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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS. QUARTERLY REPORT, 1 OCTOBER-31 DECEMBER 1983

MOBIL RESEARCH AND DEVELOPMENT CORP.
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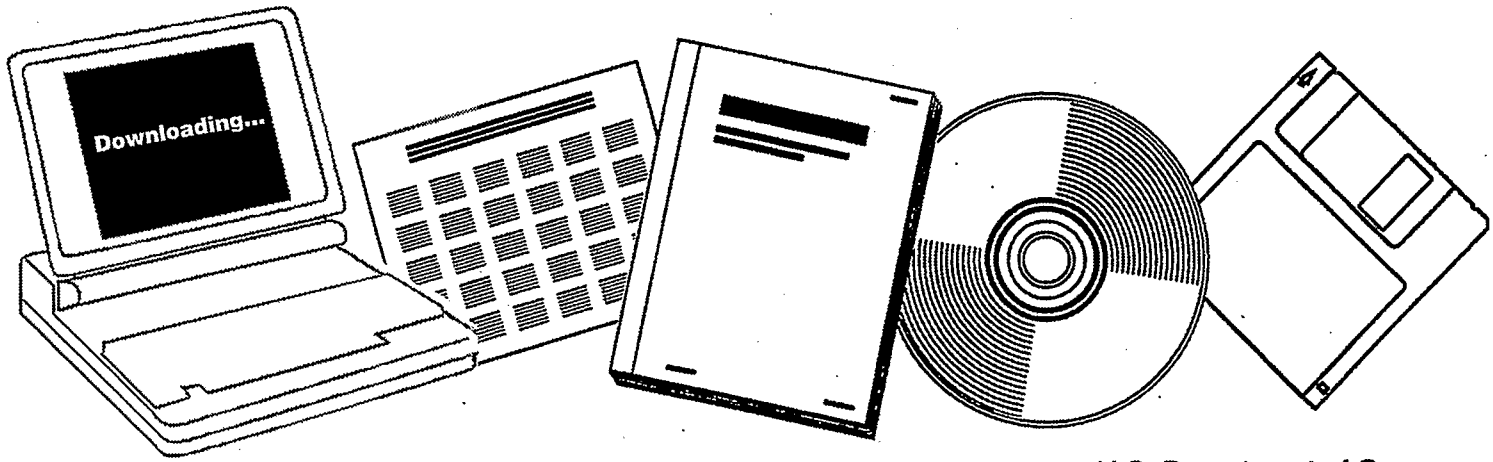

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TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS

QUARTERLY REPORT FOR THE PERIOD
1 OCTOBER - 31 DECEMBER, 1983

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I. Abstract

The status of the Slurry Fischer-Tropsch two-stage pilot plant and the two tall hot-flow models is discribed. A new Fischer-Tropsch catalyst was evaluated in a small bubble-column reactor, and the run is detailed in this report. Also, a new device for measuring the particle size distribution of catalyst was tested.

Photographs of bubble patterns in the small hot-flow models are presented, qualitatively illustrating the effects of orifice and sintered-metal-plate feed-gas distributors, and the superficial gas velocity. In addition, Fischer-Tropsch reactor-wax from the two-stage BSU was used in the hot-flow studies for the first time, and the results verify that different waxes can behave very differently in similar systems.

Finally, a mathematical model was used to evaluate a series of continuous stirred-tank Fischer-Tropsch reactors as an alternative to bubble-column reactors.

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 ratio synthesis gas, of the type produced in a coal gasification system, into maximum yield of transportation fuels. To accomplish this objective, the following tasks will 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 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

The two-stage pilot plant (Unit CT-256) is currently being modified to improve DP-measurements, Fischer-Tropsch reactor-wax separation, and to allow steam co-feeding to the slurry reactor. Work will be completed by mid-February. Construction of the two large hot-flow bubble-columns (5.1 and 10.2 cm ID x 9.1 m height) began in October and was nearly completed at the end of this Quarter. Shakedown will begin in January.

A new Fischer-Tropsch catalyst, designated as I-D (containing $Fe/Cu/K_2CO_3$), was evaluated in a small bubble-column reactor (2.7 cm ID x 1.9 m height). The catalyst performed well, producing methane + ethane yields of 1.8 to 3.8 wt % of hydrocarbons produced, and reactor-wax yields of 60 - 80 wt % over 385 hours. The space velocity, however, was difficult to determine, possibly due to catalyst losses. In-situ aditions of fresh F-T catalyst were also carried out, resulting in substanial increases in H_2+CO conversion with little effect on the methane + ethane yield. However, the conversion increases were lower than expected.

A particle size analyzer which can be used on slurry Fischer-Tropsch catalysts was identified and tested with two standard samples. The results showed good agreement with size distributions measured by a standard method. Two samples, one fresh and the other spent F-T catalyst, were sent for analysis.

Scoping hydrodynamic studies continued in a short hot-flow glass column (5.3 cm ID x 2.2 m height). The F-T reactor-wax from Run CT-256-5 gave gas holdups many times lower than those produced by an F-T derived paraffin wax, FT-200 (also known as Vestowax EH-100)[1] Also, in the small bubble-column reactor described earlier, a reactor-wax from Run CT-256-4 gave holdups 2-3 times lower than the paraffin wax FT-200. This illustrates that not all reactor-waxes behave alike.

In addition, photographs of bubble flow patterns are presented here, showing that an orifice distributor gives wider bubble size distributions than does a sintered-metal plate. The photos were taken during the hot-flow studies described in the last Quarterly Report.

Lastly, the concept of using a series of CSTR's

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

(continuous stirred-tank reactors) as an alternative reactor design was examined using a mathematical model. Using the kinetics obtained at the beginning of Run CT-256-3 as a basis for case calculations at high H_2+CO conversion (86 mol %), it was found that:

- the benefit from the elimination of the mass-transfer resistances is rather minor because the overall mass-transfer resistances in the bubble-column base case is small.

- The major penalty of a CSTR system is the back-mixing which results in a substantial increase of the total reactor volume even after the benefit of eliminating the mass-transfer resistance is included. However, the extent of this penalty can be reduced (as indicated by a decrease in the total reactor volume) by increasing the number of the CSTR's in series. Nevertheless, for systems with three or more reactors, the changes in the total reactor volume are rather small.

- With the same catalyst loading, the total reactor volume of seven CSTR's in series is about equal the volume of a single bubble-column reactor.

IV. Detailed Description of Technical Progress

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

1. Bench-Scale Unit Modifications - Status

The design of modifications to the two-stage bench-scale pilot plant (Unit CT-256) has been completed. All equipment has been purchased. The construction has started and is expected to be completed by mid-February. 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 Confidential Appendix of this report.

The new DP-cell set-up shown in Figure 1 will consist of six purgeless DP-cells, with their high pressure sides contacting the reactor slurry. This will eliminate the plugging which was previously experienced in the purged DP-legs, and also the nitrogen dilution effect. The low pressure sides of the DP-cells will be equilibrated with the pressure at the reactor top. Thus, each DP-cell will measure the static pressure of the slurry above it. The resulting small pressure prop across the cell membrane assures accurate DP-readings.

Steam co-feeding will allow testing of the in-situ water-gas shift concept. The hardware consists essentially of a pump feeding water at constant rate to a vaporizer-superheater. From there, the steam generated is mixed with the feed synthesis gas before entering the slurry reactor pre-heater.

2. Studies in Support of Process Studies in The Bench-Scale Unit

a. Preliminary Evaluation of a New Fischer-Tropsch Catalyst in a Small Bubble-Column Reactor

A new F-T catalyst, designated I-D (containing $Fe/Cu/K_2CO_3$), was evaluated using a 5.7 cm ID x 1.9 m tall bubble-column reactor (Unit CT-225). This unit does not contain

a second-stage ZSM-5 reactor. The run, designated as CT-225-112, was started on December 6, 1983, and concluded after sixteen days on stream.

The following are major highlights of the run:

- The catalyst was activated at the same conditions as those for synthesis (250°C, 2.17 MPa).
- The ranges of operating conditions were:

Temperature, °C	250-255
Pressure, MPa	2.17
H_2/CO molar feed ratio	0.67
Superficial feed-gas velocity cm/s	0.9-1.8

- The H_2+CO conversion ranged from 23 to 58 mol %, and the methane + ethane yield from 1.7 to 3.5 wt % of the hydrocarbons produced.
- The reactor-wax yield was high, ranging from 60 to 80 wt % of the hydrocarbons produced.
- In-situ additions of fresh catalyst increased conversion, but not by the expected amounts. This may have been due to undetected catalyst losses.

Run CT-225-112 started with a slurry containing 136 g of Catalyst I-D, and reactor-wax from Run CT-256-4. Aside from a general evaluation, it was desired to observe the catalyst performance at high pressures, where commercial reactors may operate. Also, it would be commercially desireable for a catalyst to be able to activate without a separate pretreatment step. For these reasons, the catalyst was brought on stream at 2.17 MPa (300 psig) pressure and 250°C temperature. The space velocity was 4.5 NL/gFe-hr, which allows for a high gas throughput.

Figure 2 shows the conversion and methane and ethane selectivities for the run. Over the first 22 hours, the conversion rose to 41%, while the methane + ethane selectivity was maintained at 2-3 wt % of the total hydrocarbons produced. At that point, the reactor-wax build-up necessitated its removal from the unit.

To remove reactor-wax from the unit CT-225, a batch settling system similar to that used in Runs CT-256-4 and 5 was employed. The settling pot was a 300 cm^3 pressure-vessel with a dip-tube extending halfway down for decanting the wax. The pot was situated 30 cm below the level of the reactor bottom. Slurry was brought from a drain at the 1.5 m level to fill the pot. When settling was completed (usually 45 minutes), the upper layer of the wax was decanted and the remainder pressurized quickly back into the reactor bottom. A maximum of about 160 cm^3 of wax could be decanted in each batch, in contrast with the maximum reactor slurry capacity of about 1500 cm^3 (including the disengagement zone).

The first reactor-wax withdrawal at 22 HOS resulted in the accidental removal of 100 g of concentrated slurry from the settling pot. This was immediately placed back into the pot and pressurized into the reactor. Only 50 g of reactor-wax was decanted. However, some damage to the catalyst may have occurred due to its exposure to the air. This may explain the abrupt leveling-off of the H_2+CO conversion after 22 HOS.

Reactor-wax was withdrawn once every one to two days on the average. Figure 3 is a plot of the cumulative reactor-wax withdrawn. The slope of this curve, combined with the conversion data, indicates that the reactor-wax yield averaged from 60 to 80 wt % of the hydrocarbons produced. Solids analyses were done on each batch of wax removed.

Also, make-up fresh catalyst was added twice in-situ, at 238 and 333 HOS. On this basis the space velocity was determined. At the run's end, however, extensive solids analysis on the slurry and subsequent reactor rinses indicated that there was only about 40% of the original and added catalyst in the slurry. This leads to the possibility that the catalyst deposited in the settling pot or another part of the system undetected. In any case, this result made the space velocity a question mark for all but the very beginning of the run.

The difficulty we had in evaluating the activity of the catalyst in this small bubble-column is illustrated by the conversion at 20 and 200 HOS. Based on feed-gas flowrate and the estimated catalyst inventory obtained by deducting the catalyst loss in the withdrawn wax, the estimated space velocity at 200 HOS was 3.4 NL/gFe-hr, or 75% of that at 20 HOS. In addition, the temperature was raised by 5°C. This should have resulted (based on a first-order kinetic estimate) in H_2+CO conversions of 65-75 mole %. The actual conversion, (about 42 mol %) however, was roughly the same at both times.

The methane + ethane yield during the run, however, remained low, ranging from 1.7 to 3.5 wt % of hydrocarbons produced. This shows that the catalyst which was active was aging very slowly, much the same as did Catalyst I-C in run CT-256-5, which was also run at 250°C most of the time. During previous catalyst evaluations, we have observed that a drop in H_2+CO conversion due to catalyst aging is usually accompanied by a rise in the methane + ethane yield. This also supports the catalyst-loss hypothesis to explain the decreased H_2+CO conversion.

At 275 HOS, a large decrease in the H_2+CO conversion occurred. This was probably due to the following reasons:

- The conversion drop came after a series of five reactor-wax withdrawals which totalled nearly one-half the reactor contents. We have already seen that catalyst losses may have occurred during reactor-wax removals.

- After the fifth withdrawal, the concentrated slurry was accidently left in the settling pot for ten hours, possibly in contact with air for some of that time. Previous experience has shown that F-T catalyst can de-activate under such conditions. The catalyst in the pot may have been 30% of the total catalyst in the reactor.

In-situ additions of fresh catalyst were carried out at 238 and 333 HOS. The following conslusions can be drawn:

- The H_2+CO conversion increased both times, the first time by 22% (63 g catalyst added) and the second time by 35%(50 g catalyst added). By comparison, conversion in Run CT-256-4 increased by only 5% after about a 50% increase in catalyst loading due to in-situ addition of fresh catalyst I-B.

- The conversion increases were not as high as was expected based on the proportions of fresh catalyst added. This may have been due to incomplete activation due to lower H_2 and CO partial pressures.

- The methane + ethane yield was not significantly affected.

b. Evaluation of a Method for Measuring F-T Catalyst Size Distribution

The catalyst particle size distribution in a F-T slurry is essential for determining the catalyst settling characteristics. We identified a particle size analyzer (Sedigraph 5000E made by Micromeritics, Inc.) which can be applied to slurry F-T catalysts. This analyzer uses a low intensity X-ray beam to measure the size of solid particles settling in a liquid, and it has the following important features:

- The instrument limit on the minimum particle size is 0.1 μm, which allows detection of the small particles in F-T slurries.
- The catalyst sample can be suspended in any hydrocarbon liquid,provided the density and viscosity of the liquid at room temperature are known.

The second feature may be especially useful, since catalyst can be separated from the reactor-wax by diluting the slurry with solvent and centrifuging several times.

The Sedigraph 5000E analyzer was used to analyze a sample of fresh F-T catalyst I-B (Figure 4). The mean particle size was 4.2 μm, the range being .15-40 μm. A sample of spent catalyst used in Run CT-256-3 (after 86 DOS) and separated from reactor-wax by centrifuging in toluene, has been sent to Micromeritics for analysis. Preliminary results indicate that the particles are smaller than 3 μm, and a significant portion is in the submicron range. Based on this, it appears that there was substantial disintegration during that run.

To test the accuracy of the Sedigraph 5000E analyzer, two standard samples from the Community Bureau of Reference, Brussels (obtained through Gilson Co., Inc.), were analyzed by a standard method. These samples have quartz particles in the range .35-3.5 μm and 1-20 μm, respectively. Table 1 shows the small discrepancies between the results of the Sedigraph 5000E analyzer and the data reported on the Certificate of Measurement of the standards. Part of these discrepancies may be due to the inhomogeneity of a small sample obtained from the original standard sample.

3. Future Work

- Another evaluation of Catalyst I-D will be made in the small bubble-column reactor, using a separate pretreatment step.
- Continue effort on the F-T Catalyst particle size measurement.

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

1. Vacuum Fractionation of Reactor-Wax

As reported earlier, a 20.7 kg sample of reactor-wax from Run CT-256-4 was distilled in a laboratory vacuum still. All distilled fractions were analyzed for carbon-number distribution. This was done to observe any compositional change in the reactor-wax during distillation. The analysis of the bottom fraction is also needed to evaluate the performance of further upgrading of this fraction.

Table 2 gives the preliminary carbon-number distribution of the reactor-wax before and after distillation. The data shows that the reactor-wax became heavier after the vacuum distillation. This unlikely result may have been due to inaccuracies in the analysis of the heavy fractions of both the before- and after-distillation wax. Since the same chromatographic method was used in both cases, we are currently re-evaluating and attempting to improve it.

2. Future Work

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

C. Task 3 - Product Evaluation

1. Fischer-Tropsch Reactor-Wax Analysis

Efforts to improve the accuracy of the analyses of the F-T reactor-wax, particularly the heavy fractions, have been initiated.

At present, the method cannot detect any hydrocarbons with carbon-numbers greater than 70. Thus a major improvement will be increased resolution of the high-boiling hydrocarbons. Some of the techniques to do this are:

1. Cold-on-column gas chromatographic analysis with the addition of internal standards, and

2. High temperature gel permeation chromatography (GPC).

2. Future Work

- Continue the effort to improve the accuracy of the analyses of the F-T reactor-wax.

- Continue providing analyses to support other Tasks.

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

1. Design and Construction of Two Tall, Hot-Flow, Non-Reacting Columns

The Engineering Flow, and Piping and Instrumentation diagram for the two tall hot-flow bubble-columns described in the previous Quarterly Report (June-September 1983) have been completed. The fabrication of all vessels was completed by November, 1983. The on-site construction was initiated in October and was completed at the end of this quarter except for insulation of all steam-traced lines.

Figure 5 is a partial Engineering Flow, and Piping and Instrumentation diagram showing the 10.2 cm ID hot-flow non-reacting column. As reported previously, both the 5.1 and 10.2 cm ID columns have identical features. Figure 5 gives only the main features of the column. Hence, it does not show the N_2 gas-feed system, the DP-cell arrangement, or the slurry sampling and loading systems. The feed N_2 is passed through the gas preheater E-14 and enters the column below the gas distributor. As shown in Figure 5, six slurry sample lines (marked "S") are provided at 152 cm intervals along the column. These sample lines connect to the sample-bombs, not shown in the diagram. The lines marked "DP" are the DP-cell N_2 purge lines used to prevent the plugging of the DP-legs by the wax or slurry. The DP-measurement allows the estimation of the gas holdup along the column.

The upper glass section between the 610 and 914 cm levels permits the visual observation of the expanded slurry. When the liquid level is below the 610 cm level, it cannot be visually observed. Hence 21 thermocouples were installed in the steel section between the 442 and 602 cm levels at 7.6 cm intervals. These thermocouples allow us to measure the slurry level within 7.6 cm, since the thermocouple readings are expected to increase when the expanded slurry reaches there. Also shown in the diagram are the hot-condenser/disengager E-7 at the top of the column and the down-stream cold-condenser/scrubber SG-4. The off-gas is bubbled through the scrubber to remove any heavy hydrocarbons stripped by the gas from the column. The scrubbed off-gas is finally metered by gas meter E-30. The control-valve CV-2 just before the gas meter regulates the column back-pressure.

2. Scoping Hydrodynamic Studies Using Small Bubble-Column Reactors

a. Photographic Analysis of Bubble-Column Hydroynamics

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

The flow patterns from both a 100 μm sintered-metal-plate (SMP) and a single 0.25 mm orifice gas distributor were photographed in the 3.2 cm ID column. The superficial gas velocities were varied from 1 to 4 cm/s.

The pictures reveal the following:

- The 100 μm sintered-metal-plate distributor produced uniform small bubbles at all velocities, with bubble density (bubbles per unit volume) 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 sintered-metal plate distributor. Less foaming was observed when a SMP of larger opening was used.

a.1 Single-Orifice Distributor

Figure 6 shows the photographs of the bubbles produced by a single-orifice distributor of diameter 0.25 mm. 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 6a), 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 6b or 6c.

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).

a.2 Sintered-Metal Plate Distributor

Figure 7 shows the bubbles produced by the sintered-metal-plate distributor, which had an average pore size of 100 μm. 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 coalescense that took place toward the top of the expanded column at the higher velocities. This is in contrast with the orifice results, 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. By comparison, earlier studies showed that a sintered-metal-plate distributor with an average pore size of 15 μm produced bubbles much smaller than even those seen in the photographs (with a corresponding increase in the bubble density), yet no visible coalescense took place.

The overall gas holdups produced by both of these distributors were reported in the last quarterly report; 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.

a.3 Foam Formation

Foam formation has always been observed in our small hot-flow models when using sintered-metal plate distributors. When the average bubble size is very small (like when using a 15 μm sintered-metal plate), 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 μm sintered-metal plate, 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 8 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.

It was reported in the last Quarterly Report that the foaming tendency was greatly reduced when the orifice-type distributors were used.

b. Hydrodynamic Studies Using Reactor-Wax in a Small Hot-Flow Column

In the last quarterly report the effect of different gas distributors on gas holdup was studied using the paraffin wax FT-200. Here we report results of similar studies, using reactor-wax from Run CT-256-5 in the small 5.3 cm ID hot-flow model. Four different gas distributors were used and the results are given in Figure 9. The gas holdup was less than 12 vol% in all cases. Also, the 60 μm 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 paraffin wax FT-200, which produced substantial foam when a 60 μm SMP was used.

The results obtained with the orifice-type distributors showed the same general trends as those observed with the paraffin wax FT-200 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 which can be commercially applied. These results indicate that studies using small orifice distributors may be applied to the commercial orifice distributors.

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.

c. Gas Holdups in a Small Reactive Bubble-Column

The new DP-cell arrangement in our small (2.7 cm ID x 1.9 m L) bubble-column reactor permits the measuring of gas holdups (see the last Quarterly Report). We used it to measure the gas holdup in a sample of reactor-wax taken from Run CT-256-4.

Using a 20 μm sintered-metal plate as a gas distributor, gas holdups were measured using nitrogen and hydrogen at 177°C and nitrogen at 232°C. The pressure was 1.14 MPa (150 psig). Figure 10 shows the results of this study. The gas holdups produced under these conditions are well below that produced by the paraffin wax FT-200 in the small hot-flow columns using a 15 μm sinterer-metal-plate distributor. The leveling off of the curve at a superficial gas velocity of about 2 cm/s may indicate the onset of slugging.

Results from the scoping hydrodynamic studies reported in this and the last Quarterly Report indicate that the various bubble-column mediums behave quite differently in gas holdups and other hydrodynamic features. To see if these hydrodynamic differences were the result of the differences in physical properties of the medium, the properties, such as density, surface tension, viscosity and the average carbon number of the three mediums used thus far are summerized in Table 3. Only the viscosity shows significant variation among the mediums. Based on the literature correlations (Shah, et al. 1982) the bubble-column gas holdup is inversely proportional to a 0 to 0.17 power of the viscosity. The maximum variation on the gas holdup is about 23%, based on the variation of the viscosities of the three mediums at 204°C. The observed variation of the gas holdups among these three mediums is much larger than this. Further investigations in this area are needed.

3. Evaluation of Continous Stirred-Tank Reactors Using a Mathematical Model

In a search for slurry F-T reactor designs that may give better performance than bubble-column (BC) reactors, continuous stirred-tank reactors (CSTR's) in series were investigated using a mathematical model. A series of CSTR's has several potential advantages over BC reactors:

- Higher catalyst loading.
- Reduced mass transfer resistances.
- Established scale-up experience.

Possible disadvantages of series of CSTR's are gas and liquid-phase backmixing, and increased operating cost due to power requirements for stirring.

In this work the effect of the gas and liquid-phase backmixing and the elimination of the mass-transfer resistances was investigated using a multi-component mathematical model for a series of slurry CSTR's. The results were compared with predictions of the BC multi-component model (Kuo, 1983). The base conditions of all calculations are: I-B catalyst, 260°C, 2.14 MPa, 15 wt % catalyst loading, 0.7 feed H_2/CO ratio and 86 mol % H_2+CO conversion. The major highlights from the calculations are:

- The benefit of eliminating the mass-transfer resistances by using a CSTR system is rather minor because the overall mass-transfer resistances in the bubble-column base case is small.
- The major penalty of a CSTR system is the gas- and liquid-phase backmixing which results in a reduction of the H_2 and CO partial pressures. The extent of this penalty can be reduced, as indicated by a decrease in the total reactor volume, by increasing the number of CSTR's in series.
- By increasing the number of CSTR's in series, it is possible to have a total reactor volume less than that of a single bubble-column reactor to achieve the same conversion. In this case study, the crossover point is seven CSTR's in series.

a. Description of the CSTR Mathematical Model

Except for the perfect mixing in the gas- and liquid-phase, the major assumptions are similar to those used for the BC multi-component model (Kuo, 1983):

- Mass transfer resistances to H_2, CO, CO_2, and H_2O diffusion at the liquid side of the gas-liquid interface.
- Two consecutive reactions:

Fischer-Tropsch:

$$CO + (1+m/2)\ H_2 = (-CH_m) + H_2O \qquad (1)$$

$$r_1 = k_1[H_2][CO]/([CO] + k_3[H_2O]) \qquad (2)$$

Water-Gas Shift:

$$CO + H_2O = CO_2 + H_2 \qquad (3)$$

$$r_2 = k_2([CO][H_2O]-[H_2][CO_2]/k_4)/([CO]+k_3[H_2O]) \qquad (4)$$

- Molar contraction due to synthesis reaction is a linear function of synthesis gas conversion.
- Constant bubble-size and gas holdup.
- Steady-state isothermal and isobaric operation.
- Perfectly mixed gas- and liquid-phase.

Material balances for the gas- and liquid-phase of the components H_2, CO, CO_2 and H_2O (denoted by subscripts 1, 2, 3, 4, respectively), yield:

$$Q^i C_{gi}{}^i - Q^e C_{gi}{}^e = k_{Li} a_g (C_{gi}{}^e/K_i - C_{Li}) V/N, \quad i = 1,....,4 \qquad (5)$$

for the gas-phase, and

$$k_{Li}a_g(C_{Li}-C_{gi}^e/K_i) = (1-\epsilon_g)(1-v_c)C_{Fe}\sum_j S_{ij}r_j, \quad i = 1,....4 \quad (6)$$

where r_1 and r_2 are, respectively, the F-T and the water-gas shift reaction rates given by Equations (2) and (4), and S_{ij} ($i = 1,...,4$; and $j = 1,2$) are elements of the stoichiometric matrix.

Assuming that the molar contraction due to the F-T reaction is linear with respect to the H_2+CO conversion, the following relation between the gas flow rate and the H_2+CO conversion was obtained:

$$Q^e = Q^i(1 + \alpha X_{H_2+CO}) \quad (7)$$

where α is the constant molar contraction factor.

In dimensionless form, Equations (5) to (7) become:

$$\bar{Q}\bar{C}_{gi}^e - \bar{C}_{gi}^i + St_{di}(\bar{C}_{gi}^e - \bar{C}_{Li}) = 0 \quad (8)$$

$$St_{di}(\bar{C}_{gi}^e - \bar{C}_{Li}) + \sum_j S_{ij}St_{kj}\bar{r}_j = 0 \quad (9)$$

for $i = 1,...4$

A solution for this set of non-linear algebraic equations can be obtained using a conventional Newton-Raphson iteration routine. The convergence criterion of the iterative scheme is that the successive approximations for the dependent variables be within 0.1% of each other. The calculation procedure for a series of CSTR's is as follows:

1. Choose a total reactor volume, V, and a number of CSTR's, N.
2. Solve Equations (8)-(9) for the first CSTR.
3. Use output from each CSTR as input to the next, and solve Equations (8)-(9) for remaining CSTR's.

In a mechanically agitated slurry reactor, the hydrodynamics can be controlled independently of the gas throughput by varying the stirring speed. Increasing the stirring speed increases the gas-liquid interfacial area and this decreases the mass transfer resistance (e.g., Joshi et al., 1982). At sufficiently high stirring speeds, the mass transfer resistance becomes negligible and equilibrium is achieved between

the bulk gas and the gas absorbed in the liquid. This special case of no mass transfer resistance can be described by the following dimensionless material balance equations:

$$\bar{C}_{gi}^{e} = \bar{C}_{Li} \tag{10}$$

$$\bar{Q}\bar{C}_{gi}^{e} - \bar{C}_{gi}^{i} = \sum_{j} S_{ij} St_{kj} \bar{r}_{j} \tag{11}$$

for $i = 1,\ldots,4$

The solution procedure and convergence criteria for Equations (10)-(11) are identical to those of Equations (8)-(9) described above.

b. Comparison of Bubble-Column Reactor and Series of CSTR's

The correlations used to estimate the model parameters are the same as those in Tables 27 and 28 in Kuo (1983). The kinetic constants k_1, k_2, k_3, and k_4 were estimated from the two-stage pilot plant data (Section VII.E in Kuo (1983)) and are given in Table 4, together with other pertinent parameters used in the calculations. Note that the same gas holdup correlation developed by Deckwer et al. (1980) for a bubble-column (Table 27 in Kuo (1983)), is also used to predict the gas holdup in the CSTR model. The assumption is that for the same gas throughput, there is a stirrer speed for which each gas holdup (or higher) can be achieved in the CSTR.

Figure 11 shows the effect of mass-transfer resistance on H_2+CO conversion. For a series of five CSTR's at the base conditions, there is little gain in eliminating the mass transfer resistance. Note that this result is only valid at the base conditions, and different results may be obtained at other conditions, as the extent of the mass transfer limitations is a function of the operating conditions.

In Figure 12, series of CSTR's with no mass transfer resistances are compared at base conditions with a single BC reactor. Increasing the number of reactors in a CSTR system decreases the conversion difference between the BC system and the CSTR system. This is due to the reduction of the gas- and liquid-phase backmixing. Thus, a system of three CSTR's requires only about a 10% larger reactor volume to achieve 86 mol % H_2+CO conversion than the BC case; one and two CSTR's require 20 and 80% larger volumes, respectively, than the BC. Calculations show that seven or more CSTR's require a slightly less reactor volume than a BC to achieve 86 mol% H_2+CO conversion.

4. Future Work

- The shakedown of the hot-flow columns (Unit CT-284) will begin in early January, 1984.

- The hydrodynamic studies using the 5.1 ID tall bubble-column will be initiated by late January, 1984. A 20 μm sintered-metal-plate distributor will be used, the same as that in the reacting bubble-column in Unit CT-256. Initially, the liquid medium will be the paraffin wax FT-200, followed by F-T reactor-waxes produced in Unit CT-256.

- Scoping hydrodynamic studies using various reactor-waxes will be conducted.

- A single-orifice gas distributor will be evaluated for the first time in a small reactive bubble-column.

- Work is planned to quantify the performance of a series of CSTR's with respect to higher catalyst loading and power requirements for stirring.

V. NOMENCLATURE

a_g	Gas bubble interfacial area, $6\epsilon_g/d_B$, (cm^2 gas-liquid area/cm^3 expanded slurry)
C	Concentration, (mol/cm^3 liquid or gas)
C_{Fe}	Iron loading, (gFe/cm^3 liquid)
$\bar{C}_g$	$C_g/C_{g1}{}^i$
$\bar{C}_L$	$C_LK/C_{g1}{}^i$
d_B	Bubble diameter, (cm)
f	Molar H_2/CO ratio at reactor inlet
K	Solubility coefficient $C_g{}^*/C_L{}^*$, (cm^3 liquid/cm^3 gas)
k_1, k_2	Intrinsic kinetic rate constants for F-T and water-gas shift reactions, respectively, used in Equations (2) and (4), (cm^3 liquid/s-gFe)
k_3, k_4	Constants used in the rate expressions (2) and (4)
$\bar{k}_3$	k_3K_2/K_4
$\bar{k}_4$	$k_4K_1K_3/K_2K_4$
k_L	Liquid side mass transfer coefficient, (cm^3 liquid/ s-(cm^2 gas-liquid area))
m	Average H/C atomic ratio of F-T products
N	Number of CSTR's in series
P	Pressure, (Pa)
Q	Gas volumetric flow rate, (cm^3/s)
$\bar{Q}$	Q/Q^i
R_d	Transport resistance from gas-liquid interface to bulk liquid phase, K/k_La_g, (s-cm^3 expanded slurry/ cm^3 gas)
R_k	Kinetic resistance, $K_1/k_jC_{Fe}(1-\epsilon_g)(1-v_c)$, (j=1,2), (s-$cm^3$ expanded slurry/cm^3 gas)

r_1 Kinetic rate of F-T reaction, given as Equation (2), (mol/s-gFe)

r_2 Kinetic rate of water-gas shift reaction, given as Equation (4), (mol/s-gFe)

$\bar{r}_1$ $\bar{C}_{L1}\bar{C}_{L2}/(\bar{C}_{L2}+\bar{k}_3\bar{C}_{L4})$

$\bar{r}_2$ $K_1(\bar{C}_{L2}\bar{C}_{L4}-\bar{C}_{L1}\bar{C}_{L3}/\bar{k}_4)/K_4(\bar{C}_{L2}+\bar{k}_3\bar{C}_{L4})$

S_{ij} Elements of stoichiometric matrix, i = 1,...,4; and j = 1,2

T Temperature, (°C)

u Superficial velocity, (cm/s)

$\bar{u}_g$ u_g/u_g^i

V Expanded slurry volume in each reactor, (cm^3 slurry and gas)

v_c Volumetric fraction of catalysts in slurry, $\rho_L w_c/(\rho_s+w_c(\rho_L-\rho_s))$, ($cm^3$ catalyst/cm^3 slurry)

w_c Weight fraction of catalyst in slurry, (gCat/g slurry)

X_{H_2+CO} Molar H_2+CO conversion

Greek Letters

α Contraction factor, molar contraction per mole of H_2+CO converted, defined in Equation (7)

ϵ_g Gas holdup, (cm^3 gas/cm^3 expanded slurry)

ρ Density, (g/cm^3)

ρ_s Catalyst solid density, (gCat/cm^3 catalyst solid)

Dimensionless Numbers

St_d Stanton number (diffusion resistance), V/NQ^iR_d

St_k Stanton Number (kinetic resistance), V/NQ^iR_k

Acronyms

BC	Bubble-Column
BSU	Bench-Scale Unit
CSTR	Continous Stirred-Tank Reactor
DOE	Department of Energy
DOS	Days on Stream
DP	Differential Pressure
F-T	Fischer-Tropsch
GPC	Gel Permeation Chromatography
HOS	Hours on Stream
SMP	Sintered-Metal Plate

Superscripts

i	At reactor inlet
e	At reactor exit
*	At gas-liquid interface

Subscripts

g	Gas
i	Components, i = 1,2,3,4, for H_2, CO, CO_2, H_2O, respectively
L	Liquid

VI. Literature

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Kuo, J. C. W., "Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline", Mobil Research And Development Corporation, Final Report, DOE Contract No. DE-AC22-80PC30022, June, 1983.

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

Table 1

Testing of Sedigraph 5000E Particles Size Analyzer with Standard Samples[1]

Wt% Less Than	Particle Size, μm		Error (%)
Standard A (.35-3.5μm)	Sed. 5000E	Standard[2]	
10	.84	.57±.12	46.9
50	1.45	1.13±.20	28.3
90	2.37	2.15±.30	10.1
Standard B (1-20μm)			
10	1.54	1.20±.25	28.3
50	3.10	2.92±.30	5.8
90	7.20	7.27±.60	1.0

(1) Samples were obtained indirectly from the Community Bureau of Reference, Brussels, Belgium.

(2) Data reported in the Certificate of Measurement issued by the Community Bureau of Reference (November 6, 1979).

Table 2

Overall Reactor-Wax Composition (Run CT-256-4)

Carbon Number Range	Before Distillation	After Distillation
C_{10} - C_{20}	11.1	4.8
C_{21} - C_{25}	20.3	5.8
C_{26} - C_{30}	22.9	17.5
C_{31} - C_{35}	19.8	31.0
C_{36} - C_{40}	12.5	21.3
C_{41} - C_{45}	6.9	12.1
C_{46} - C_{50}	2.9	4.5
C_{51} - C_{55}	1.7	1.8
C_{56} - C_{60}	0.9	1.2
C_{61} - C_{70}	0.9	0.0
Mol. Avg. C-No.	28.2	32.1
Peak C-No.	27.0	34.0

Table 3

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),	2.1/-	3.0/5.3	7.2/14.6
Molar Avg. C-No.	36.0	29.3	29.6

(1) At 204°C.

Table 4

Parameters Used in Fischer-Tropsch CSTR Mathematics Model Calculations

	Base
T, °C	260
P, MPa	1.48
u_g^i, cm/s[1]	4
w_c, wt %	15
f	0.7
m	2.24
k_1, cm^3 liquid/gFe-s	0.50
k_2, cm^3 liquid/gFe-s	1.35
k_3	0.20
k_4	37.5

[1] Used only for the Bubble-Column base case calculation.

FIGURE 1

SCHEMATIC ARRANGEMENT OF NEW DP-CELLS FOR LIQUID LEVEL AND GAS HOLDUP MEASUREMENT

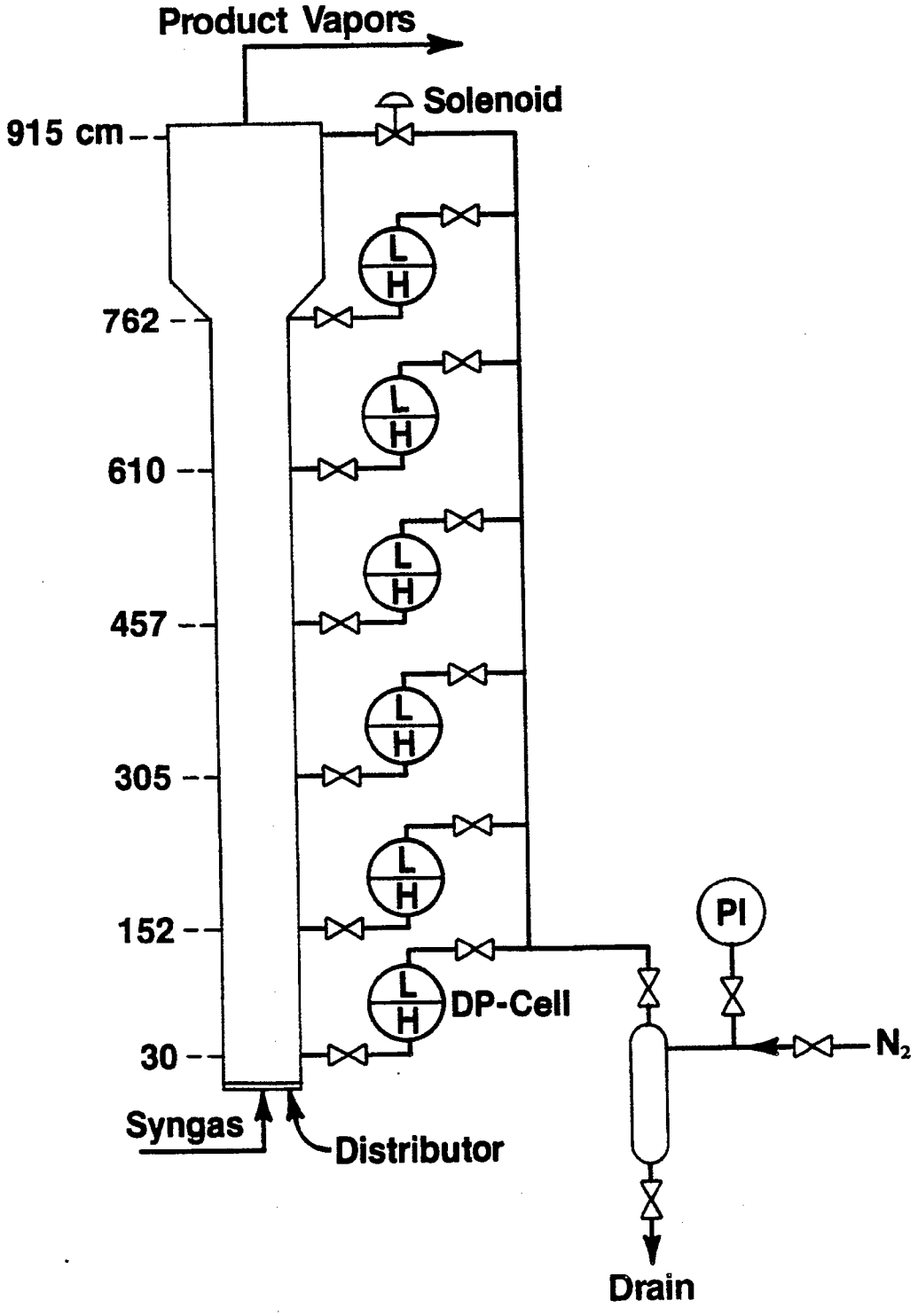
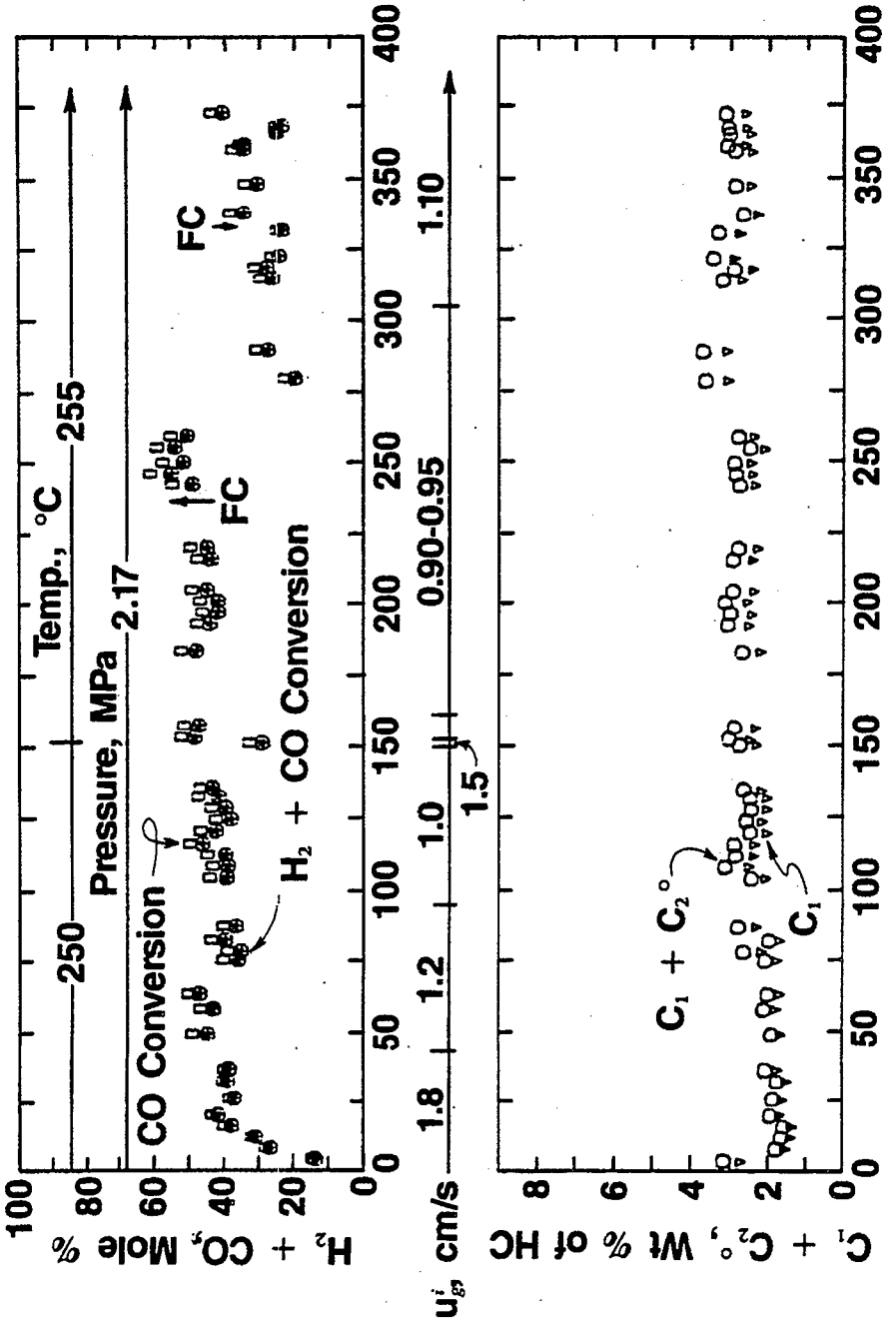


FIGURE 2

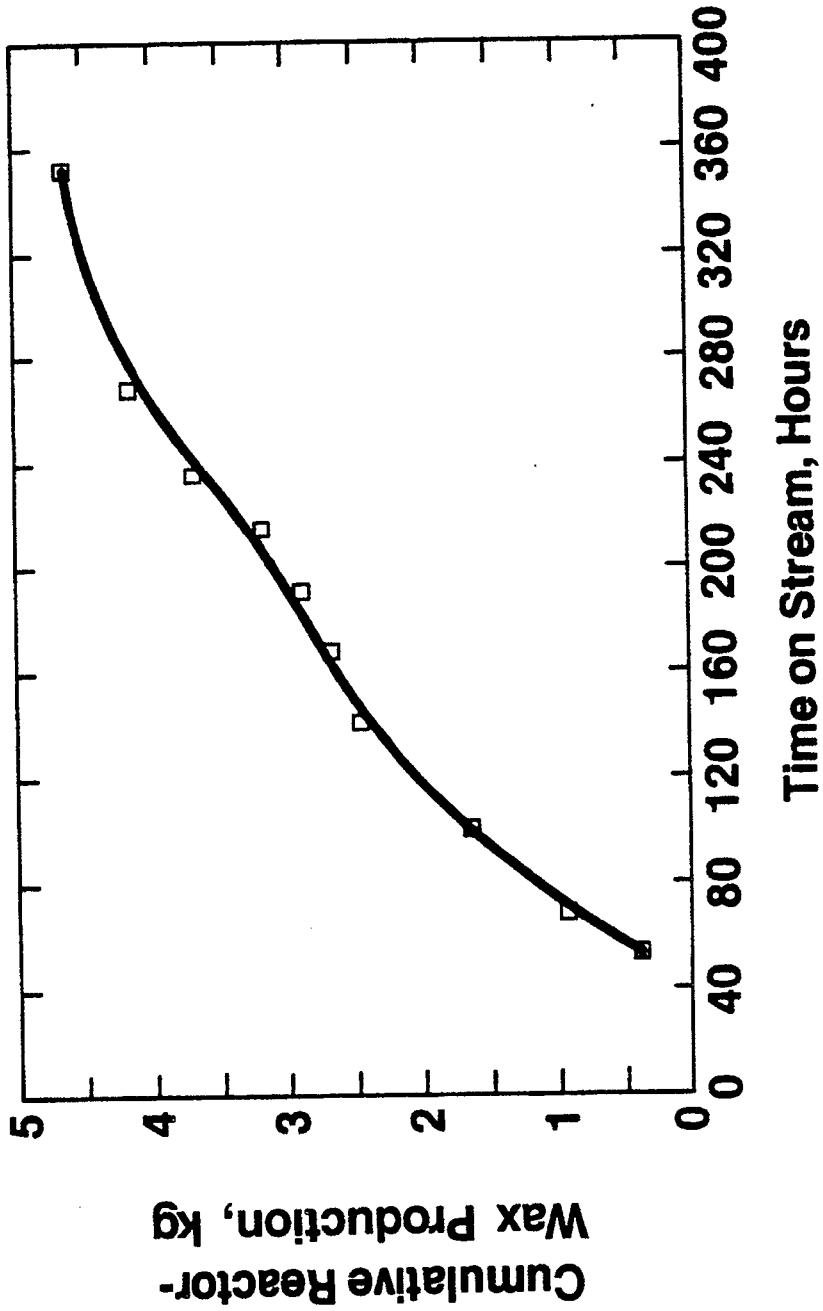
SYNTHESIS GAS CONVERSION AND METHANE AND ETHANE YIELD (RUN CT-225-112; CATALYST I-D: PPTD Fe/Cu/K_2CO_3)



FC: Fresh Catalyst Added

FIGURE 3

CUMULATIVE REACTOR-WAX PRODUCTION, RUN CT-225-112



PARTICLE SIZE DISTRIBUTION OF FRESH CATALYST I-B MEASURED BY SEDIGRAPH 5000E PARTICLE SIZE ANALYZER

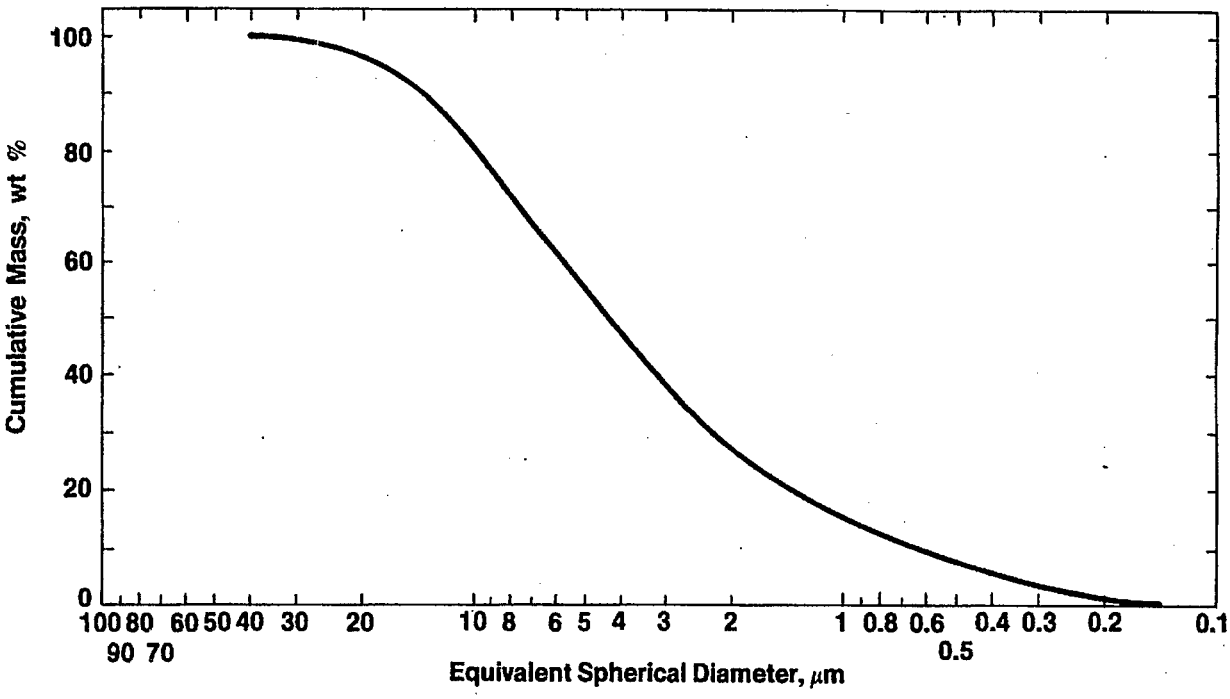


FIGURE 5

ENGINEERING FLOW, AND PIPING AND INSTRUMENTATION DIAGRAM, CT-284

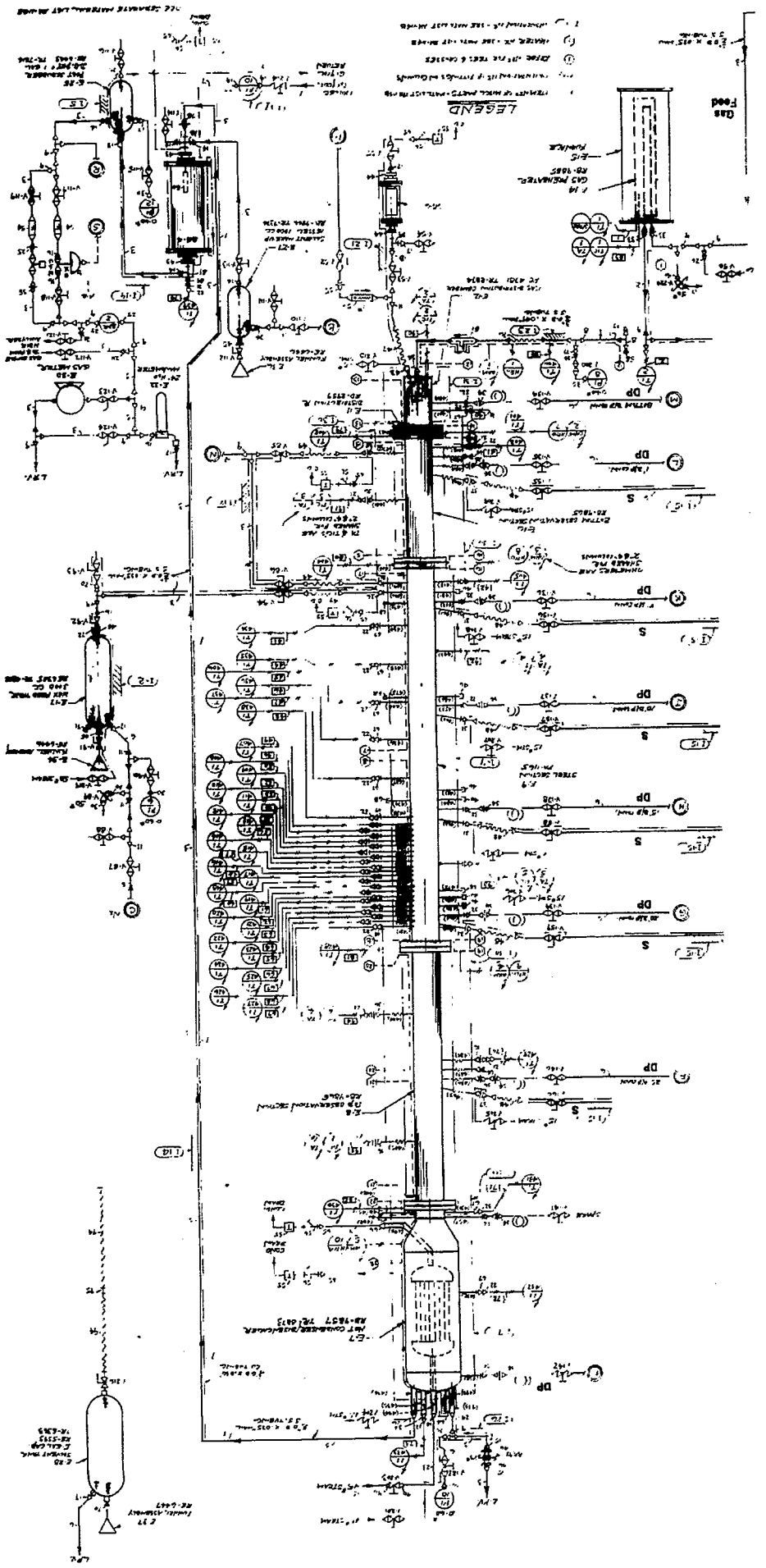


FIGURE 6

BUBBLES PRODUCED BY 0.25mm ORIFICE DISTRIBUTOR

a. 1 cm/s

3.2 cm

b. 2 cm/s

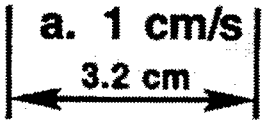
c. 3 cm/s

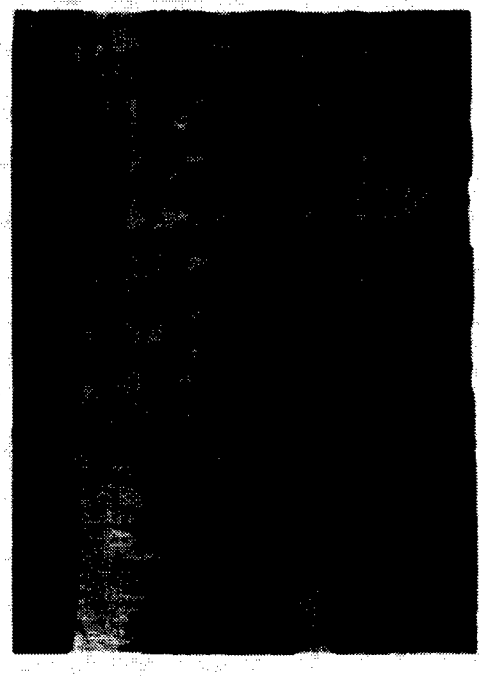
d. 4 cm/s

FIGURE 7

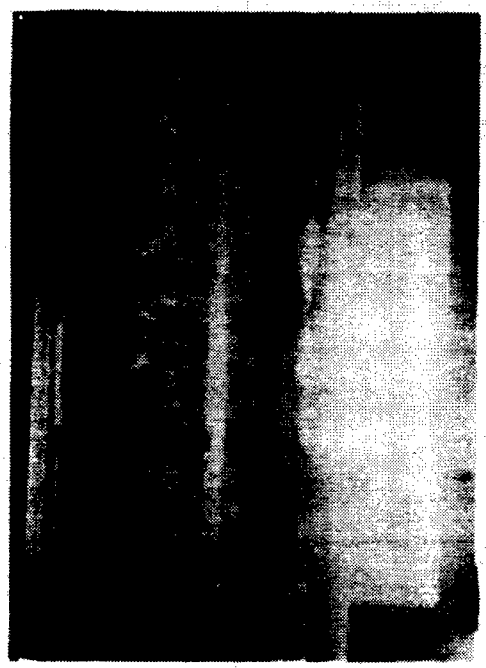
BUBBLES PRODUCED BY 100μm SINTERED-METAL-PLATE DISTRIBUTOR

a. 1 cm/s

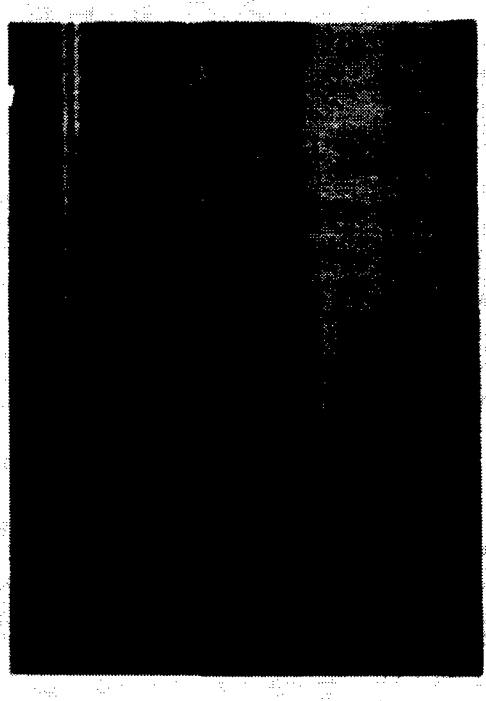




b. 2 cm/s



c. 3 cm/s



d. 4 cm/s

FIGURE 8

FOAM PRODUCED BY 100μm SINTERED-METAL-PLATE DISTRIBUTOR

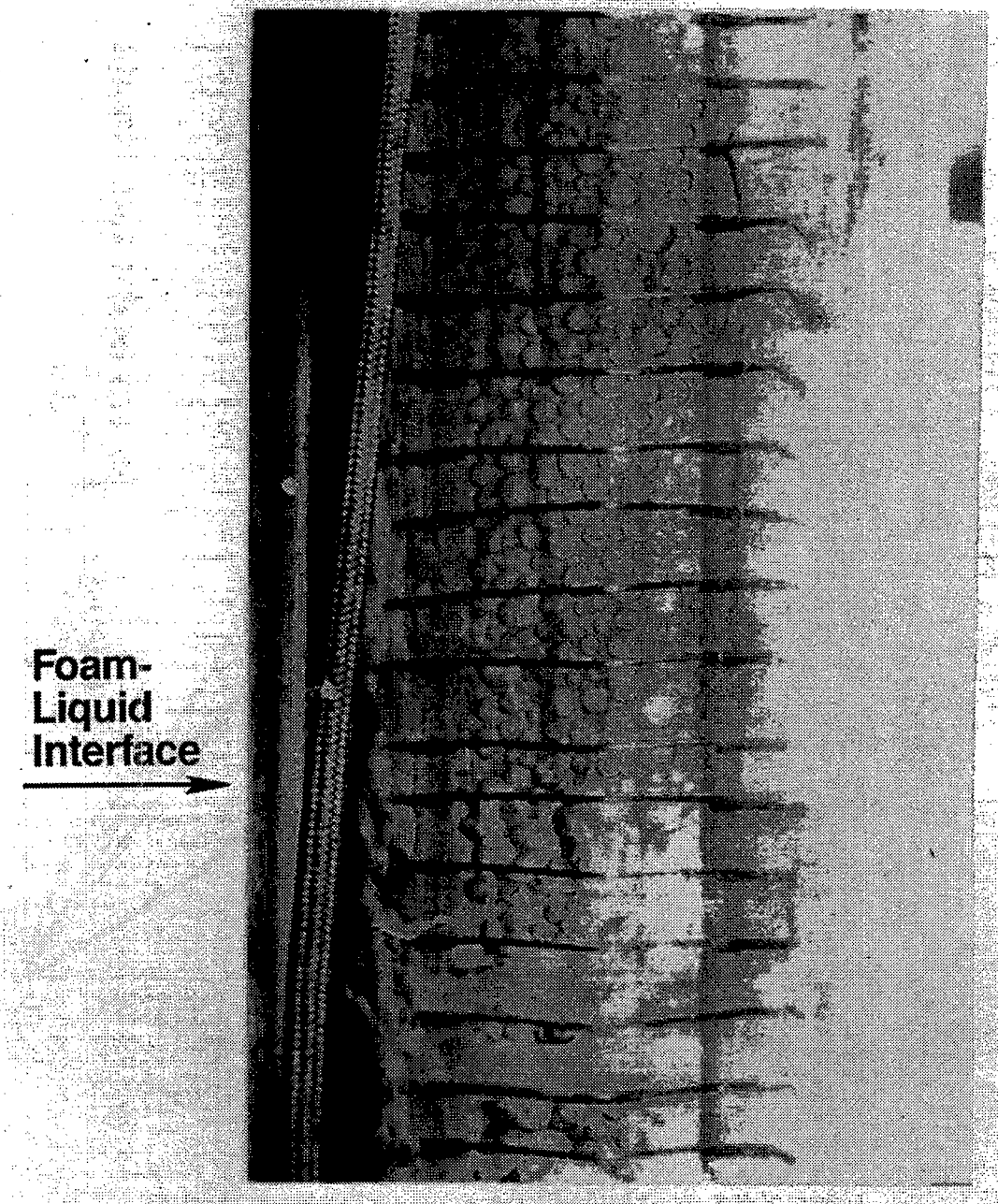


FIGURE 9

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

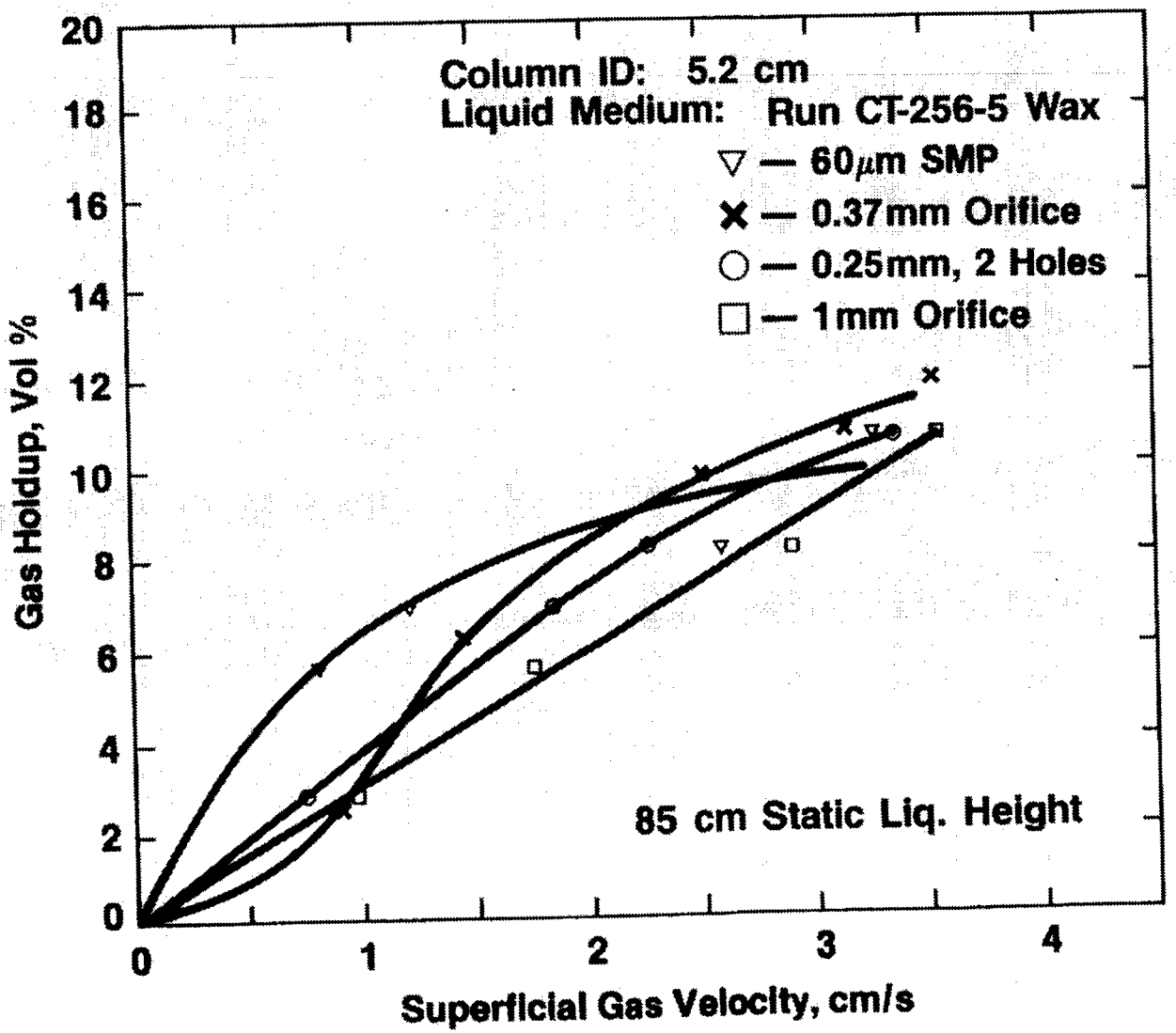


FIGURE 10

GAS HOLDUP IN A SMALL BUBBLE-COLUMN REACTOR USING REACTOR-WAX

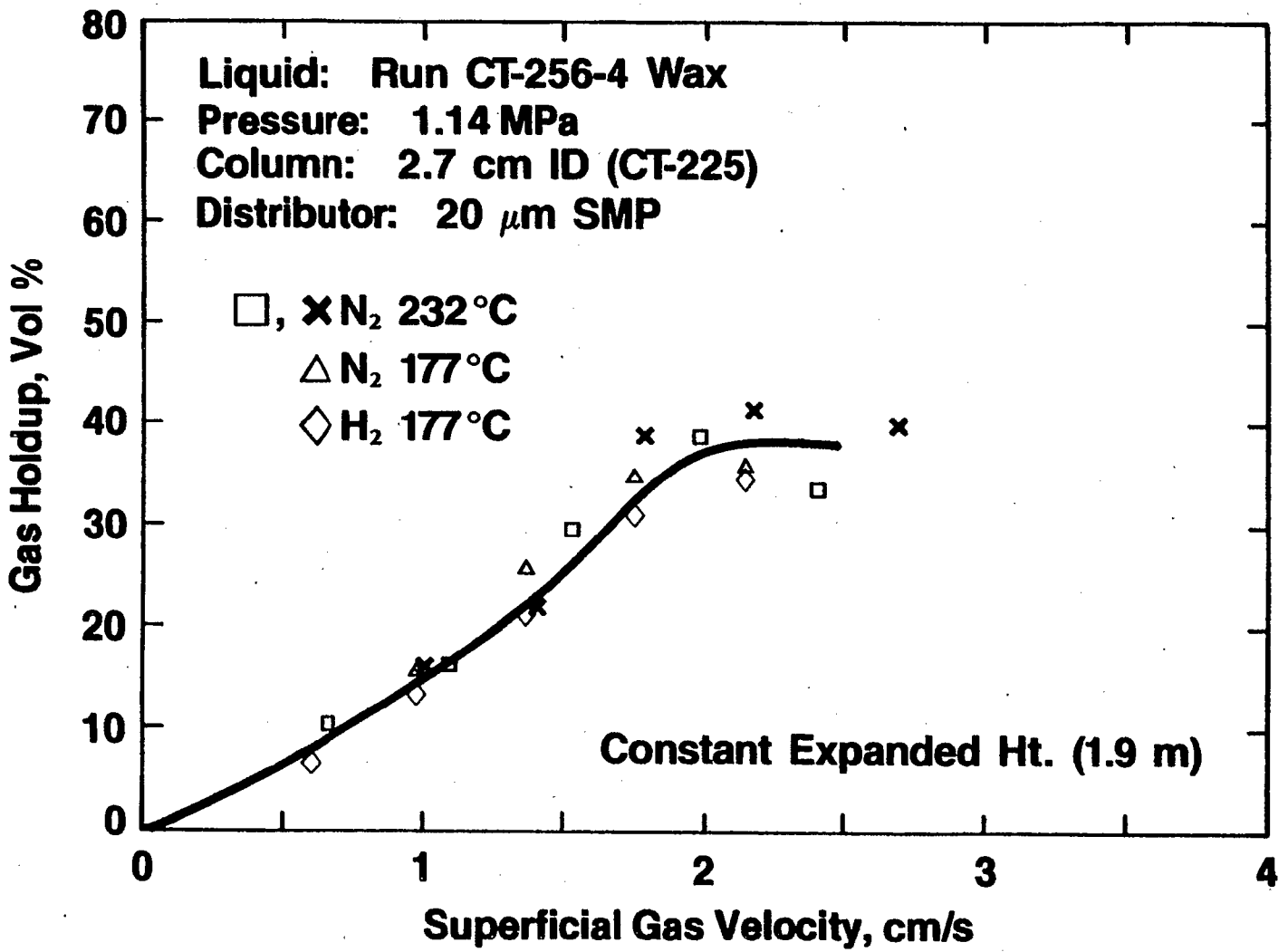


FIGURE 11

EFFECT OF MASS TRANSFER RESISTANCE ON CONVERSION FOR A SERIES OF CSTR'S

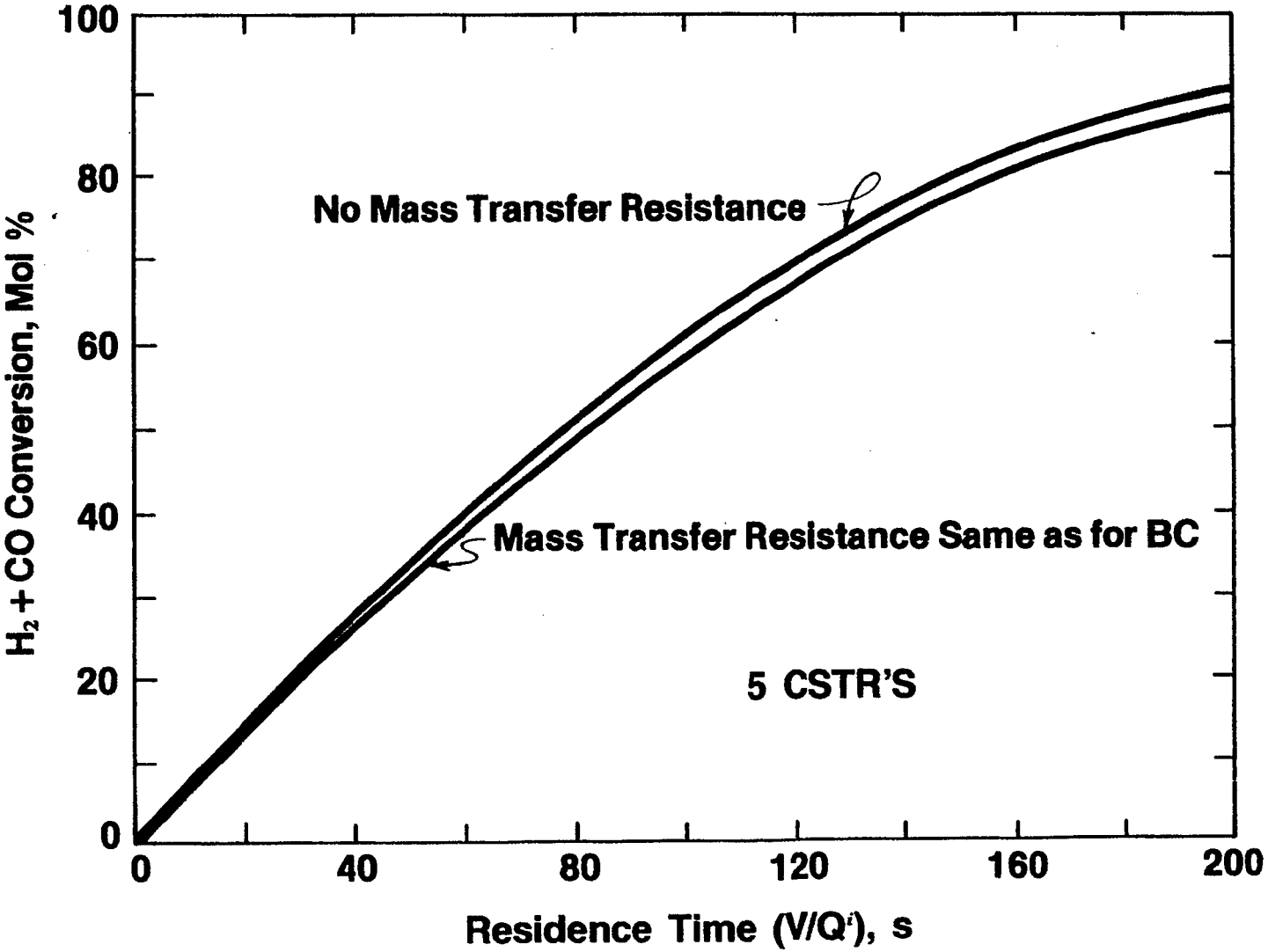
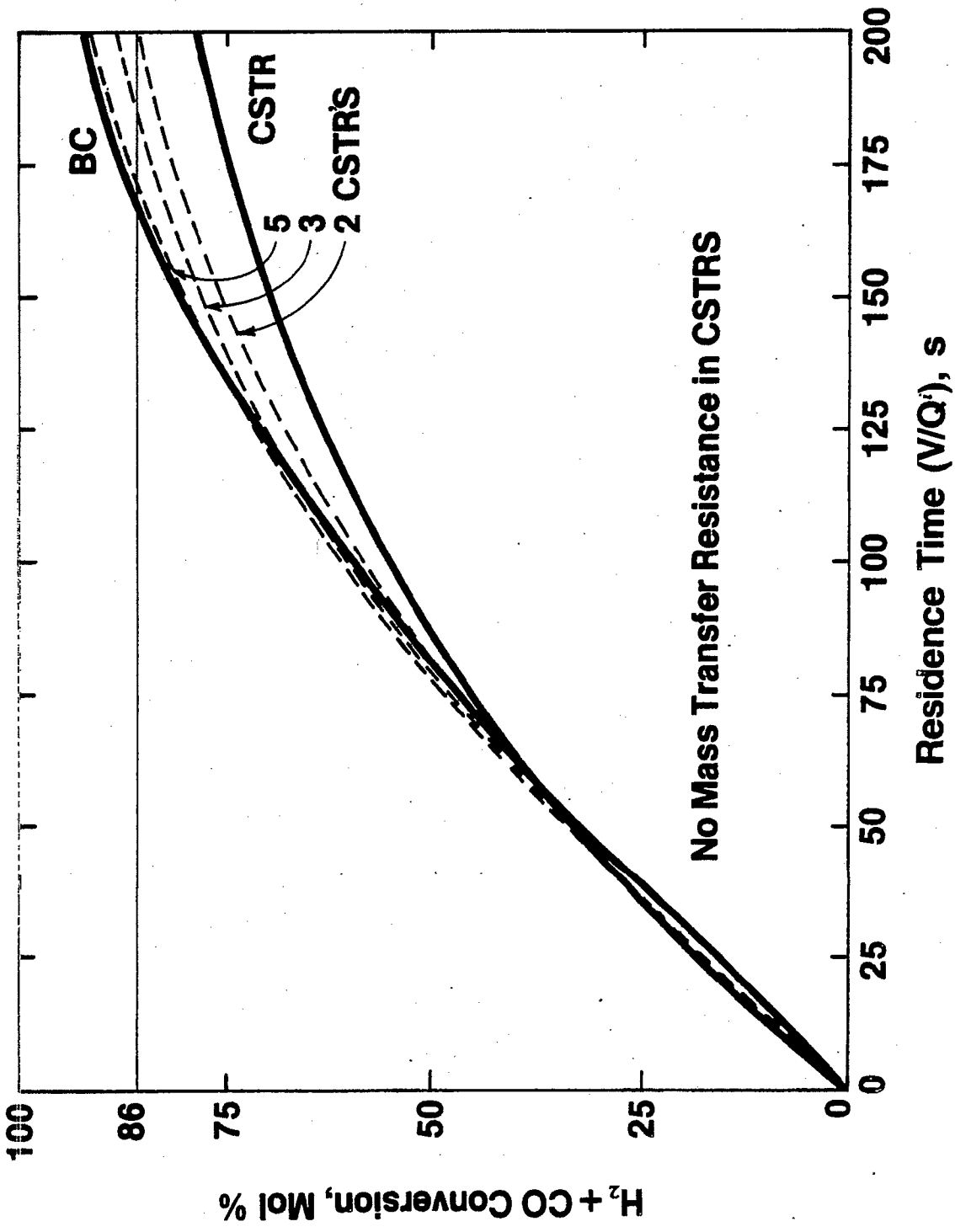


FIGURE 12

COMPARISON OF BC AND SERIES OF CSTR'S



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