE YIELD (RUN CT-225-113; CATALYST I-D: PPTD Fe/Cu/K_2CO_3)

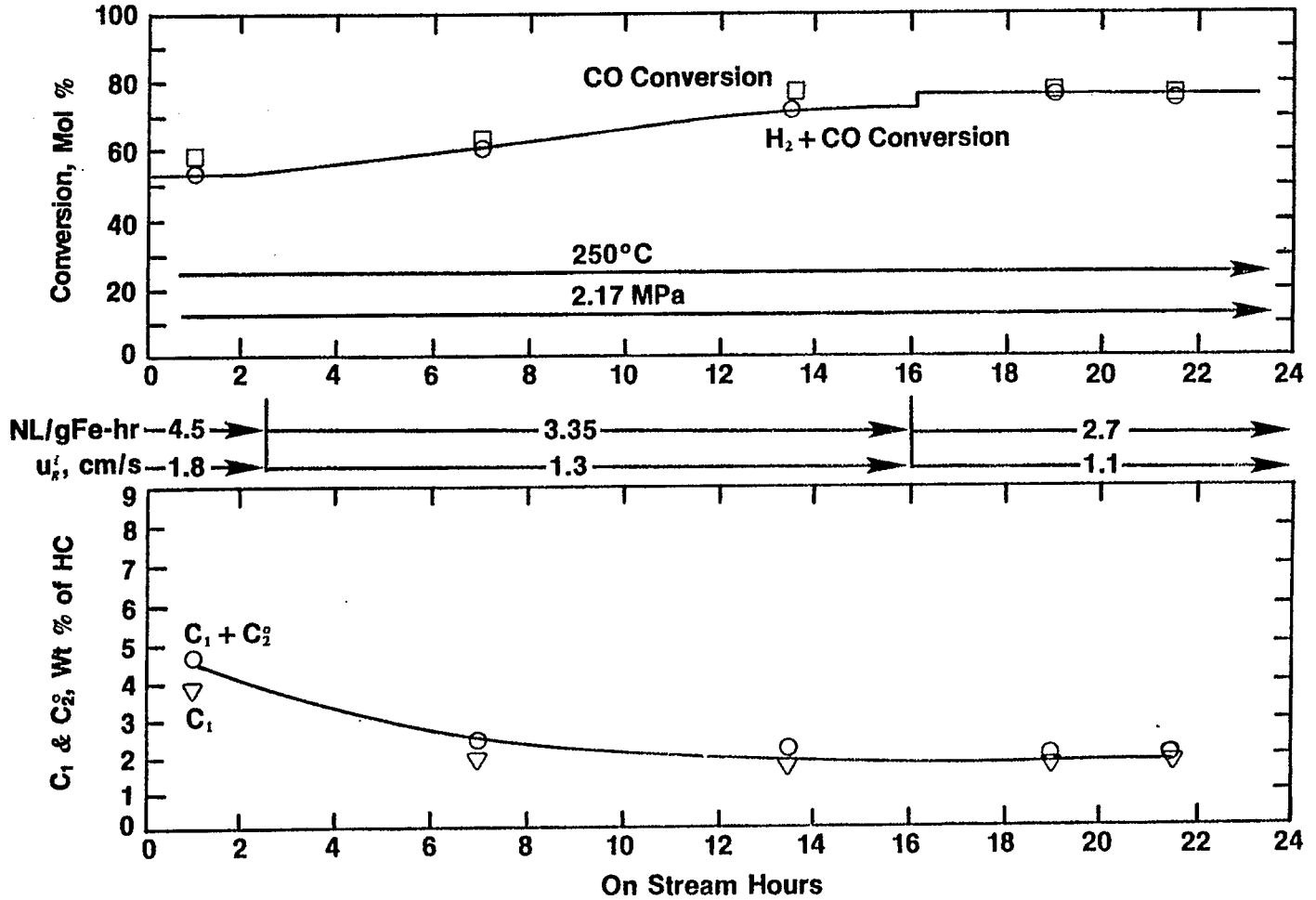


Figure 3

PRETREATMENT OF FISCHER-TROPSCH CATALYST I-D
(RUN CT-256-6)

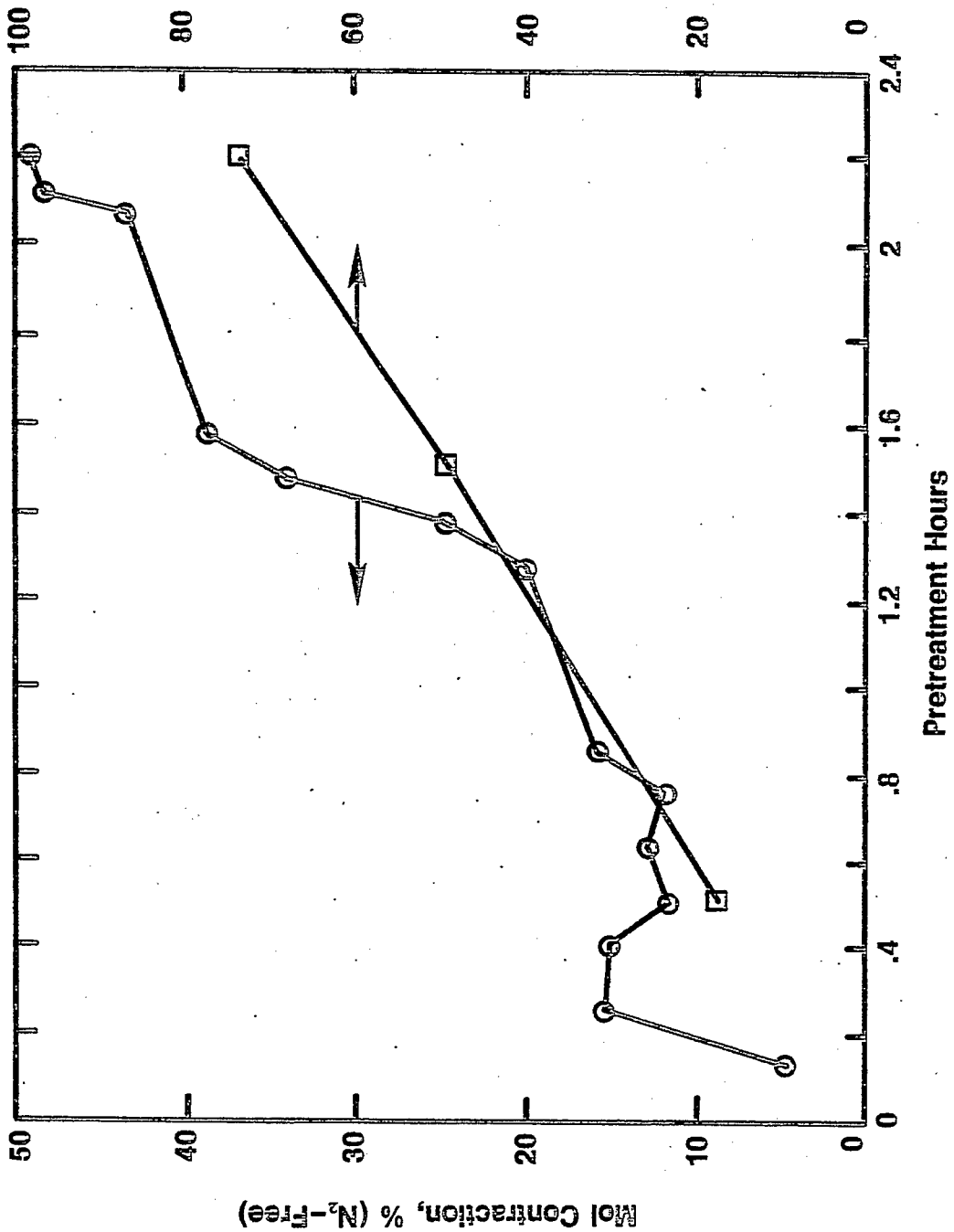


Figure 4

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

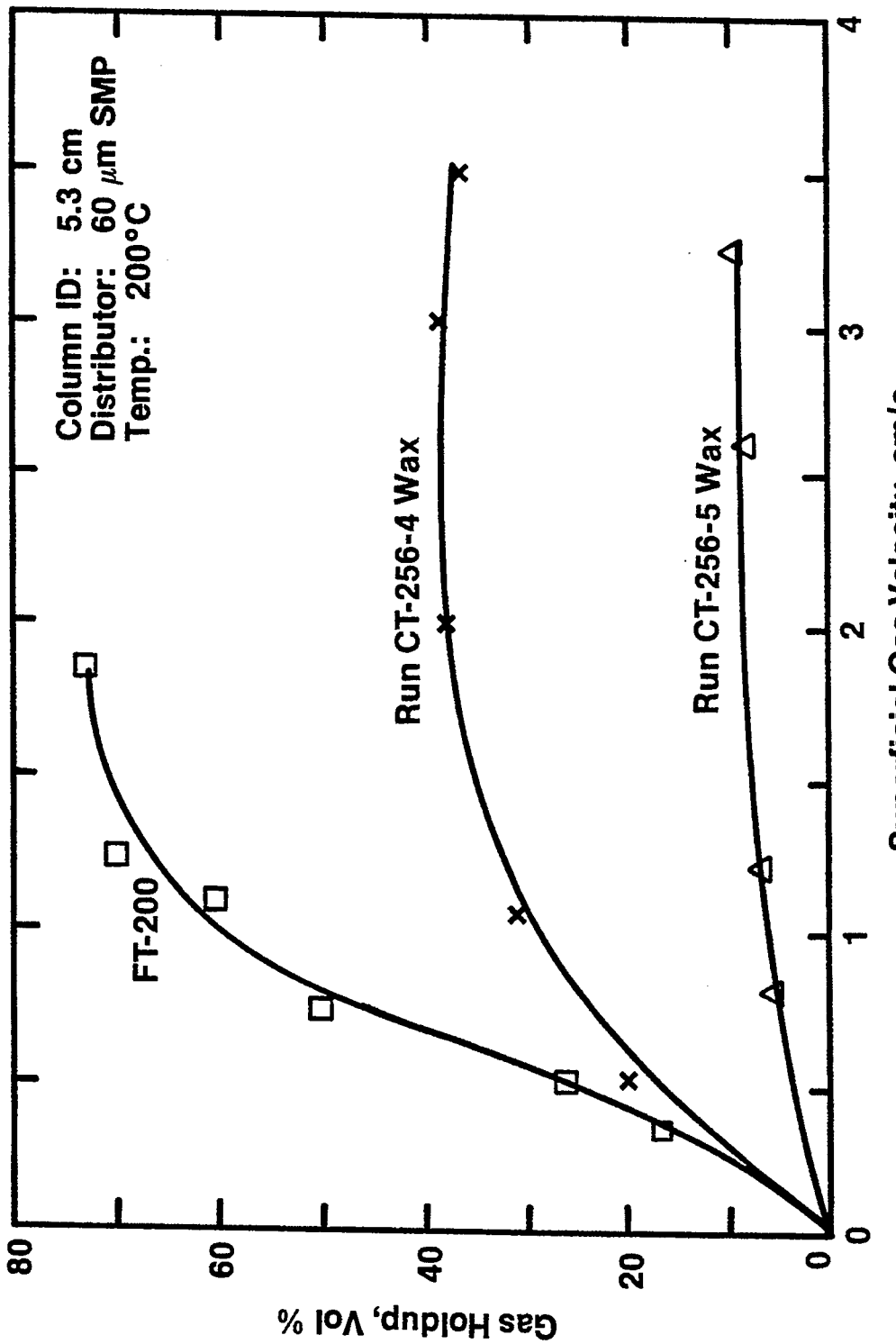


Figure 5

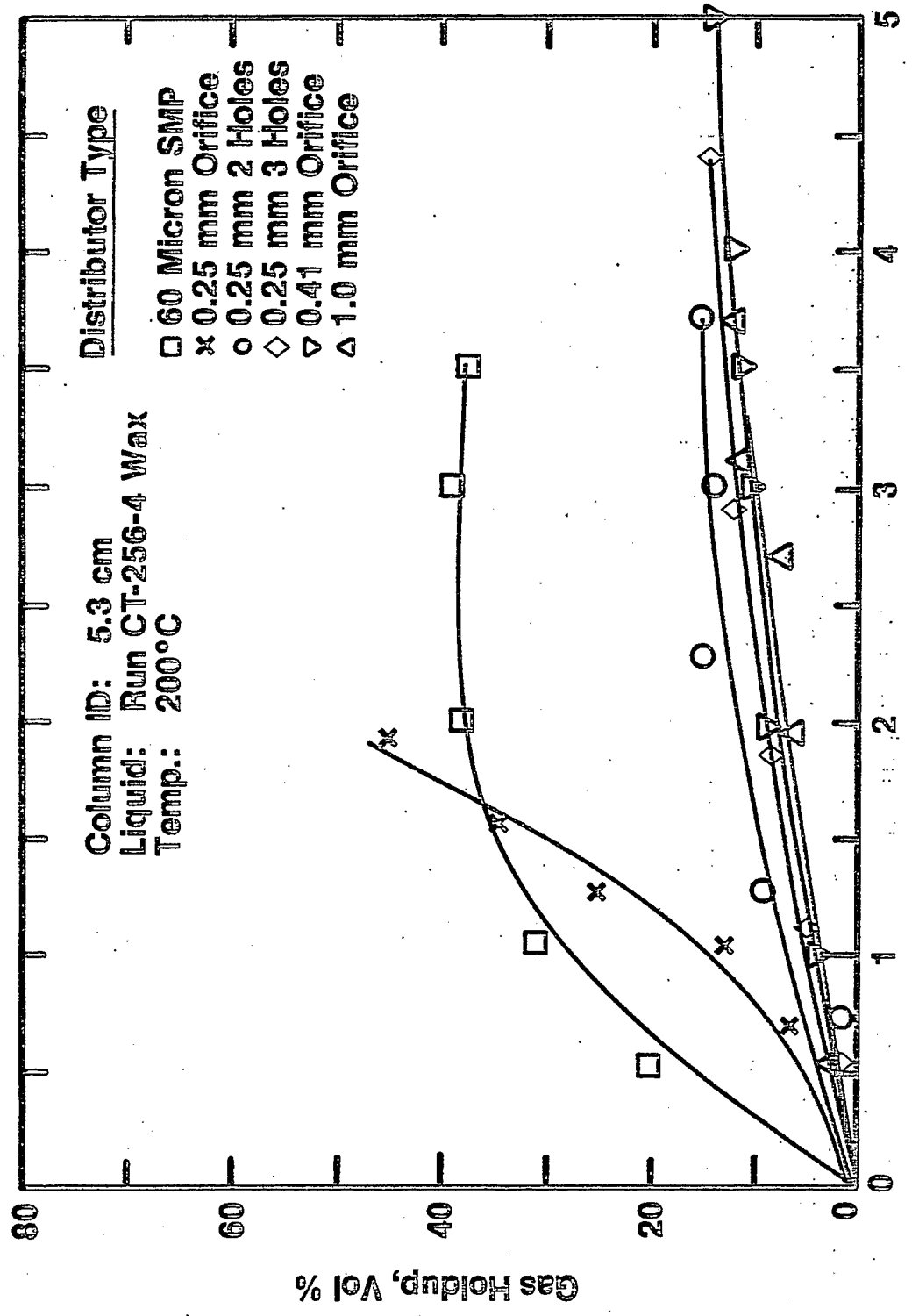

GAS HOLDUP IN SHORT HOT-FLOW COLUMN
Column ID: 5.3 cm
Liquid: Run CT-256-4 Wax
Temp.: 200°C
Distributor Type
□ 60 Micron SMP
× 0.25 mm Orifice
○ 0.25 mm 2 Holes
◇ 0.25 mm 3 Holes
▽ 0.41 mm Orifice
△ 1.0 mm Orifice
Gas Holdup, Vol %
Superficial Gas Velocity, cm/s
0
20
40
60
80
0
1
2
3
4
5

Figure 6

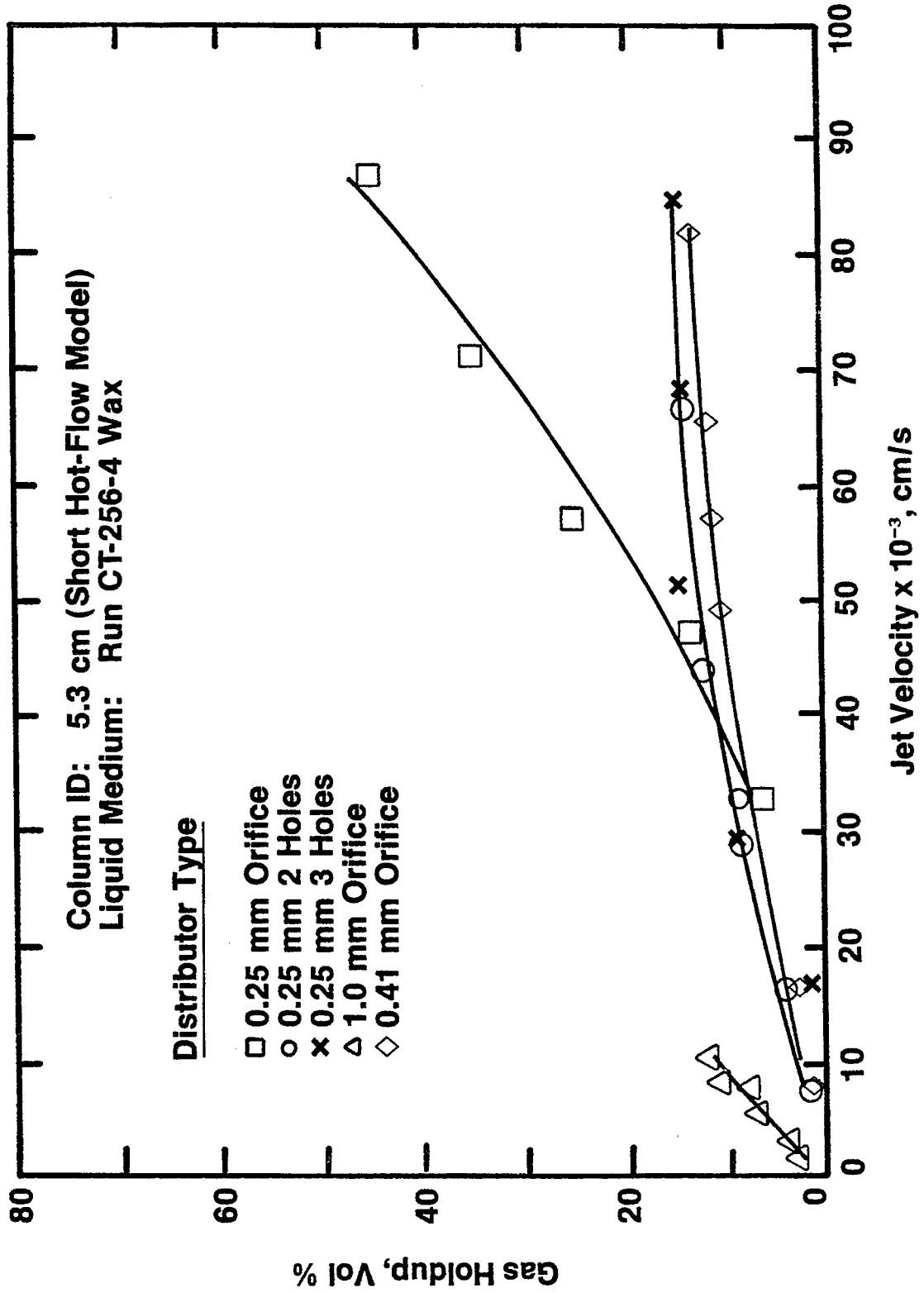

GAS HOLDUP vs. JET VELOCITY
Column ID: 5.3 cm (Short Hot-Flow Model)
Liquid Medium: Run CT-256-4 Wax
Distributor Type
□ 0.25 mm Orifice
○ 0.25 mm 2 Holes
× 0.25 mm 3 Holes
△ 1.0 mm Orifice
◇ 0.41 mm Orifice
Gas Holdup, Vol %
0
20
40
60
80
Jet Velocity x 10⁻³, cm/s
0
10
20
30
40
50
60
70
80
90
100

Figure 7

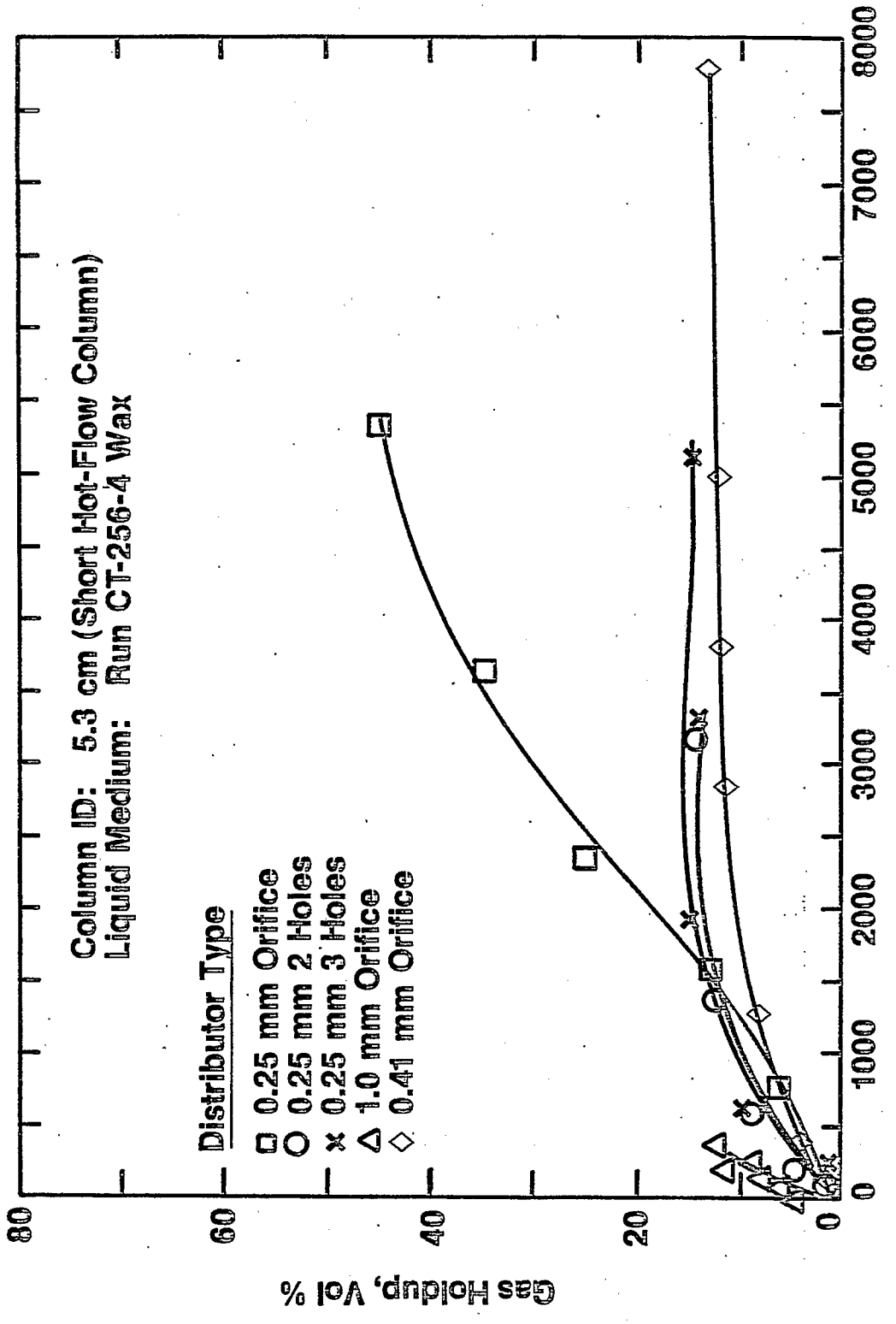

GAS HOLDUP vs. WEBER NUMBER
Column ID: 5.3 cm (Short Hot-Flow Column)
Liquid Medium: Run CT-256-4 Wax
Distributor Type
0.25 mm Orifice
0.25 mm 2 Holes
0.25 mm 3 Holes
1.0 mm Orifice
0.41 mm Orifice
Gas Holdup, Vol %
Weber No.
0
20
40
60
80
0
1000
2000
3000
4000
5000
6000
7000
8000

Figure 8

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

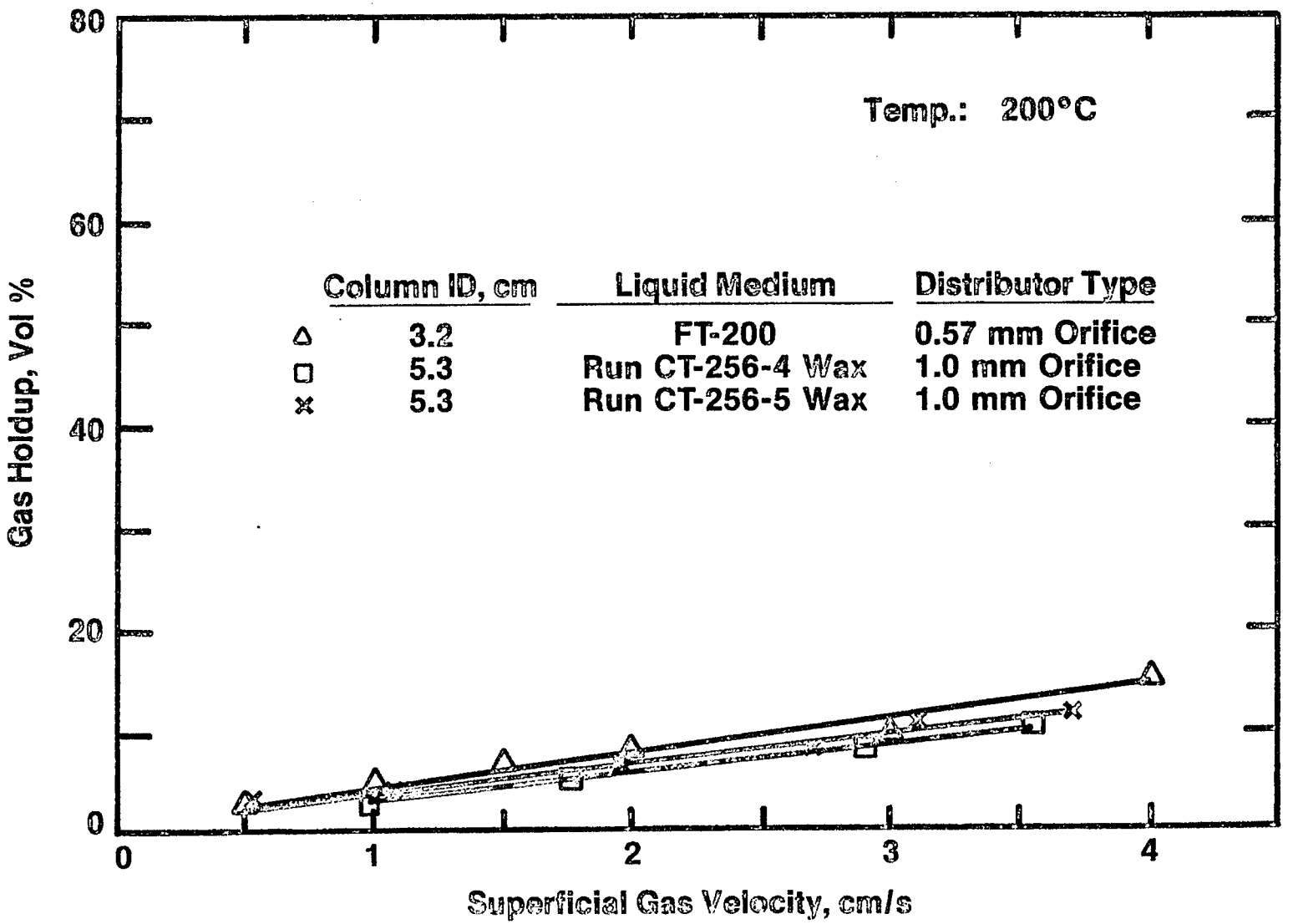


Figure 9

GAS HOLDUPS WITH HEXADECANE
IN TALL HOT-FLOW COLUMN
(5.1 cm COLUMN ID)

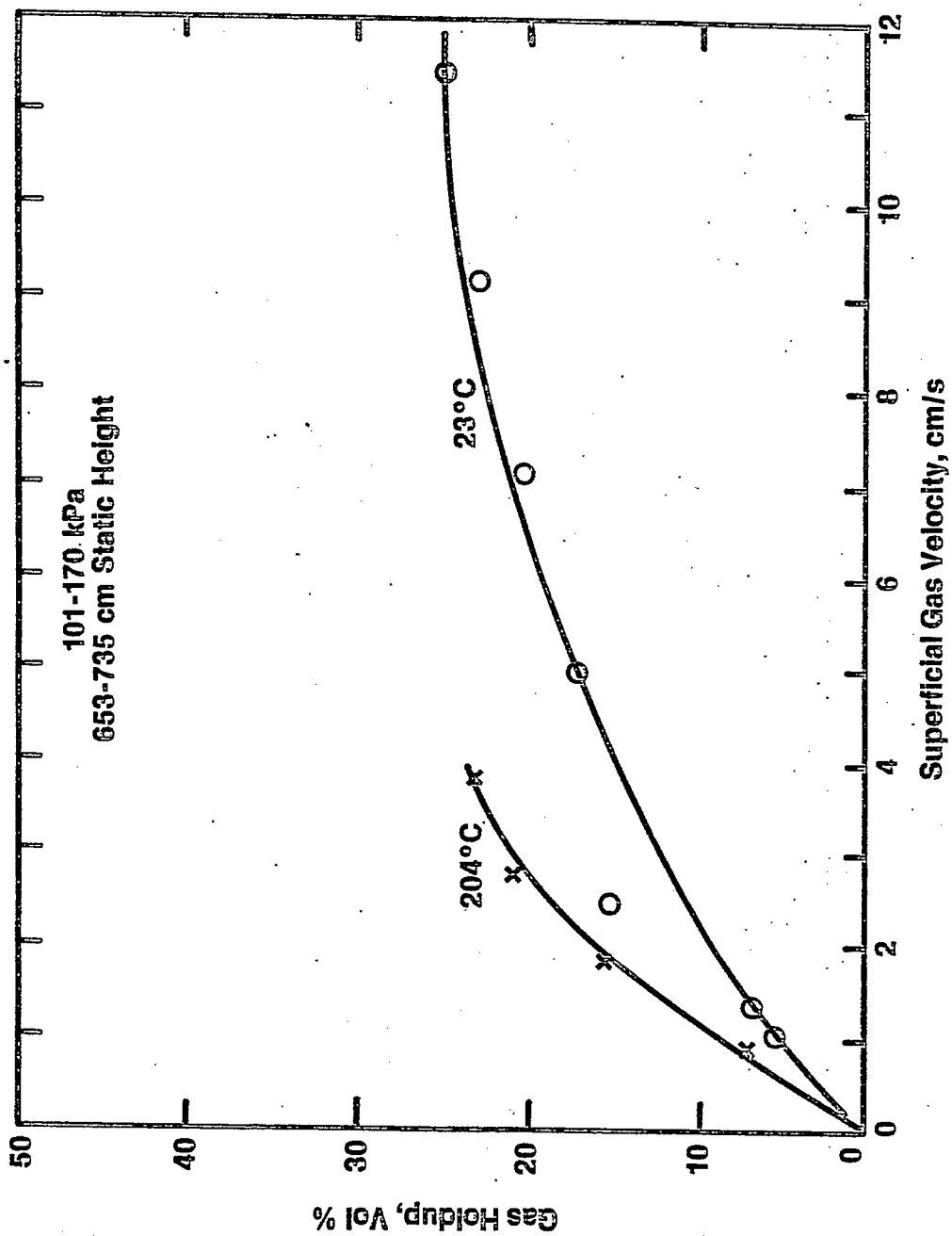


Figure 10

EFFECT OF DISTRIBUTOR TYPE

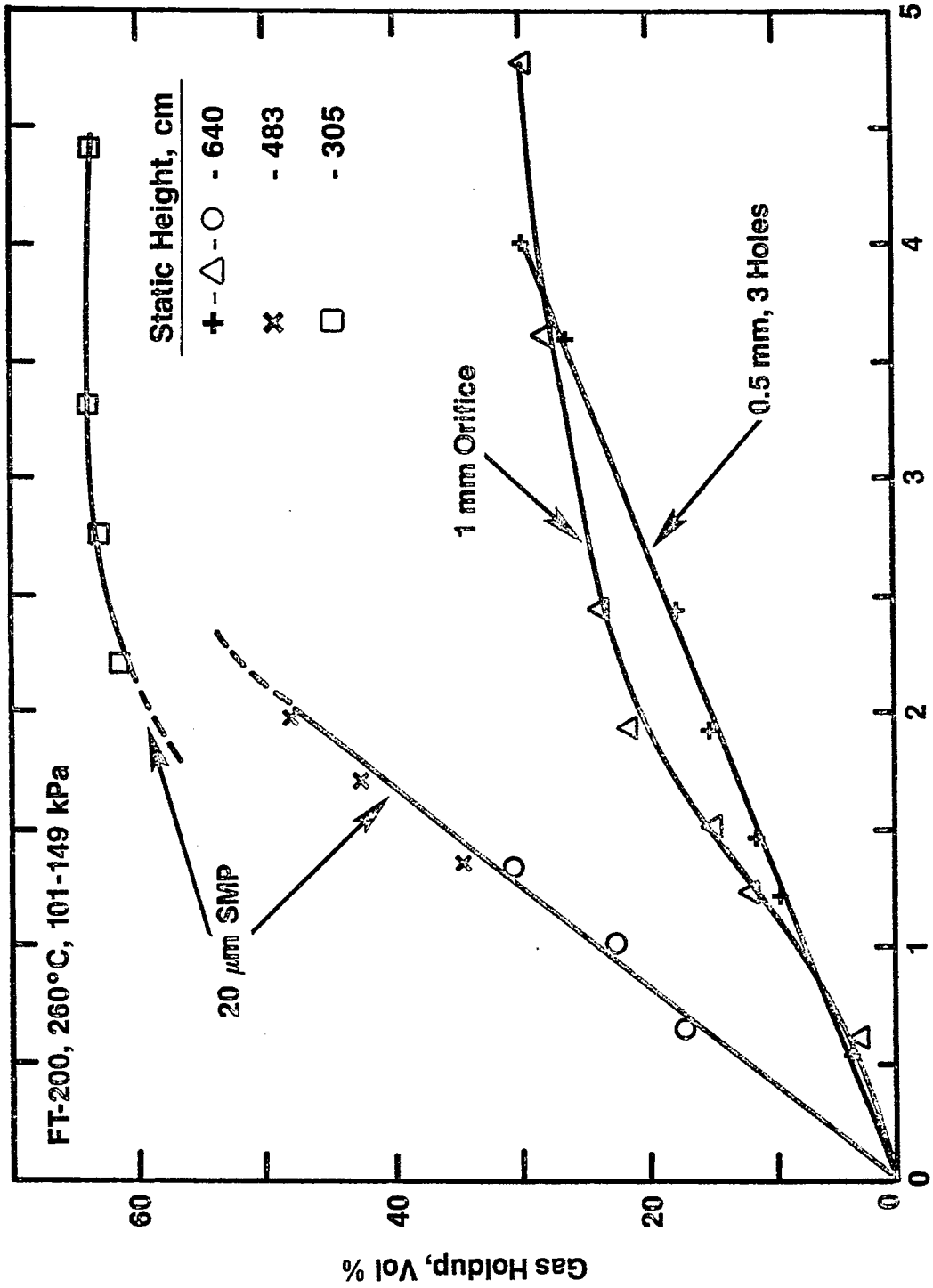


Figure 11

COMPARISON OF ORIFICE DISTRIBUTORS

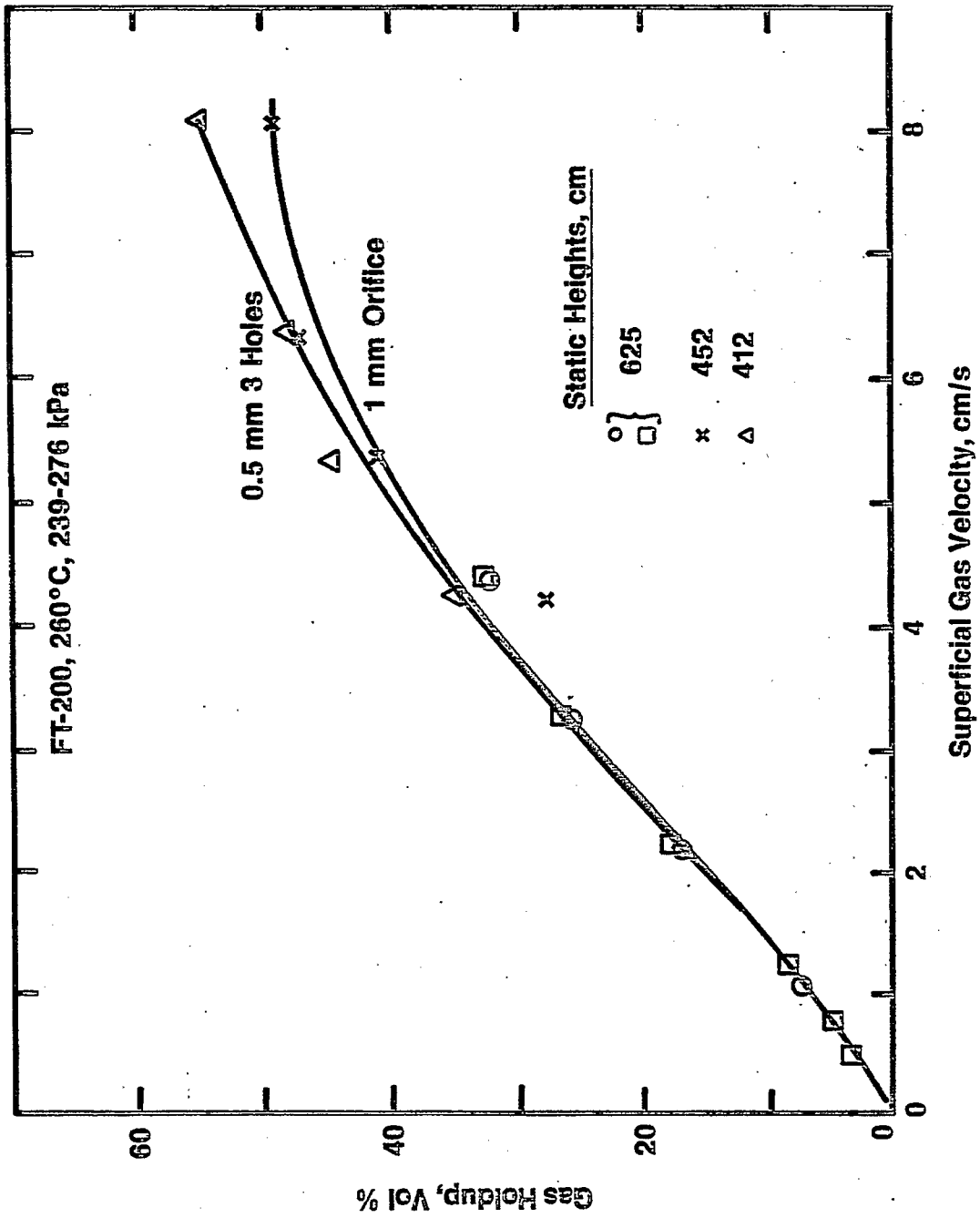


Figure 12

COMPARISON OF ORIFICE DISTRIBUTORS

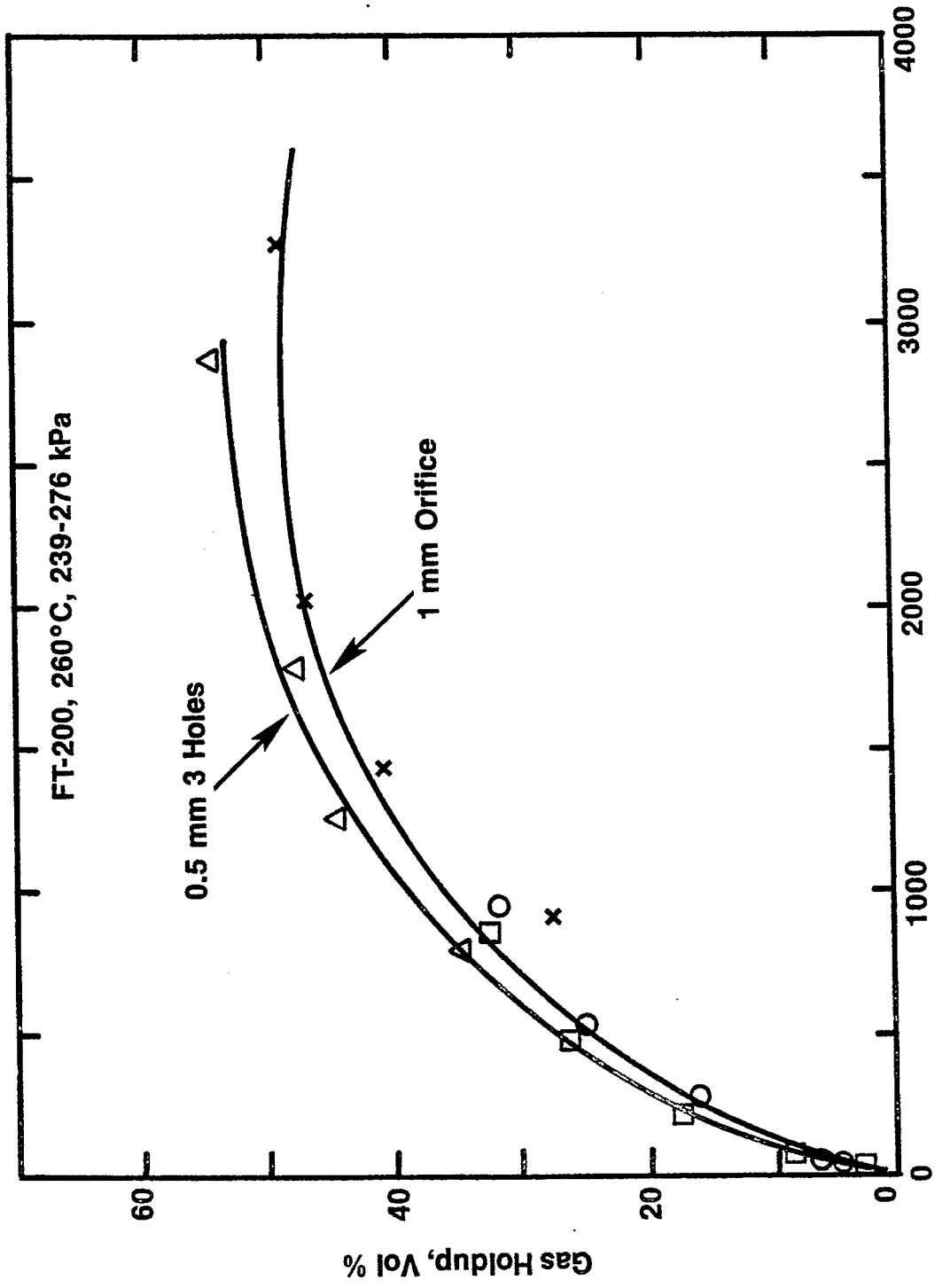


Figure 13

COMPARISON OF ORIFICE DISTRIBUTORS

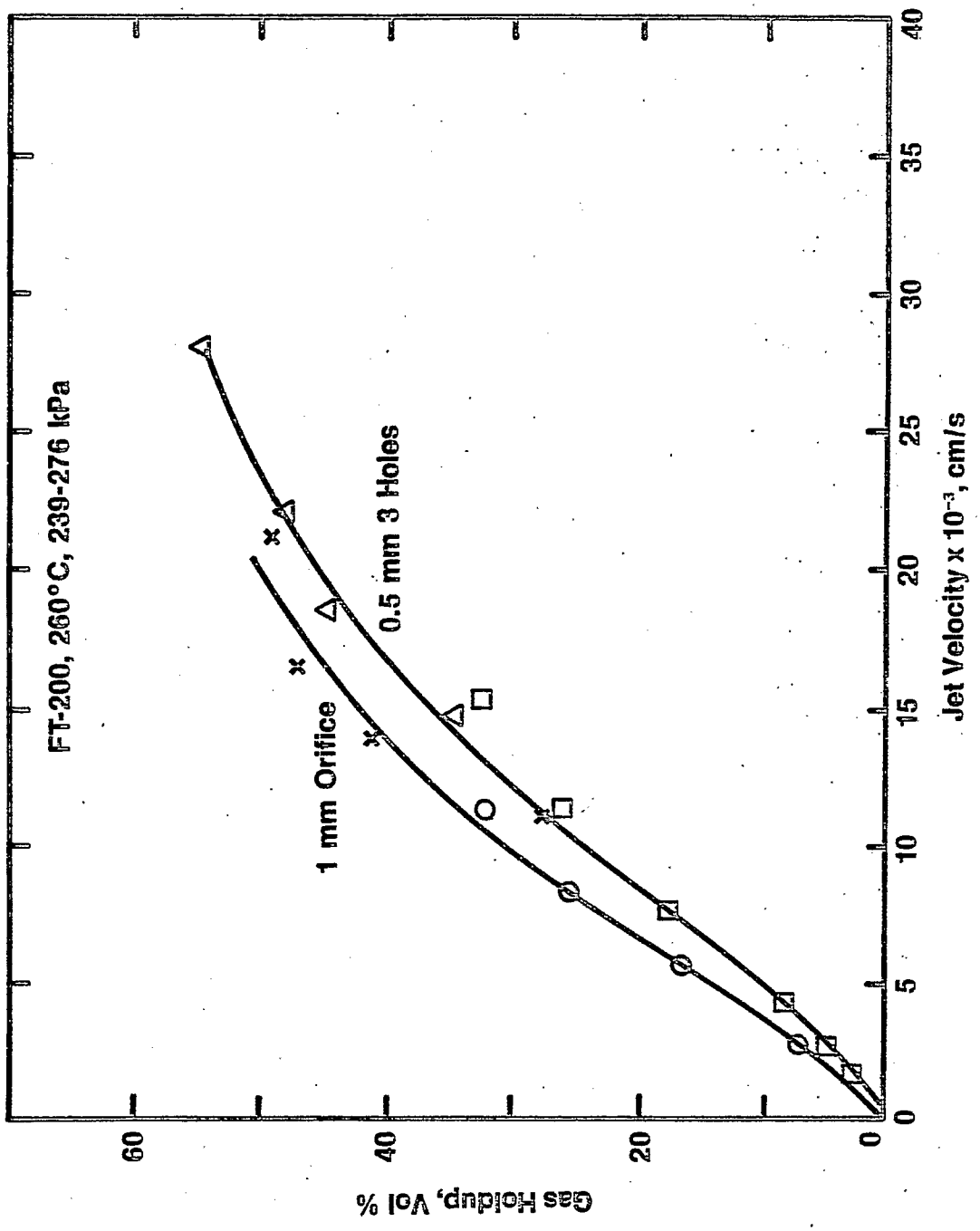


Figure 14

EFFECT OF STATIC LIQUID HEIGHT

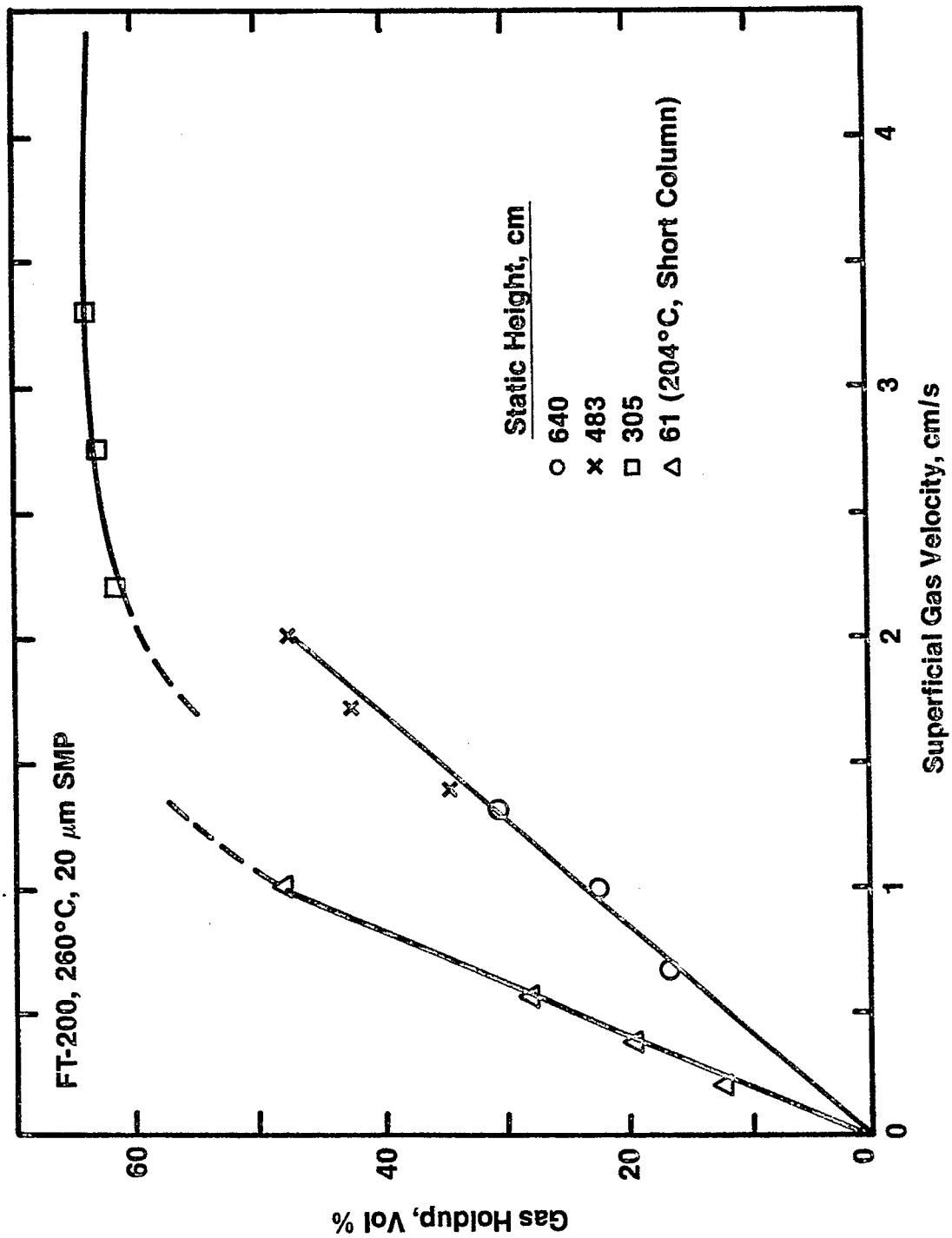


Figure 15

EFFECT OF STATIC LIQUID HEIGHT
(1 mm ORIFICE)

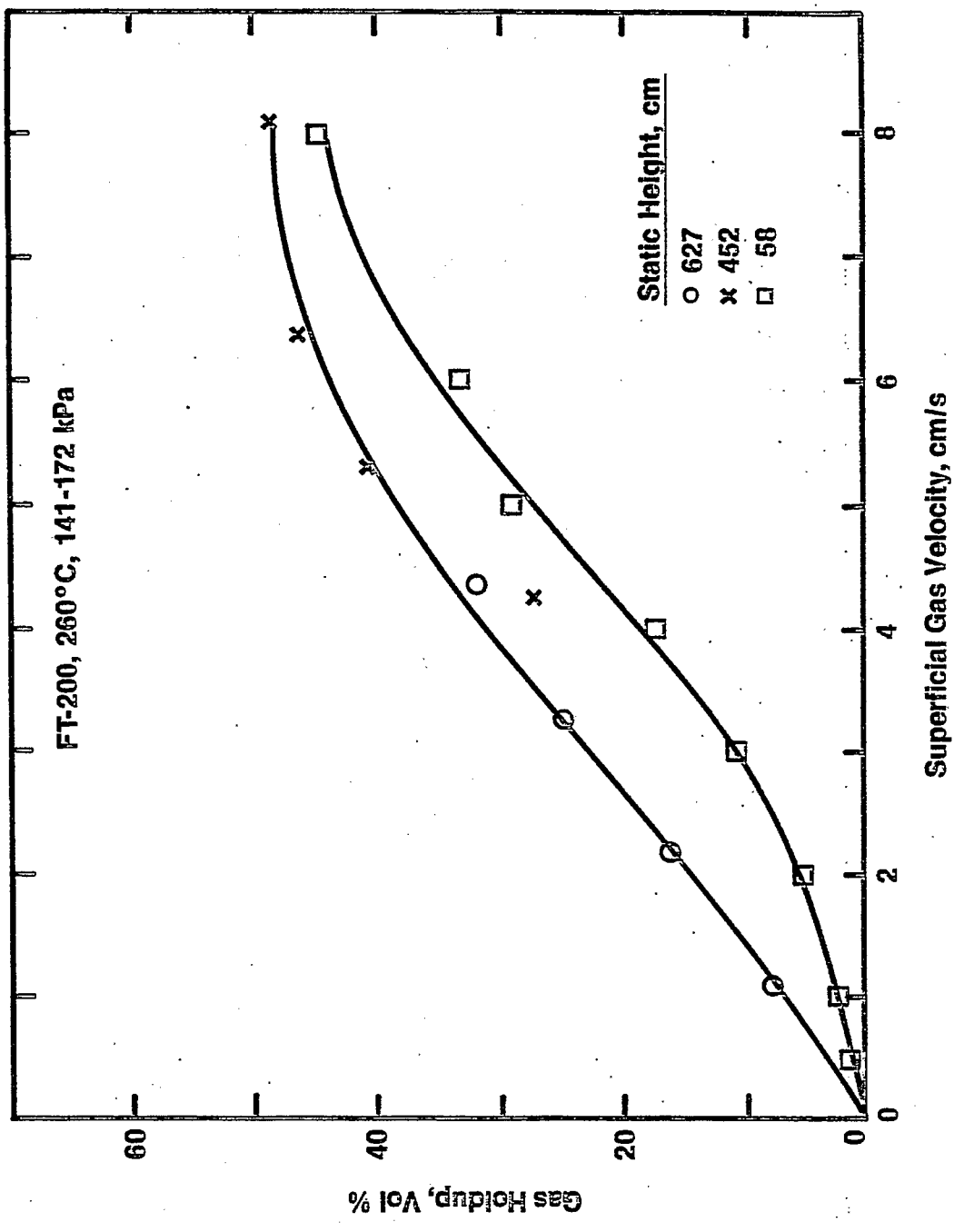


Figure 16

EFFECT OF PRESSURE (20 μm SMP)

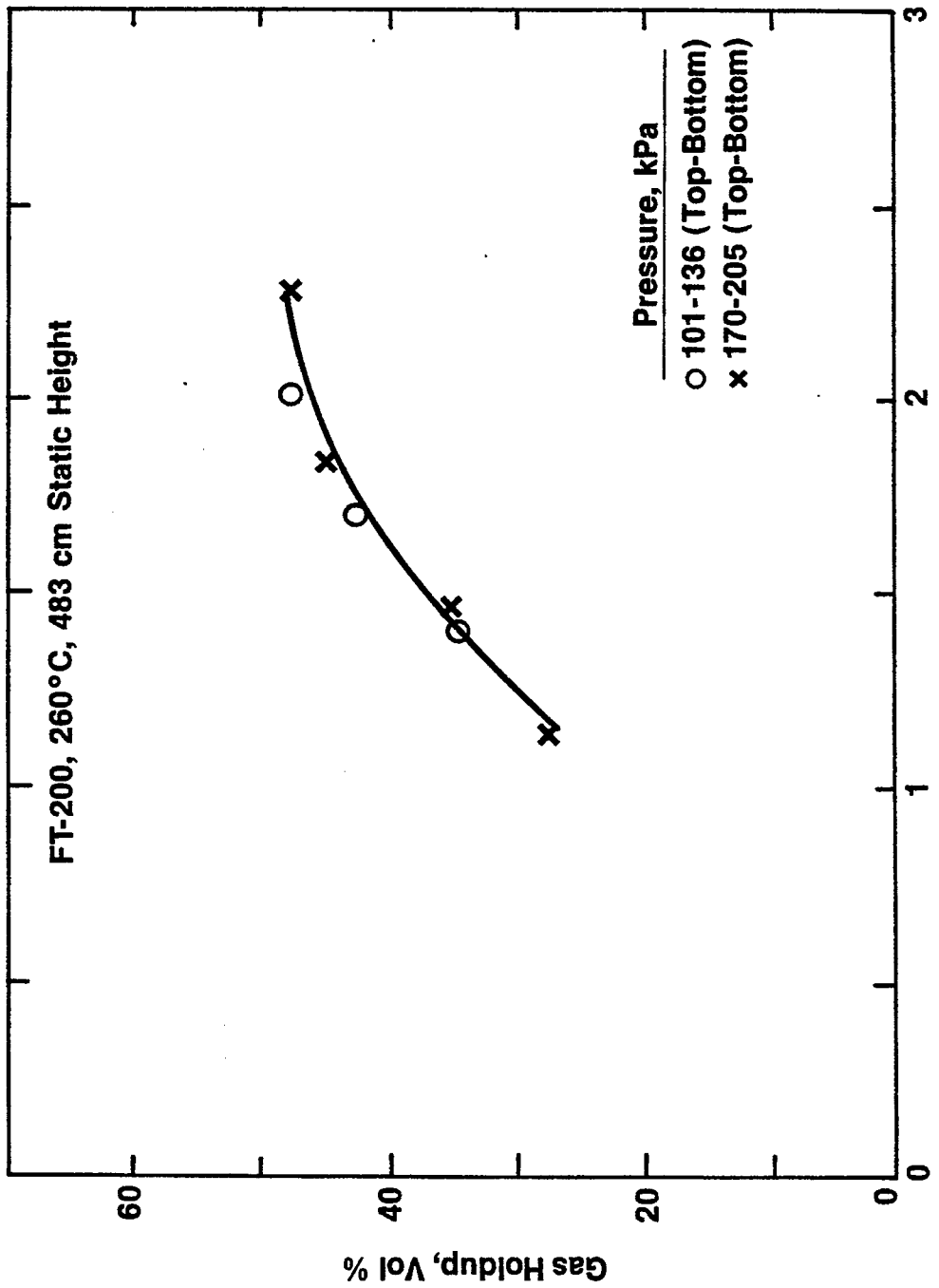


Figure 17

EFFECT OF PRESSURE (1 mm ORIFICE)

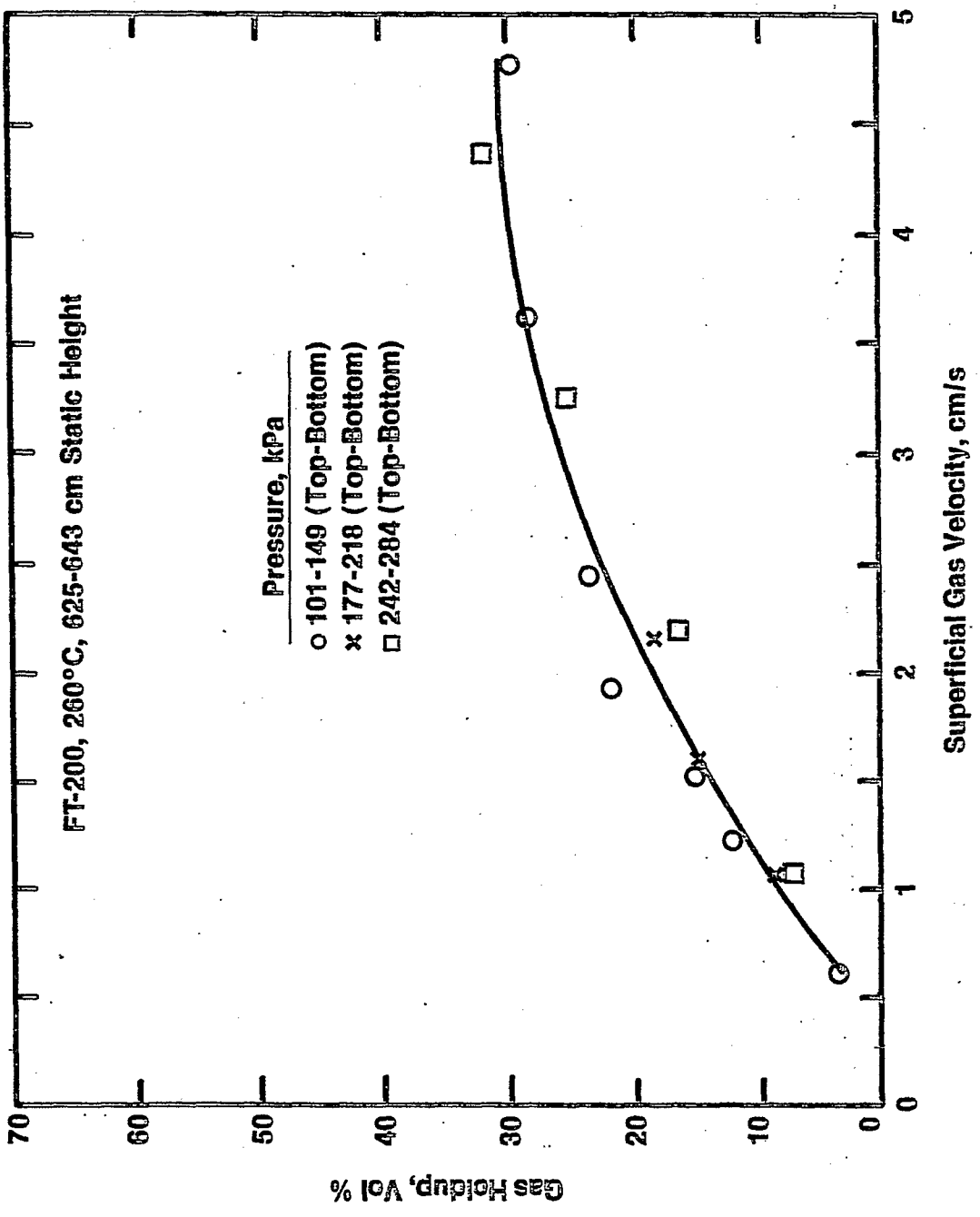


Figure 18
EFFECT OF TEMPERATURE ON GAS HOLDUP
(20 μm SMP)

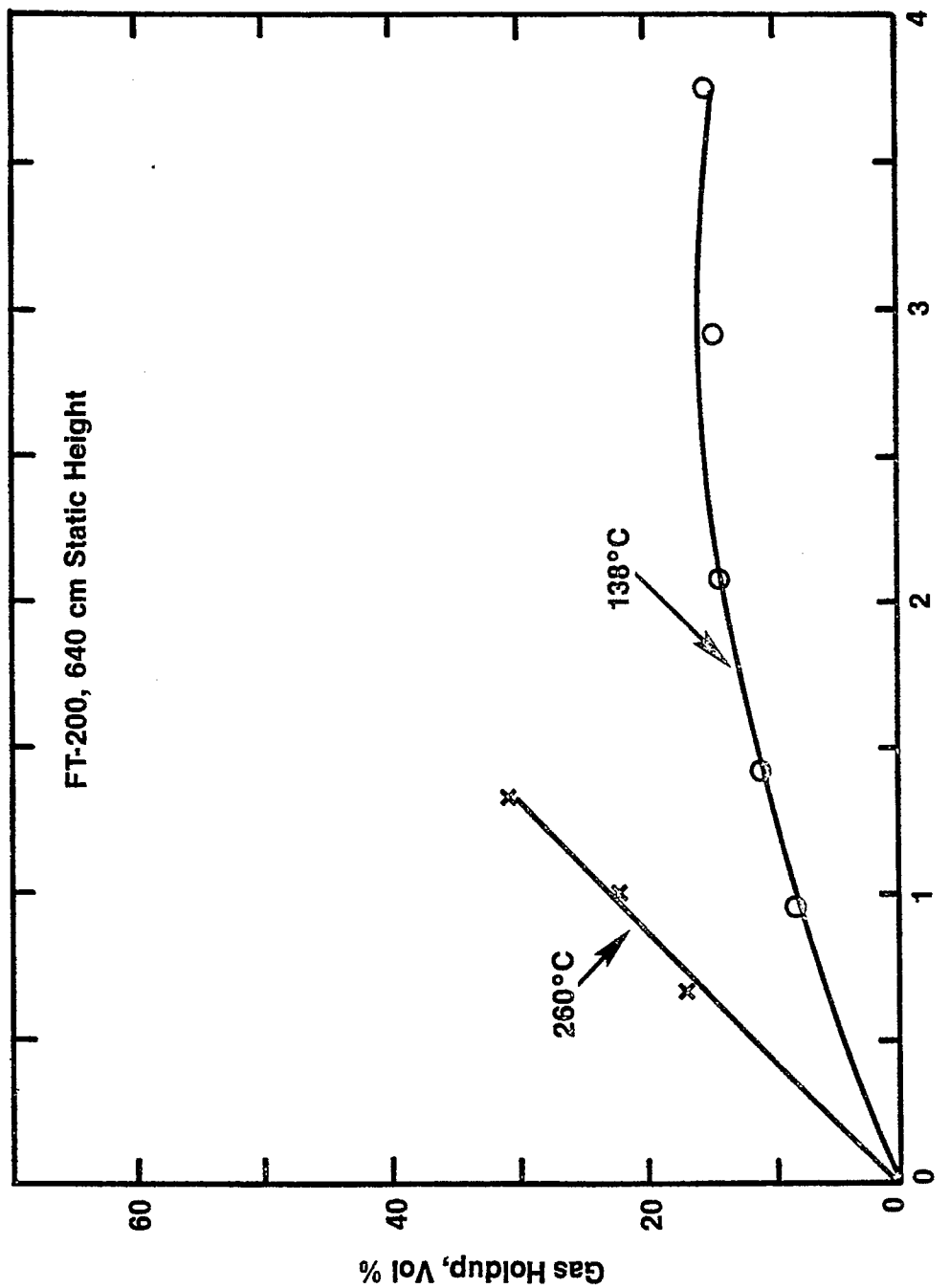
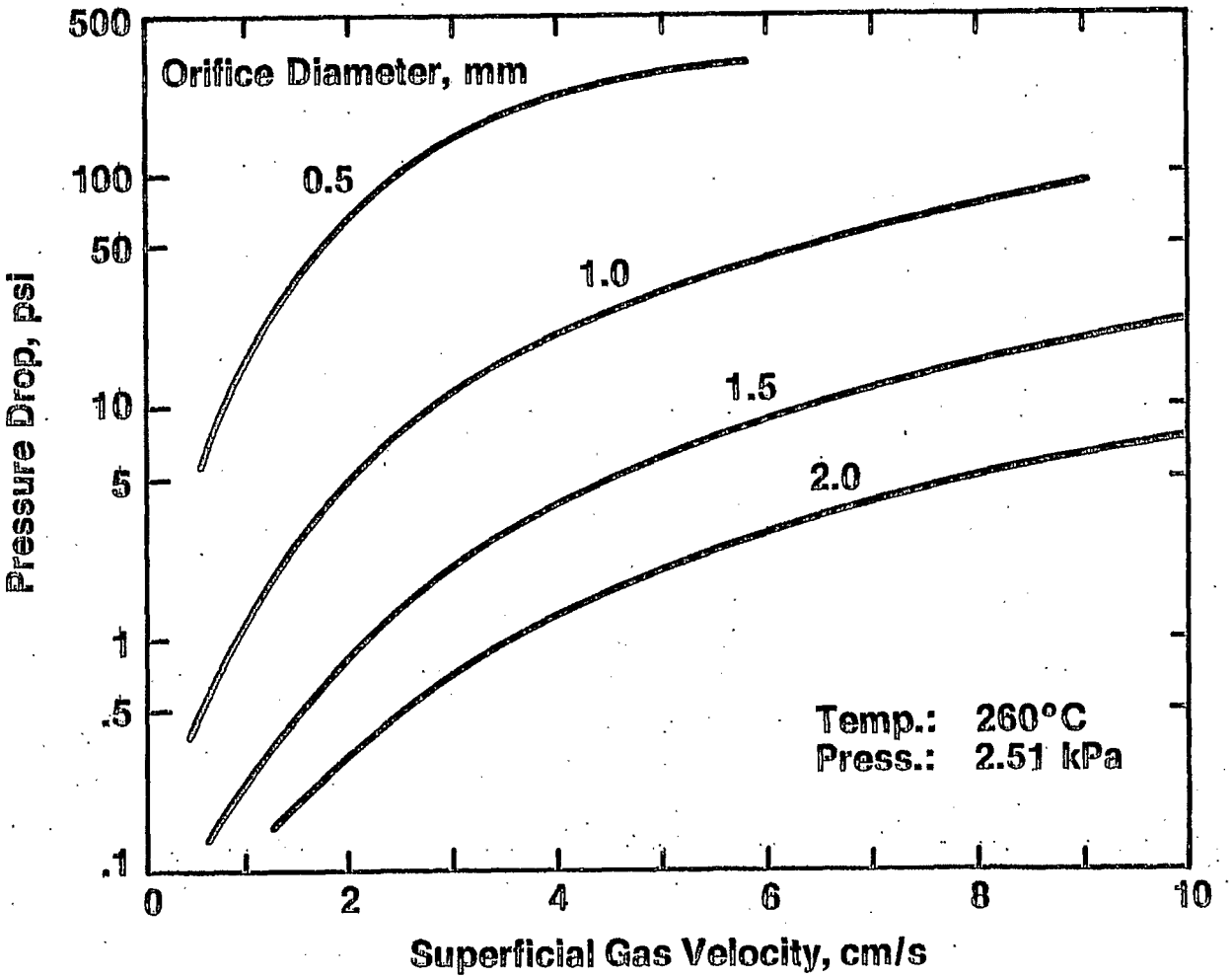


Figure 19

CALCULATED PRESSURE DROPS ACROSS ORIFICE DISTRIBUTORS IN PILOT PLANT COLUMN



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