

DE85015201



TWO-STAGE PROCESS FOR CONVERSION OF SYNTHESIS GAS TO HIGH QUALITY TRANSPORTATION FUELS. QUARTERLY REPORT, JULY 1-SEPTEMBER 30, 1984

MOBIL RESEARCH AND DEVELOPMENT CORP. PAULSBORO, NJ

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DE85015201 DOE/PC/60019-5 (DE85015201)

Distribution Category UC-90d

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

QUARTERLY REPORT FOR THE PERIOD 1 JULY - 30 SEPTEMBER, 1984

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DATE PUBLISHED - NOVEMBER 1984

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC22-83PC60019

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I. Abstract

The seventh run of the two-stage Fischer-Tropsch pilot plant continued during this quarter, thus far accumulating 86 days on stream. Mathematical model calculations on the effects of water-gas shift activity were performed, and a new technique for analyzing heavy reactor-waxes was utilized. Experiments using hot-flow bubble-columns and also our bubble-column reactor have yielded new information on bubble size and gas holdup. We are continuing our investigations into the use of series of CSTRs as an alternative for 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The methods for upgrading the reactor-wax which is withdrawn from the slurry Fischer-Tropsch reactor will be evaluated.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.

<u>Task 4 - Slurry Fischer-Tropsch Reactor Hydrodynamic</u> 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 of Progress to Date

This quarter has seen significant developments in all of the major tasks. In process studies, Run CT-256-7 continued, and even though the single orifice gas distributor which was being tested for the first time was found to be leaking during the run, very low methane and ethane selectivity has been maintained for over 86 days. Also, mathematical model studies into the effect of water-gas shift activity on H_2+CO conversion have led to a series of important conclusions on this topic.

In product analysis, a new technique has enabled the resolution of the C55⁺ content of our heavy reactor-waxes for the first time.

In hydrodynamic studies, we have reported more results of our work with the tall hot-flow bubble-column, including photographs of the bubble-flow patterns, gas holdup profiles using DP-cell data, and measurements of bubble sizes using a dynamic gas-disengagement technique. Gas holdup during Run CT-256-7 was measured using the new purgeless DP-cells, and the pressure drop across the orifice gas distributor was found to conform to our calculations. Finally, the basis of our new mathematical model for evaluating CSTR as alternatives to bubble-column reactors is described here.

IV. Detailed Description of Technical Progress

A. <u>Task 1 - Process Studies in Two-Stage</u> <u>Bench-Scale Unit</u>

1. <u>Run CT-256-7-Continuation</u>

The seventh run of the two-stage pilot-plant, designated as CT-256-7, has accumulated 86 days on stream thus far. The run was started on May 31, 1984, and a one-month shutdown occurred at 76 DOS. The run was restarted following the shutdown, since the first-stage slurry had been allowed to cool in-situ. The major objective of the run was to achieve high conversion and low methane + ethane selectivity using catalyst I-B at high pressure and moderate temperatures. Catalyst I-B had been used in Run CT-256-3 as a gasoline-mode catalyst, and it showed excellent long-term stability. It was therefore felt that operating at high pressures would substantially reduce the methane + ethane yield without affecting the catalyst stability.

Also of importance in this run was the testing, for the first time in the pilot plant, of a single-orifice feed-gas distributor in the first-stage slurry reactor. This is important because orifice-type distributors are most practical for commercial units.

The major highlights of the run to date are:

- Methane + ethane selectivity has been maintained at less than 6.0 wt % over the entire run. Reactor-wax yields have been 35-65 wt %.
- No definitive conclusions on the effects of a single-orifice distributor could be drawn, due to leakage around its perimeter, which was discovered during the shutdown at 76 DOS. The distributor was repaired before the run was restarted.
- H₂+CO conversion has ranged from 40 to 86 mole %, with the higher conversions occurring early in the run (0-20 DOS). The leaking distributor may have caused gas-flow maldistribution as well as catalyst losses, which combined to lower the conversion.
- Additions of a new batch of catalyst I-D, as well as potassium, had little effect on the H2+CO conversion.

• Fischer-Tropsch operation at high (277°C) temperature, with little effect on methane + ethane selectivity, was shown toward the end of the run.

- A new proprietary reactor-wax removal system was successfully demonstrated.
- The second-stage ZSM-5 fixed-bed reactor was run for 25 days with a new batch of catalyst. However, an erratic GC analysis did not allow proper adjustment of the reactor inlet temperature for maintaining a constant severity, and consequently no second-stage data are reported here.

a. First-Stage Fischer-Tropsch Reactor Operation

The last quarterly report (April-June, 1984) outlined the startup and catalyst pretreatment of Run CT-256-7. This will not be repeated here. What follows is a detailed description of the entire synthesis operation.

are:

The range of operating conditions for the run to date

Temperature, °C	255-277
Pressure, MPa	2.51
H2/CD Feed Molar Ratio	0.67
Superficial Feed-Gas Velocity, cm/s	2.7-4.0
Space Velocity, NL/gFe-hr	2-7
Catalyst Loading, wt % (Average)	14
H ₂ +CO Conversion, Mole %	35-86
Methane + Ethane Yield, wt % of HC	2.4-6.0
Reactor-Wax Yield, wt % of HC	35-65
Hydrocarbon Production, gHC/gFe	>900

Figure 1 shows the conversion and methane + ethane selectivities, as well as the temperature, pressure, space velocity and superficial gas velocity for the run. A summary of the major events during the run is given in Table 1. It is seen on the run plot that the methane + ethane selectivity has remained low (<6.0 wt %) throughout the run. This is the longest period for which we have maintained such low methane + ethane yields. This of course also corresponds to the production of heavier hydrocarbons, and consequently the reactor-wax yield ranged from 35 to 65 wt %. This high wax production was successfully handled by a new proprietary wax removal system, which continuously withdrew up to 7 kg of clean (<0.1 wt % solids) reactor-wax per day.

Figure 2 is a plot of the accumulated reactor-wax which was removed from the first-stage slurry reactor. It can be seen that the slope of this curve generally lessens with time on stream, which corresponds, among other things, to increasing methane + ethane yields. By measuring the slope at a given point and knowing the H_2+CO conversion, the reactor-wax yield as a function of methane selectivity can be calculated. This has been done for other runs, and our data for Run CT-256-7 is compared with them, as well as literature results, in Figure 3. These data cover a wide range of methane selectivities, which were achieved using a variety of catalysts and operating conditions.

Early in the run, the catalyst activity was comparable to previously studied F-T catalysts. This appeared to indicate that the orifice distributor produced no ill effects on activity. However, measurements of the pressure drop across it turned out to be less than that predicted by pressure-drop correlations (see Section 4.3), possibly indicating that the distributor had developed a leak around its edge.

Over the first twenty days on stream, the H_2+CO conversion was between 80 and 86 mol %. The next twenty days, however, saw the conversion drop steadily to about 40 mol %, and it remained there for almost 25 days. The cause of this decline is uncertain, but evidence seems to indicate that a loss of catalyst, combined with gas flow maldistribution caused by the leaking distributor, was responsible. This will now be discussed.

The run plot shows that the space velocity climbed from about 4.0 to over 6.0 NL/gFe-hr between 22 and 36 DOS. The amount of catalyst in the reactor was obtained by sampling the slurry at different points along the column, and then integrating the concentrations with respect to column height. Over this time period, the catalyst concentration dropped, indicating that catalyst was being lost from the reactor. Also, the catalyst concentration profiles were becoming steeper (higher concentration toward the bottom of the column) with time. This is shown in Figure 4, which is a sample of catalyst profiles taken throughout the run. It clearly shows the steep, non-uniform profiles during most of the run, and the more uniform profiles early in the run and after the distributor was repaired. This was an indication that gas flow was improperly distributed when the orifice plate was leaking.

When we suspected that the distributor was leaking (around 30 DOS), we began to check the volume below the plate for any slurry which may have leaked around it. Using a small drain attached to the vessel, any accumulated slurry was removed once per day. A plot of the accumulated slurry removed is shown in Figure 5. From 30 to 45 DOS, nearly 250 g of catalyst was lost. At that point, the superficial gas velocity in the column was increased, with the rationale that the higher flow would cause less slurry "weeping" around the plate. This had limited success, as shown in the figure, and catalyst continued to be lost. After the repair work at 76 DOS, the leakage was stopped completely. We attribute the conversion drop during the run to catalyst loss and hydrodynamic factors. The fact that the methane + ethane selectivity remained steady during the decline indicates that the catalyst was not damaged.

In an effort to raise the H₂+CO conversion, both fresh catalyst and potassium additions were tried. A new batch of catalyst I-D was tested for catalyst addition, but while significant increases in conversion were seen using an earlier batch of this catalyst in Run CT-256-6, addition of the catalyst in the current run appeared to have only a small effect on conversion. This was done twice, at 37 and 50 DOS, and both times the amount added was more than half of the prevailing catalyst inventory. This indicates that the new batch of catalyst I-D may have been different from the old batch.

A potassium salt was then added in an attempt to promote activation of the added catalyst. Three such additions, done from 56 to 62 DOS, appeared to have little influence on the H_2+CO conversion, though the methane + ethane selectivity seemed to stabilize.

At 63 DOS, the reactor temperature was increased to 277°C for eight hours in an attempt to activate the catalyst in-situ. As seen in Figure 1, this was not successful. The conversion dropped to the same low level when the temperature was reduced.

After this, we attempted to increase conversion by raising the reactor temperature. This usually results in a higher catalyst aging rate and higher methane + ethane yields. As seen in the run plot, however, raising the temperature to 277°C at 67 DOS nearly doubled the H₂+CO conversion, while the methane + ethane yield remained at its low level of about 4.7 wt %. This may indicate that catalyst I-D (the principle catalyst in the reactor at the time) is stable at high temperatures. We plan to investigate this further.

The unit was shut down at 76 DDS (the slurry was allowed to cool in-situ), and the distributor was removed and examined.

It was found that several screws which hold down the distributor plate were loose, which in turn caused leakage around the perimeter of the plate. To correct this, the plate was cleaned off and then welded in place before being placed back in the reactor. The unit was then restarted. The improvement was immediately evident; Table 2 shows the smoother reactor temperature profile which was achieved and higher distributor pressure drop, which corresponded to our calculations. Subsequent catalyst profiles were also considerably less steep (Figure 4) than before the shutdown. Figure 5 shows that the leakage was halted after the repair. After the restart, the H_2+CO conversion was 40 mol %, and the methane + ethane selectivity had climbed only slightly, to 6.0 wt %. We feel that this was not a consequence of the new distributor. While this was the first time that a cold shutdown and restart was performed in the two-stage pilot plant, there have been other occasions where the H_2 and CO flows were cut and the unit was "idling" under nitrogen. In those cases the conversion dropped and the methane + ethane yield increased somewhat when the synthesis gas was re-introduced. It appears that the catalyst is affected when removed from the H_2+CO environment. This could also have contributed to the lower conversion observed after the restart.

The run is continuing, with the main effort being to try and increase the conversion.

b. Second-Stage ZSM-5 Fixed-Bed Operation

The second-stage ZSM-5 reactor was run for 25 days early in the run, using a fresh load of catalyst. Unfortunately the GC system did not work properly, so adjustments to the reactor inlet feed temperature for maintaining constant catalytic severity could not be made accurately. Therefore, none of the data from the second-stage operation are presented here.

2. Effect of Water-Gas Shift Activity on Conversion: Mathematical Model Calculations

Since the F-T catalyst is also a water-gas shift catalyst, it can be used with a low H_2/CO ratio synthesis gas to obtain high (H_2+CO) conversion. Thus, the water gas shift activity plays an important part in the performance of the two-stage slurry reactor. We have used our multi-component mathematical model to establish the relative importance of the shift activity and F-T activity of the catalyst.

The model is based on the following kinetic rate expressions (Kuo, 1983):

F-T: $r_1 = k_1 [H_2] [C0] / ([C0] + k_3 [H_20])$ (1)

Shift: $r_2 = k_2([C0][H_20] - [H_2][C0_2]/k_4)/([C0] + k_3[H_20])$ (2)

The k_1 and k_2 are the F-T and shift kinetic rate constants, k_3 is the ratio of water and CO adsorption constants, and k_4 is the shift equilibrium constant. We have varied k_1 and k_2 over a wide range to study their relative effects on the H₂, CO, H₂+CO conversion and H₂/CO usage ratio. In the slurry reactor, the variation in k_1 and k_2 can be a result of either temperature variation or catalyst aging. The major conclusions are:

- H₂/CO usage ratio increases with declining shift activity (i.e., decreasing k₂).
- Low H₂ conversion is the result of low F-T activity irrespective of shift activity.
- Low shift activity with good F-T activity gives high H₂ conversion but low (H₂+CO) conversion.
- When the effect of temperature on both k_1 and k_2 is considered for Run CT-256-3 start-of-cycle catalyst, the water-gas shift activity is sufficient to maintain a low H₂/CO usage ratio at temperatures > 245°C. The activation energies for k_1 and k_2 were 100 and 140 kJ/mol, respectively.

In the following the detailed results are discussed.

Figures 6 and 7 show the effect of F-T activity, k_1 , on the H₂+CO conversion for a very low and a very high shift activity ($k_2 = 0.1$ and 2.4 cm³ liquid/s-gFe) respectively. From these two plots, it can be seen that the H₂+CO conversion drops rapidly as the F-T activity (i.e., k_1) declines at both low and high levels of shift activity. The main difference between the low and high shift activity is in the H₂/CO usage ratio. This fact is more clearly borne out by Figures 8 and 9, where the conversion is plotted as a function of shift kinetic constant, k_2 , (i.e., shift activity) at two levels of F-T activity.

These two figures show that shift activity has significant effect on H_2+CO conversion only when it is very low (<0.5 cm³ liquid/s-gFe). In this case, the H_2/CO usage ratio increases substantially and hence even though the H₂ conversion increases with decrease in k₂, the overall conversion decreases. As seen here, the lower shift activity does not reduce the H₂ conversion. Hence, a low H₂ conversion is always due to lower F-T activity. On the other hand, a drop in CO conversion with the H₂ conversion staying the same is a result of decreasing shift activity.

From the above, it follows that lower shift activity increases the H₂/CO usage ratio. The higher H₂/CO usage ratio results in lower H₂/CO ratio in the reactor than was in the feed. This may affect the F-T activity, which in turn may further decrease the overall H₂ + CO conversion. Hence, a higher shift activity is desired.

Since both F-T and shift kinetic constants decrease with temperature, it is important to study the effect of temperature on the overall conversion. Figure 10 shows the effect of temperature on conversion through decrease in both F-T and shift activity. Unlike previous parametric studies where only one kinetic constant was changed at a time, both k1 and k2 were varied with temperature assuming appropriate activation energies (Deckwer et al. (1982), and Newsome (1980)). As expected, the H2+CD conversion decreases substantially with a decrease in temperature. But it is important to note that at temperatures > 245° C the H₂/CO usage ratio is still lower than the feed H_2/CO ratio. Thus, the H_2/CO ratio in the reactor is higher than the feed ratio. A higher H_2/CO ratio in the reactor is always preferrable to minimize catalyst aging. At temperatures below 245°C the H2/CO usage ratio is higher than the feed ratio. It may be advisable to avoid this to prevent any catalyst aging due to the lower H2/CO ratio environment. Thus, for a 0.67 H_2/CO feed ratio gas reaction temperatures should be maintained above 245°C. Of course, if a feed gas of higher H_2/CO ratio is used, then temperature lower than 245°C can be tolerated.

- 3. Future Work
- Continue Run CT-256-7
- Continue long-term stability studies for low methane + ethane operation.
- Evaluate repaired 1 mm orifice gas distributor.
 - B. <u>Task 2 Scoping Studies of</u> Fischer-Tropsch Reactor-Wax Upgrading
 - 1. <u>Thermal Cracking, Hydrocracking, Fluid Catalytic</u> Cracking, and Hydrodewaxing

Preliminary results from proprietary hydrocracking, fluid catalytic cracking, hydrodewaxing, and thermal cracking studies to upgrade F-T reactor-wax are described in the Mobil Proprietary Appendix.

- 2. Future Work
- Continue scoping studies for F-T reator-wax upgrading using conventional refinery processes.
- Analyze data from three thermal cracking runs.

C. Task 3 - Product Evaluation

1. Field Ionization Mass Spectrometry for Fischer-Tropsch Reactor-Wax Analyses

As reported in our previous quarterly report, the reactor-waxes produced during Runs CT-256-4 and -5 were relatively heavy. Also, due to analytical limitations, we were not able to obtain carbon-number distribution for these waxes beyond C55. However, we were able to estimate the C55⁺ content of these waxes. In order to obtain the carbon number distribution beyond C55, we have investigated the application of Field-Ionization-Mass-Spectrometry (FIMS).

We have analyzed wax samples from Runs CT-256-3, -4, The analysis was carried out by an outside laboratory and -5. (SRI International). For each sample two spectrums covering two molecular weight ranges were obtained. The wide range spectrum covers a molecular weight-range of 100-2000. The raw FIMS spectrums for reactor-waxes from Run CT-256-3, -4, and -5 are shown in Figures 11, 12, and 13, respectively. In these figures the corrected intensity is plotted as a function of molecular weight. Because of the wide range of molecular weights, a unit-mass resolution cannot be obtained for these spectrums. The corrected intensity is proportional to the molar content. In all these cases the response factors for different hydrocarbon types (like olefins, paraffins, oxygenates, etc.) is unknown. The area under the curve gives the total mass. To compare these results to the GC results, we have estimated the C55⁺ content from these spectrums. Table 3 summarizes the results. Clearly, the very high C55+ content of CT-256-4 and -5 reactor-wax estimated by the GC method was confirmed. In the case of Run CT-256-3 reactor-wax, however, the FIMS analysis shows significant C55⁺ content (the long tail in Figure 11 past molecular weight 772). The GC result in this case was reconfirmed by repeating the analysis. Hence, the FIMS analysis will be repeated to resolve the discrepancy. Table 3 also gives number average and weight average molecular weights for these reactor-waxes. The increasing molecular weight for these waxes (from Run CT-256-3 to Run -5) is consistent with the increasing viscosity observed (and reported earlier).

Since the wide-range spectrum did not resolve intensity peaks for each mass, no digitized data other than the spectrums shown here was provided by SRI International. In order to obtain a carbon-number distribution plot (or molecular weight-distribution), it is necessary to obtain the area under each peak. However, it is very difficult to do this for peaks below "800 molecular weight, since they are very crowded. Hence, only the peaks beyond molecular weight 800 were considered. The carbon-number distribution below molecular weight 800 was obtained from another, higher resolution, spectrum.

Figure 14 shows a typical high-resolution spectrum obtained over a molecular weight range of 100 to 800. In this range a unit-mass resolution is achieved, but the range is limited to 700 up to the molecular weight of 1300. The y-axis for this high-resolution spectrum is the percent of total moles seen by the spectrometer (i.e., between 100 to 800 molecular weight). Once again, as in the case of wide-range spectrum no correction has been made for response factor of different hydrocarbon types, for effect of different molecular weights, and also for C^{13} isotope contribution. Since the content of C^{13} isotope increases with increasing molecular weight, it becomes increasingly important to take this into consideration for the higher molecular weight hydrocarbons. For example, the C50 hydrocarbon contains about 33% C^{13} carbon atoms.

Since no response factors of hydrocarbon types and of molecular weights over this molecular weight range are available, we have used those obtained up to C20 (molecular weight <250). The high-resolution spectrum thus gave a carbon number distribution over the molecular weight range of 100-800. By combining the distribution obtained from the low-resolution (or wide-range) data for the molecular weight range >800, a complete carbon-number distribution was obtained as given in Figure 15. As seen in the figure, a bimodal carbon-number distribution is revealed for the Run CT-256-5 wax. The second hump at carbon-number of about 105 has been observed for the first time for Fischer-Tropsch waxes. As evident from the wide-range spectrums (Figures 11 to 13), the Run CT-256-3 reactor-wax did not exhibit a second hump. The carbon number distribution below C55 agrees well with that obtained from the modified GC method. The presence of a second hump in the carbon-number distribution cannot be explained at this time.

Based on our evaluation of FIMS technique, the following limitations have been identified:

• The extent of fragmentation of the heavy reactor-waxes is unknown

- The response factors of different hydrocarbon types is unknown
- High-resolution data can be obtained only up to molecular weights of 1300
 - 2. <u>Analyses of Oxygenates in Fischer-Tropsch</u> Reactor-Wax

a. Low Temperature Liquid Chromatography (LC)

For light waxes, a low temperature LC method was initially developed and used. An extraction is performed prior to LC to remove as much as possible the components with a carbon number greater than C40. This is necessary to prevent the high carbon number hydrocarbons from eluting with the oxygenated hydrocarbons.

Approximately 1 g of the wax was weighed into a 15 cm³ centrifuge tube. Ten cm³ of pentane was added. The wax was dispersed with a mini-spatula, after which an additional 4 cm³ of pentane was added. The centrifuge tube was capped and carefully shaken prior to centrifuging it for 15 minutes. The supernatant pentane was removed and the extractiion was repeated two additional times. The pentane soluble consists mostly of C40⁻ hydrocarbons and oxygenates. The amount of pentane soluble material was obtained by difference after drying and weighing the insoluble fraction.

The combined pentane soluble fractions were further fractionated on a 30 cm x 1.1 cm (ID) Michel-Miller glass column (Ace Glass, Vineland, NJ) packed with 25 cm of 20-44 micron Bio-Sil A silica gel (Bio-Rad, Richmond, CA). Prior to use, the silica gel was activated overnight at 150°C. The column was eluted sequentially with 250 cm³ pentane to remove the hydrocarbons, 250 cm³ methylene chloride to elute esters and ketones and 150 cm³ methanol to elute alcohols. A Kuderna-Danish concentrator was used to remove the bulk of the solvents. The cuts were then brought to dryness in preweighed inverted rim breakers with a slight nitrogen purge.

b. High Temperature Liquid Chromatography

Reactor-waxes containing greater than 5 wt % C60+ hydrocarbons were difficult to extract with pentane. In addition, these waxes may contain higher molecular weight oxygenates which may not be completely extracted into pentane. As a result a general high temperature liquid chromatographic method applicable to most F-T waxes was developed.

Approximately 2.5 g of finely dispersed F-T waxes was loaded on a Michel-Miller column as described above. The column was packed with 40-63 micron Woelm silica gel. The sample was mixed with silica gel on top of the bed to prevent plugging of the column. The temperature was controlled with heating tape and a powerstat. The column was initially eluted with 100 cm^3 of n-nonane at 80°C to elute the hydrocarbons and then 75 $\rm cm^3$ of n-propanol to elute the oxygenates. The temperature of the eluting solvents was monitored with a thermometer immediately at the column exit. After an initial run, the temperature settings were readily reproduced for a given column system. The hydrocarbon and oxygenates were brought to dryness as indicated above. Total percent hydrocarbons, oxygenates and loss and/or residue remaining on the column was reported. Table 4 summarizes oxygenates results by the high temperature method for two F-T waxes.

3. Future Work

- FIMS analysis of samples containing paraffins only (such as F-T derived FT-200 wax)(1)
- FIMS analysis of samples containing oxygenates only
- FIMS analysis of standards containing known ratios of paraffins and olefins
 - D. Task 4 -Slurry Fischer-Tropsch Reactor
 - 1. <u>Photographic Analysis of Bubble Flow Patterns</u> in Bubble-Columns

During the evaluation of three feed-gas distributors in the 5.1 cm ID hot-flow bubble-column, the bubble flow patterns within the glass sections of the column were photographed. The bottom 152 cm glass section permitted the observation of bubble flow patterns forming at the distributor. The top glass section between the 610 and 914 cm levels revealed the well-developed flow patterns at the top. The bubble flow patterns were very similar in the case of the two orifice-type distributors (1 mm single-orifice and 0.5 mm-3 hole). Hence, photographs of only the 0.5 mm-3 hole distributor case have been shown here.

Figure 16 shows bubbles produced by a 20 micron SMP distributor. As reported earlier (Quarterly Report, January-March, 1984), the bubbles formed at the distributor are uniformly small and they stay uniform throughout the column. Figure 16 clearly shows the uniform, densely packed bubbles. The bubble size distribution did not change noticeably at different locations along the column or at different superficial gas velocities. Hence, only one typical photograph is shown here. The bubble size from the photographs for the SMP case was found to be less than 1 mm.

(1) A F-T paraffin wax with an average molecular weight of 600.

In contrast to the uniformly small bubbles produced by the SMP, the orifice-type distributors give a wider bubble size distribution as shown in Figure 17. In this photograph the bubble flow patterns at three different locations along the column have been shown using a 0.5 mm-3 hole gas distributor operating at 1.2 cm/s superficial gas velocity. In the zone very close to the distributor (between 13 to 25 cm) large bubbles can The black vertical strips seen in the photograph are be seen. the heating rods used to heat the column. These heating rods are 8 mm in diameter and can be used as a reference for bubble size measurement. From the photograph (13-25 cm above the distributor) a few bubbles as large as 6-7 mm can be seen. Around these large bubbles a lot of small bubbles (~2 mm) can be observed. As seen from the middle photograph in the figure (127-142 cm above the distributor), the large bubbles seem to have broken up into smaller bubbles. In the very top zone (663-678 cm from the distributor) bubbles appear to be of more uniform size (~1 to 2 mm). However, even the small bubbles in the top zone are larger than those observed with the SMP. Consequently, the gas holdups with the orifice distributors are lower than those with the SMP. Also, the larger bubbles at the top zone in the case of orifice-type distributors substantially reduced the foam height.

As reported earlier, the slugging at constant frequency was observed with all three distributors. A typical photograph of the slug is shown in Figure 18 produced by 0.5 mm-3 hole distributor at 4 cm/s. Since a slug is a lot more transparent, it appears as a white patch in the photograph. A lot of small bubbles can be clearly seen to be moving around the rising slug. Due to presence of very small bubbles around a slug, the overall gas holdup can be still substantially high.

2. Gas Holdup Profiles in Hot-Flow Columns

a. <u>Gas Holdup Profiles in the 5.1 cm ID</u> Hot-Flow Bubble-Column

In the 5.1 cm ID hot-flow bubble-column we have measured gas holdup profiles using a DP-cell arrangement. The overall holdup was obtained by visual observation of the expanded slurry height. The local gas holdup along the length of the column was measured using DP cells. Figure 19 gives local gas holdup along the bubble-column at various superficial gas velocities for the 1 mm single-orifice distributor. The data at lower gas velocities of 2.2 and 3.3 cm/s were taken with a higher static height of 627 cm. The rest of the data at higher superficial velocities were taken at the lower static height of 452 cm. In all cases the gas holdup was found to increase along the length of the bubble-column. This observation is quite consistent with the bubble flow patterns shown in the previous subsection. In the case of orifice-type distributor the bubbles formed at the bottom are large (~6-7 mm) giving lower holdup at the bottom. These large bubbles tend to break up as they rise upward. Hence the gas holdup increases along the height of the column.

The lower gas holdup in the bottom zone also substantiates our earlier results showing the effect of static liquid height. Figure 20 is the same plot shown in the previous quarterly report (Figure 15, Quarterly Report, January-March, 1984) illustrating the effect of decreasing static liquid height on the gas holdup. Additional local holdups (marked by V and Δ) in the bottom zone (between 30-305 cm) for the higher static height case have also been shown on the same plot. The local gas holdup in the bottom zone compares well with the overall gas holdup at lower static height. Thus, the bubble flow patterns in the lower zone close to the distributor seems to be similar at all static liquid heights. This supports our explanation of lower gas holdup for very low static height.

b. <u>Gas Holdup in First-Stage Bubble-Column</u> Reactor

In the last quarterly report, we reported that a new purgeless DP-cell system had been installed along the first-stage bubble-column reactor of the two-stage BSU. During Run CT-256-7, gas holdups were measured using this system. A plot of the overall gas holdup as a function of time is presented in Figure 21. The scatter in the data is substantial, thus preventing the development of a correlation for gas holdup as a function of superficial gas velocity.

It is clear, however, that the gas holdup jumped from an average of 25 vol % to 40 vol % after the feed-gas distributor was repaired at 76 DOS (See Section IV.A.1). This indicates that smaller bubbles were being formed following the repair, a direct consequence of higher gas jet velocity.

3. <u>Dynamic Disengagement for Bubble-Size Measurement</u> in Hot-Flow Bubble-Columns

. Theory

Sriram and Mann (1977) developed a dynamic disengagement technique to measure bubble-rise velocity in bubble-columns. The technique requires measurement of the steady state gas holdup ϵ_{g0} , and measurement of the transient gas holdup ϵ_{g} following the interruption of the gas flow. The transient gas holdup can be measured by recording with a video camera the expanded liquid level as a function of time.

Sriram and Mann (1977) showed that for a certain bubble-size distribution f(dB), and in absence of liquid flow and axial nonhomogeneity,

$$\epsilon_{go} = u_g / \int f(d_B) u_B dd_B$$
(3)

$$\epsilon_g = \epsilon_{go} \int f(d_B) [1 - tu_B / L(t)] dd_B$$
(4)

The term in brackets in equation (4) represents the fraction of bubbles of size dB remaining in the column after time t. This term is taken as zero for tuB>L(t).

For a narrow uni-modal bubble-size distribution (f(dB)=1 in Equation (3)), the average bubble-rise velocity is:

$$\bar{\mathbf{u}}_{\mathrm{B}} = \mathbf{u}_{\mathrm{g}} / \epsilon_{\mathrm{go}} \tag{5}$$

From correlation of \overline{u}_B vs \overline{d}_B (e.g. Abou-el-Hassan (1983), Mendelson (1967)), the average bubble-size \overline{d}_B can be calculated.

For narrow bi-modal distributions, Equation (4) can be rewritten as

$$\epsilon_{g} = \epsilon_{go} [f_{S}(1 - t \bar{u}_{BS}/L) + f_{L}(1 - t \bar{u}_{BL}/L)]$$
(6)

where S and L stand for small and large bubbles, respectively. It can be shown that Equation (6) can be rewritten as L (the dynamic expansion height) versus t:

$$L/L_{o} = 1 - (\epsilon_{go} \overline{u}_{BS} + \epsilon_{go} L\overline{u}_{BL}) t/(1 - \epsilon_{go}) Lo; t \le t^{*}$$
 (7a)

$$L/L_{o} = (1 - \epsilon_{go}) / (1 - \epsilon_{goS}) - \overline{u}_{BS} \epsilon_{goS} t / (1 - \epsilon_{goS}) Lo; t > t^{*}$$
(7b)

where t^* is the time taken by the large bubbles to disengage, and ϵ_{goS} is the fraction of the gas holdup occupied by small bubbles.

Some publications present Equation (6) as a linear function of t (e.g. Godbole et al., 1982), by substituting the initial height L_0 for L. This, of course, is only valid for low ϵ_{g0} , where L does not change much. Our derivation, Equations (7a) and (7b), are valid for any ϵ_{g0} , and L/L₀ is always a linear function of t.

To evaluate ϵ_{gos} , \overline{u}_{BS} , \overline{u}_{BL} , \overline{d}_{BS} , \overline{d}_{BL} , the following procedure is recommended:

- a. Find breakpoint ϵ_g^* , t*
- b. Find \overline{u}_{BS} and ϵ_{goS} from Equation (7b)
- c. Find uBL from equation (7a)
- d. Use correlation between \overline{d}_B and \overline{u}_g to calculate \overline{d}_{BS} and \overline{d}_{BL}

b. <u>Application to 5.1 cm ID Hot-Flow</u> Bubble-Column

To obtain information about the bubble-size distribution, dynamic gas-disengagement experiments were carried out using the 5.1 cm ID bubble-column. In this experiment, upon shutting off the feed gas the decrease in the expanded liquid height was monitored by a video camera and a timer. Figure 22 is a plot of expanded liquid height as a function of elapsed time for the 0.5 mm-3 hole distributor. Any foam at the top was not considered for this experiment; i.e., the decrease of foam-liquid interface was recorded instead of the top of the foam. The experiments were carried out at two superficial gas velocities (1.2 and 2.2 cm/s). At higher velocities the gas holdup was very large and hence it required a longer length of the column to be recorded by a video camera. Due to the space limitation the video camera setup could not cover the necessary length of column.

As seen in the figure the data can be fitted by a straight line, except for the last few seconds. As shown in the previous subsection, the straight line plot indicates that bubble-size distribution is very narrow. The following equation describes the dynamic decrease in the expanded liquid height:

$$L = L_0 - (L_0 - L_s) \overline{u}_B t / L_s$$
(8)

where L_s is the static liquid height and u_B is the average bubble-rise velocity. Table 5 gives the average bubble rise velocity obtained from the slope of the plots.

By using a literature correlation of up versus dp by Abou-el-Hassan (1984), the average bubble size can be deduced from the bubble rise velocity. Even though the correlation was not developed for F-T wax mediums, due to lack of any other data, we have used this correlation. The average bubble diameter (of 1.2 and 2.2 mm) obtained here agrees well with the photographic observation.

For a uniform bubble size distribution the overall gas holdup is related to superficial gas velocity by Equation 5. Thus, a plot of $\epsilon_{\rm g}$ versus $u_{\rm g}$ should have a slope = $1/\bar{u}g$. The plot of ϵ_g versus ug was reported in a previous quarterly report (January-March, 1984, Figure 11) and is given here in Figure 23. The data can be described by a following correlation:

$$\epsilon_{g} = 6.5 u_{g}^{1.1} \tag{9}$$

The above correlation indicates that the bubble rise velocity is not quite constant over the full range of superficial gas velocity. However, by fitting a straight line to this data, the average bubble rise velocity (= 1/slope) can be determined to be 14 cm/s. Clearly this average bubble rise velocity compares well with that obtained from dynamic disengagement data.

4. <u>Pressure Drop Across an Drifice Distributor</u>, Run CT-256-7

As described in the January-March Quarterly Report, a correlation from the literature was adapted to calculate the pressure drop across orifice distributors. When the 1 mm orifice used in Run CT-256-7 was repaired after 76 days on stream, pressure drops across it were measured using nitrogen and synthesis gas at various pressures and temperatures. The results were then compared with the calculated values, as shown in Figure 24. The agreement is excellent, and the wide range of pressure drops indicate that the correlation may be used with confidence.

5. Status of Tall, Hot-Flow Bubble-Columns

On August 14 an accidental fire on the 10.2 cm ID x 9.1 m tall hot-flow bubble-column forced the shutdown of both the hot-flow bubble-column unit and the two-stage BSU. At the time, an evaluation of a 20 micron SMP feed-gas distributor using FT-200 wax was in progress. The fire was caused by the contact of the hot wax spurting from a broken glass outlet (for a thermocouple) at the 76 cm level with a nearby electric junction box. It caused minor damages to both units. Modifications to the unit, which include replacement of all glass sections having protruding outlets with straight glass sections were carried out. The damage to the electrical outlet and utility lines was repaired in about two months along with a complete safety inspection. After the modifications both hot-flow bubble-columns were shaken down. An evaluation of a 2 mm single orifice feed-gas distributor using the 5.1 cm ID column was then initiated.

6. <u>CSTR's as Alternative to Fischer-Tropsch</u> <u>Bubble-Column Reactor:</u> <u>Mathematical Model</u> <u>Development</u>

Series of continously stirred tank reactors (CSTRs) have several potential advantages over bubble-columns, as previously reported (Quarterly Report, October-December, 1983). In the current modeling effort, the potential advantage of increased catalyst loading in CSTRs is studied by using a new mathematical model.

The major features of the new model are

- Hydrodynamic correlations which integrate the effect of both mechanical agitation and gas sparging.
- Nonlinear kinetics which include CO₂ rate inhibition in addition to previously used H₂O inhibition. Furthermore, the effect of total pressure is also included.
- The same basic model is used for CSTR and bubble-column calculations. The number of stirred tanks required to simulate the bubble-column is estimated from axial dispersion correlations.

Model predictions will be used to weigh the economics of better reactor utilization (higher catalyst loading) versus increased cost (stirring power requirement).

Details of the model and calculations will be given in a future quarterly report.

7. Future Work

Evaluate a 2 mm single orifice using 5.1 cm ID hot-flow bubble-column

V. Nomenclature

dR	Bubble Size, cm
dR	Average Bubble Size, cm
f	Fraction of Bubbles of Size dB
L	Expansion Height, cm
Le	Static Height, cm
t	Time, s
up	Bubble-Rise Velocity, cm/s
ūp	Average Bubble-Rise Velocity, cm/s
ug	Gas Superficial Velocity, cm/s

Greek Letters

 $\epsilon_{\rm g}$ Gas Holdup

Subscripts

L	Large
S	Small
0	At t=0

Acronyms

CSTR	Continuous Stirred-Tank Reactor
DOE	Department of Energy
DOS	Days On Stream
DP	Differential Pressure
FIMS	Field-Ionization-Mass-Spectrometry
F-T	Fischer-Tropsch
GC	Gas Chromatography
ID	Inside Diameter
LC	Liquid Chromatography
SMP	Sintered-Metal Plate

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VI. References

Abou-El-Hassan, M.E., Chem. Eng. Commun., <u>22</u>, 243 (1983)
Deckwer, W. D., Serpemen, Y., Ralek, M., and Schmidt, B., Ind. Eng. Chem. Process Des. Dev., 21, 222 (1982).
Godbole, S.P., Monath, M.F., and Shah, Y.T., Chem. Eng. Commun, <u>16</u>, 119 (1982)
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.
Mendelson, H.D., AIChE Journal, <u>13</u>, 250 (1967)
Newsome, D. S., Cat. Rev. - Sci. Eng., <u>21</u>, 275 (1980).
Sriram, K., and Mann, R., Chem. Eng. Sci., 32, 571 (1977)

Table l

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DOS .	MAJOR EVENTS
-0.2-0	Pretreatment
0	2.52 MPa; 257°C; 0.67 H_2/Co ; 4.0 Cm/s
1.0	Wax Withdrawal Started
6.9	2nd-Stage on at 253°C
14.1	Lost \leftarrow 150 g Catalyst (leak on wax removal system)
19.9	$2.52 \rightarrow 2.00 \text{ MPa}$
20.8	$2.00 \rightarrow 1.48 \text{ MPa}$
21.7	$1.48 \rightarrow 2.52 \text{ MPa}$
25	2nd-Stage Temp \longrightarrow 327°C
36.9	600 g Catalyst I-D added
40.7	2nd-Stage Out
49.9	700 g Catalyst I-D added
56.1	Potassium added
57.8-58.8	Potassium added
60.7-61.4	Potassium added
62.5-63.0	277°C Operation
64.8-65.1	280°C H ₂ -Treatment
67.7	$257^{\circ}C \rightarrow 277^{\circ}C$
76.0	Unit Shutdown (Slurry Solidifying in-situ)
76.0+	Unit Restarted; 277°C; 2.52 MPa; 4.0 cm/s
81.1-81.7	1.14 MPa Operation
84.0	$277 \rightarrow 260^{\circ}C$

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FIM R	S Analysis of eactor-Waxes			
C55+ Content, Wt. %	<u>CT-256-3</u>	<u>CT-256-4</u>	<u>CT-256-5</u>	
	27	64	72	
C55+ Content, Wt. % (Based on GC)	7	65	75	
No. Average MW	642	814	976	
(Carbon No.)	(46)	(58)	(70)	
Wt. Average MW	951	1135	1291	
(Carbon No.)	(68)	(81)	(92)	

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CT256-4 (<u>B1ended</u>) 100 22 22 c Total Oxygenates by High Temperature Liquid Chromatography Method Table 4 (Wt %) CT256-3 (83 D0S) 100 (?) (=) 84 67) Hydrocarbons Residue/Loss Oxygenates

J			
u B, cm/s	15.4	13.1	
ng, cm/s	1.2	2.2	

B, mm

2.2

1.2

28

DYNAMIC DISENGAGEMENT RESULTS

Table 5







Reactor-Wax Yield, Wt % HC

FIGURE 4

SLURRY BUBBLE-COLUMN CATALYST CONCENTRATION PROFILES (Run CT-256-7)









Conversion, Mol %













Yjisnəjnl



FIGURE 12

Intensity





FIMS SPECTRUM OF RUN CT-256-5 REACTOR-WAX FIGURE 14



FIGURE 16

BUBBLES PRODUCED BY 20µm SINTERED-METAL-PLATE





FIGURE 18

SLUG PRODUCED BY 0.5 mm-3 HOLE DISTRIBUTOR AT 4 cm/s















COMPARISON OF EXPERIMENTAL VERSUS CALCULATED PRESSURE DROP



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