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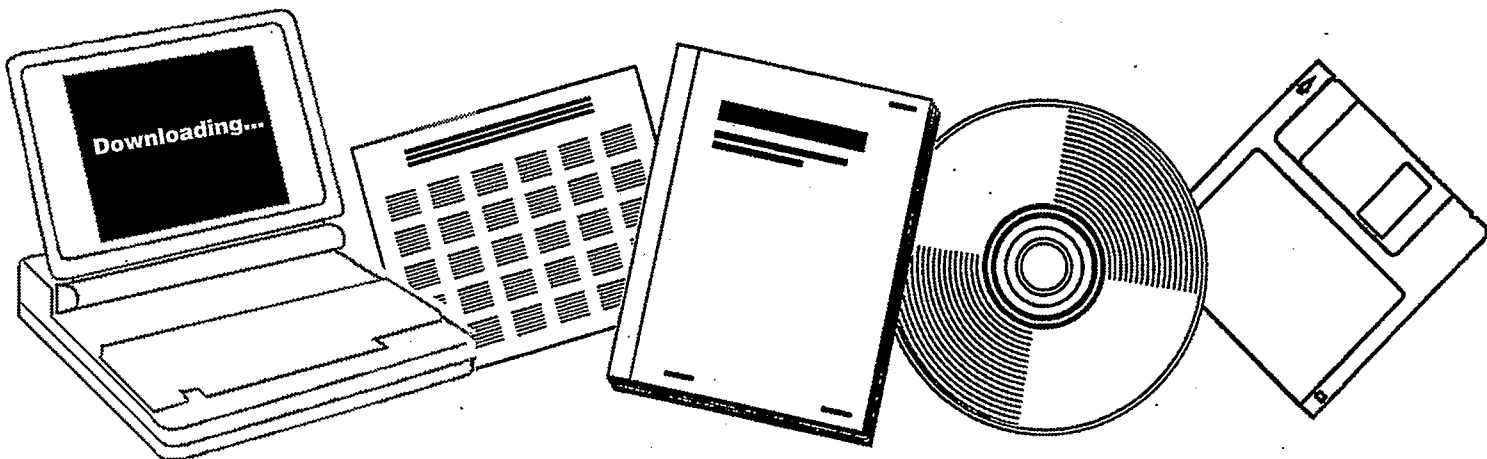
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**SLURRY FISCHER-TROPSCH/MOBIL TWO-STAGE
PROCESS OF CONVERTING SYNGAS TO
HIGH-OCTANE GASOLINE. QUARTERLY REPORT, 1
JULY-30 SEPTEMBER 1982**

**MOBIL RESEARCH AND DEVELOPMENT CORP.
PAULSBORO, NJ**

DEC 1982



U.S. Department of Commerce
National Technical Information Service

DOE/PC/30022-8
(DE83011821)

Distribution Category UC-90d

DE83011821



SLURRY FISCHER-TROPSCH/MOBIL TWO-STAGE PROCESS
OF CONVERTING SYNGAS TO HIGH OCTANE GASOLINE

QUARTERLY REPORT FOR THE PERIOD
1 JULY - 30 SEPTEMBER, 1982

REPORT PREPARED BY: J. C. W. KUO

CONTRIBUTORS:

P. M. BERGQUIST	C. P. KYAN
F. P. DI SANZO	T. M. LEIB
L. A. GREEN	J. P. WARNER
K. M. GUPTA	W. K. WONG

MOBIL RESEARCH AND DEVELOPMENT CORPORATION
PAULSBORO, NEW JERSEY 08066

DATE PUBLISHED - DECEMBER 1982

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AC22-80PC30022

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I. Abstract

The second run of the pilot plant, designated as Run CT-256-2, was concluded after twenty days on stream. In this experiment, the evaluation of the second Fischer-Tropsch catalyst, a Fe/Cu/K₂CO₃ catalyst designated as I-B, was carried out. Unfortunately, an overheating of the bottom flange of the slurry reactor and later a plugging of the feed-gas distributor forced a premature termination of the run. This upset probably resulted from a leakage at the bottom flange. The F-T catalyst was damaged during this operational upset as indicated by a lower activity and a higher methane + ethane selectivity. In the same run, an evaluation of a new second-stage ZSM-5 catalyst, designated as II-B, was also initiated. This catalyst performed satisfactorily during the run and has accumulated sixteen days on-stream time.

A new run, designated as Run CT-256-3, was immediately initiated after the termination of Run CT-256-2 using a new batch of the same Fischer-Tropsch catalyst I-B. This run had accumulated sixty-one days on stream by the end of this reporting period. High gas throughput and conversion have been demonstrated during this time. This run is being continued beyond this reporting period, although an unloading and reloading of the F-T slurry following a leakage at the bottom flange resulted in a substantial loss of catalytic activity and an increase of methane + ethane yield. Evaluation of the II-B ZSM-5 catalyst in the second-stage was also being continued with a total of fifty-seven days on-stream and two regenerations by the end of this reporting period. After both regenerations, no significant changes from the initial catalyst activity were observed.

Bubble-column gas holdups were measured using three different mediums: FT-200 Vestowax⁽¹⁾, a used slurry from Run CT-256-1, and n-hexadecane, in two existing, nonreacting glass columns. Using these small diameter (3.2 and 5.1 cm) and short (216 cm) columns, the gas holdup was found to vary strongly with the static liquid height; moderately with the solid concentration and the column diameter; and little with the slurry temperature. High gas holdups (about 60 vol %) with excessive foaming were observed for both FT-200 Vestowax and the used slurry at high gas velocity in the 3.2 cm diameter hot column. The n-hexadecane at room temperature demonstrated substantially less gas holdups than those observed for F-T waxes in the hot column.

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

Product evaluations concerning stability, i.e., gum formation and oxidation, for the raw gasoline samples from Runs CT-256-2 and -3 were initiated. Existent (heptane washed) gum contents were all within acceptable limits for conventional gasoline, as were the oxidation stabilities, indicated by the induction period method. However, total residues on evaporation (unwashed gum) were generally high, probably due to the presence of a small amount of high-boiling, heptane-soluble hydrocarbons.

II. Objective and Scope of the Project

The overall objective of the contract is to develop a two-stage slurry Fischer-Tropsch/ZSM-5 process for direct conversion of synthesis gas, of the type produced in a coal gasification system, to high octane gasoline. The specific objective is to design, construct, and operate a bench-scale pilot plant so that the economic potential of this process concept can be evaluated. To accomplish these objectives, the following specific tasks will be undertaken:

Task 1 - Design of Bench-Scale Pilot Plant

A two-stage slurry F-T/ZSM-5 bench-scale pilot plant will be designed for conversion of synthesis gas to high octane gasoline. The slurry F-T reactor will be 5.1 cm diameter and 762 cm high. The fixed-bed ZSM-5 reactor will be 5.1 cm diameter and 10-46 cm high. A distillation column will be designed to obtain stabilized gasoline products.

Task 2 - Construction and Shakedown of Pilot Plant

The pilot plant will be constructed in MRDC Paulsboro Laboratory. The unit will be shaken down when completed.

Task 3 - Operation of Pilot Plant

At least three slurry F-T catalysts will be tested in the bench-scale pilot plant. One of these catalysts may be provided by DOE's alternate catalyst development projects. The best first-stage catalyst together with a ZSM-5 class zeolite catalyst will be used for process variable studies and catalyst aging tests in the bench-scale unit. Products obtained from the unit will be evaluated to define their qualities.

Task 4 - Conceptual Design Study

A preliminary conceptual design of the process will be developed for a commercial size plant for the conversion of synthesis gas to high octane gasoline. Scoping costs of the plant will be estimated.

III. Summary of Progress to Date

The second run of the two-stage synthesis gas conversion pilot plant, designated as Run CT-256-2, was concluded after twenty days on stream. The highlights of the run were:

- The evaluation of the second Fischer-Tropsch catalyst, a Fe/Cu/K₂CO₃ catalyst designated as I-B, was carried out.
- The ranges of the operating conditions for the first-stage slurry Fischer-Tropsch reactor were:

Temperature, °C	257-263
Pressure, MPa	1.14-1.83
H ₂ /CO Feed Ratio, Molar	0.7
Superficial Feed-Gas Velocity, cm/s	3.2-4.1
Space Velocity, NL/gFe-hr	1.5-3.0

The H₂+CO conversion ranged from 60 to 88 mol % and the methane + ethane yield from 9 to 15 wt % of the total hydrocarbons produced.

- A new second-stage ZSM-5 catalyst, designated as II-B, was on stream for twenty days. It satisfactorily converted the F-T products into high octane gasoline. The ranges of the operating conditions for the second-stage fixed-bed reactor were:

Temperature, Inlet, °C	288-352
GHSV, l/hr	1,435-3,255

- After sixteen days on stream, the bottom flange of the slurry reactor was overheated to 397°C and the feed-gas distributor eventually plugged. This operational upset was attributed to a leakage at the bottom flange. A large loss of F-T catalyst activity (estimated to be roughly 40%) was observed. The methane + ethane yield also increased from about 10 wt % of the total hydrocarbons produced to 18-20 wt %.

The third BSU run, designated as Run CT-256-3, was initiated immediately after the operational upset of Run CT-256-2. A new batch of I-B Fe/Cu/K₂CO₃ catalyst (same as that used in Run CT-256-2) was used in the first stage reactor, and the same II-B ZSM-5 class catalyst was used in the second reactor. This run has been extremely successful and had accumulated sixty-one days on stream by the end of this reporting period. This run is being continued. The synthesis operation was interrupted three times during this period. The first two interruptions were minor (stoppage of synthesis gas flow for nine

and thirty-six hours, respectively) and resulted in slight loss in F-T catalyst activity and a slight increase in methane yield. During the third interruption, the slurry was unloaded, then reloaded after ten days. A substantial deterioration of the F-T catalyst activity and a substantial increase in the methane + ethane yield was observed.

In order to understand the hydrodynamics of bubble-column reactors, bubble-column gas holdups were measured using two existing non-reacting columns, a 3.2 cm diameter hot column, and a 5.1 cm diameter cold column (both about 216 cm height). Using the used slurry from Run CT-256-1 in the hot column, the gas holdup was found to decrease strongly with the increasing static liquid height, and little when the slurry temperature was varied from 200°C to 225°C. The effect of varying solid concentration on the gas holdup was somewhat irregular. At low gas velocities, the gas holdup decreased slightly with increasing solid concentration. While at high gas velocities, the gas holdup increased. Similar gas holdups were observed for both the used slurry and FT-200 Vestowax in the hot column. At gas velocities higher than 1 cm/s, both mediums exhibited high gas holdup (about 60 vol %) with excessive foaming. Using n-hexadecane at room temperature in both columns, the gas holdup decreased moderately with the increasing column diameter. Further work in this area using nonreacting columns of larger dimensions and higher temperatures is strongly recommended.

Product evaluations concerning stability, i.e., gum formation and oxidation, of the raw gasoline samples from Runs CT-256-2 and -3 were initiated. Existent (heptane washed) gum contents were 1-3 mg/100 mL, well within the 5 mg/100 mL specification for automotive gasolines. The oxidation stabilities, indicated by the induction period method (ASTM D525) were 305 to 725 minutes, well above the minimum specification of 240 minutes for automotive gasolines. However, total residue on evaporation (unwashed gum) was generally high (up to 170 mg/100 mL), probably due to the presence of small quantities of high-boiling, heptane-soluble hydrocarbons.

IV. Detailed Description of Technical Progress

A. Task 3 - Operation of the Pilot Plant

1. Run CT-256-2 - Conclusion

The second BSU run, designated as Run CT-256-2, using Catalyst I-B (containing Fe/Cu/K₂CO₃) in the first-stage bubble-column F-T reactor and Catalyst II-B (a ZSM-5 class catalyst) in a second-stage fixed-bed reactor, was concluded on July 24, 1982. In spite of the excellent performances of the catalysts, the run was terminated prematurely after twenty days on stream due to an operational upset which is described later.

Other major highlights from this run were:

- Smooth operation of the slurry F-T reactor with a high catalyst loading (19.5 wt % initially); high synthesis gas throughput; and high conversion was demonstrated over a period of seventeen days.

The ranges of the first-stage slurry F-T reactor operating conditions and performance over this seventeen-day period were:

H ₂ +CO flow rate, NM ³ /hr	1.4-2.5
Temperature, °C	257-263
Pressure, MPa	1.14-1.83
H ₂ /CO feed molar ratio	0.7
Superficial feed-gas velocity, cm/s	3.2-4.1
Space velocity, NL/gFe-hr	1.5-3.0

H ₂ +CO conversion, mol %	60-88
Methane + ethane yield, wt % HC	9-15

- The ranges of the second-stage fixed-bed reactor operating conditions were:

Temperature inlet, °C	288-352
GHSV, l/hr	1,435-3,255

This catalyst performed satisfactorily in converting the first-stage F-T products into high octane gasoline.

- A large loss of the F-T catalyst activity (estimated to be about 40%) was observed after the operational upset. The methane + ethane yield also increased from about 10 wt % of the total hydrocarbon produced to 18-20 wt %. The catalyst was obviously damaged during the upset.

a. First-Stage Fischer-Tropsch Reactor Operation

In the last Quarterly Report (April-June, 1982), the aspects of the first-stage F-T reactor operation, relating to the slurry catalyst loading, initial slurry reactor gas holdup data, F-T catalyst pretreatment and a brief description of the synthesis operation for the first five days on-stream, were reported. In this report, a detailed description of the synthesis operation for the entire period of Run CT-256-2 is presented. The major events of this run are summarized in Table 1 which includes the events leading up to the end of June, 1982 as reported in the last Quarterly Report. Table 2 lists the events of reactor-wax withdrawal and slurry loading, samplings, and unloading. Table 3 summarizes the range of the operation results and Figure 1 depicts the H_2+CO conversion and methane + ethane yield versus time on-stream. The material balances were performed daily and results are summarized in Table A-1 of Appendix A. Table A-2 gives the detailed hydrocarbon product compositions.

The synthesis operation was commenced at 260°C, 1.14 MPa (150 psig) and 3.2 cm/s. The initial H_2+CO conversion was 45 mol % and gradually increased to 73 mol % after about one day on-stream. This increase in conversion was attributed to continual activation of the F-T catalyst. To take advantage of this increase, the feed-gas superficial velocity was increased from 3.2 to 4.1 cm/s. Responding to this higher superficial velocity, the H_2+CO conversion first dropped to 61 mol % and then gradually increased, leveling off at 86 mol % after four days on-stream.

From five to seven days on-stream, the slurry reactor pressure was increased to 1.48 MPa (200 psig) while maintaining a constant feed-gas superficial velocity. The H_2+CO conversion dropped slightly to 82 mol %. The methane + ethane yield stayed fairly constant at about 10.5 wt % of the total hydrocarbons produced. A small decrease in the feed-gas superficial velocity to 3.6 cm/s brought the H_2+CO conversion back to 86 mol %.

During this seven-day period of synthesis operation, substantial reactor-wax was accumulated in the slurry reactor. Three reactor-wax withdrawals through the filter located at the 305 cm level totaled 3,225 g reactor-wax, which maintained the slurry level between 610 and 762 cm. Solid-content analyses indicated that about 68 g of catalysts were in the reactor-wax withdrawn. However, no noticeable drop in conversion was observed, probably due to continual activation of the F-T catalyst during this early period of synthesis operation.

To check F-T catalyst aging, the slurry reactor pressure was lowered back to 1.14 MPa and operated at 260°C and 3.9 cm/s from seven to twelve days on-stream. The H₂+CO conversion first dropped to 72 mol % and then gradually climbed up to 78 mol %. The methane + ethane yield also increased from 10.5 to 12 wt % of the total hydrocarbons produced. At eight days on-stream, the feed-gas superficial velocity was lowered to 3.4 cm/s. The H₂+CO conversion continued to increase and then leveled off at 86 mol % with a methane + ethane yield of about 15 wt %. Judging from the space velocity required to reach the same H₂+CO conversion as in the early part of this run, the catalyst had lost about 8% of its activity during the first eight days' operation. However, this estimated aging rate may not be meaningful in a longer time scale since, as mentioned later, stable catalyst activity was observed during the next seven days.

From twelve to fifteen days on-stream, the charge synthesis gas throughput was again increased by raising the slurry reactor pressure to 1.48 MPa while maintaining the superficial velocity at 3.4 cm/s. The operation during this period was marked by a reduction in the methane + ethane yield from 15 to 12.5 wt % of the total hydrocarbons produced. The H₂+CO conversion was very stable at 86 mol % for a seven-day period (eight to fifteen days on-stream) with slurry reactor conditions at 1.14-1.48 MPa, 262°C and 3.4 cm/s.

To further increase the sythesis gas throughput, the slurry reactor pressure was increased at fifteen days on-stream to 1.83 MPa (250 psig) while keeping the superficial velocity constant at 3.4 cm/s. The methane + ethane yield declined to 11 wt % while the H₂+CO conversion decreased slightly to about 85 mol %. Table 4 summarizes the effect of reactor pressure on the slurry reactor performance. The major effect is the decreasing methane + ethane yield with increasing pressure.

At sixteen days on-stream, 1,560 g of reactor-wax was withdrawn from the slurry reactor to maintain the slurry level at 610-670 cm. The catalyst loss, according to solid-content analyses, was 63 gm. Following the wax withdrawal, the H₂+CO conversion declined to 80 mol %. This drop in conversion was attributed mainly to the catalyst loss and partially to the lowering of the slurry level (by about 152 cm) as a result of the reactor-wax withdrawal.

At sixteen days on-stream, while operating at a pressure of 1.83 MPa, the flange at the bottom of the slurry reactor, which was normally kept at 263°C with heating tapes, began to overheat and eventually reached 397°C. The cause of this was probably a leakage of slurry at the bottom flange. At this point, the feed-gas distributor was practically plugged. The unit was then temporarily shut down to unload the slurry and

to replace the feed-gas distributor. The feed-gas distributor was found plugged with coke-like material. Figure 2 is a photograph of the feed-gas distributor and bottom-flange gasket removed from the slurry reactor after the upset.

There are two speculations regarding the causes of this upset. One speculation is that the bottom flange gasket failed with increasing time on-stream. At the higher pressure operation (1.83 MPa), the slurry leaked through the gasket, came in contact with the heating tape and began to oxidize. The oxidation reaction then heated up the flange and the distributor. The overheated distributor then promoted the Boudouard reaction resulting in coke-deposition which plugged up the distributor.

Another speculation is that the temperature controller of the bottom-flange heating tape malfunctioned and led to the overheating of the flange. This is a less likely since an over-heated flange does not normally cause a leakage. The heating tape and its controller were later checked out to be operating properly.

After a downtime of ten days, the slurry was reloaded and the slurry reactor restarted at 263°C, 1.48 MPa and 3.4 cm/s. The H₂+CO conversion was only 25 mol % and the methane + ethane yield was as high as 18 wt % of total hydrocarbons produced. The catalyst was obviously damaged during the operational upset. This damage could be attributed to several factors during the upset:

- Coking of the F-T catalysts particularly due to high temperature operation near the bottom flange.
- Loss of catalyst due to leakage through the bottom flange and slurry unloading and reloading.
- Oxidation of the catalyst by CO₂ and H₂O during synthesis gas flow stoppage and by oxygen during the slurry unloading and reloading.

In an attempt to reactivate the F-T catalyst, the slurry reactor temperature was gradually raised from 263 to 279°C to simulate a pretreatment operation. However, at 279°C, 1.48 MPa and 2.7 cm/s, the H₂+CO conversion was only 75 mol % with a methane + ethane yield of about 21 wt %.

At eighteen days on stream, an in-situ hydrogen regeneration of the F-T catalyst was tried. Run CT-256-2 was terminated after twenty days on stream with a total hydrocarbon produced estimated to be about 135 g/gFe.

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

In the last Quarterly Report, it was reported that a second-stage reactor, containing 215 g of II-B ZSM-5 catalyst, was brought on stream two hours after the start of synthesis operation. Since then, material balances were performed daily and are summarized in Table A-3 of Appendix A. Table A-4 gives the detailed product hydrocarbon compositions.

Also as mentioned in the last Quarterly Report, the catalytic severity of the second-stage operation was guided by the $i\text{-C}_4/(\text{C}_3^{\text{=}}+\text{C}_4^{\text{=}})$ molar ratio in the combined gas stream after the second-stage reactor. To achieve a ratio of 0.8-1.0, an initial temperature of 288°C to the inlet of the second-stage reactor was used. The reactor inlet temperature was then adjusted upward by about 3.3°C per day to compensate for the second-stage catalyst aging. This temperature policy was found to be adequate for the rest of the run.

Figure 3 shows the effect of second-stage operating severity, expressed as the $i\text{-C}_4/(\text{C}_4^{\text{=}}+\text{C}_3^{\text{=}})$ molar ratio in the product, on the gasoline yield. On this plot, the alkylate yield is estimated by alkylating first the $\text{C}_4^{\text{=}}$ and then $\text{C}_3^{\text{=}}$ with $i\text{-C}_4$. If there is an excess of light olefins, they are then converted to "cat-poly gasoline" using conventional catalytic polymerization process. In making this plot, the product yields are normalized after excluding the components that are either nonreactive to or bypassing the ZSM-5 catalyst, such as $\text{C}_4^{\text{=}}$ paraffins and the reactor-wax. Peak C_5^+ gasoline yields of 90-95 wt % could be achieved when the second-stage reactor operating severity was maintained at an $i\text{-C}_4/(\text{C}_3^{\text{=}}+\text{C}_4^{\text{=}})$ molar ratio of 0.6 to 1.2. The corresponding raw liquid hydrocarbon RON octanes were 89 to 92.

2. Run CT-256-3 - Startup

In Run CT-256-2, the excellent performance of the F-T catalyst I-B was demonstrated for a period of seventeen days before the unit upset. The major objectives of Run 3 were to confirm the performance of this same F-T catalyst over an extended period of time and then to perform process variable studies.

Run CT-256-3 was smoothly started up on July 27, 1982 with a high catalyst loading, a high synthesis gas throughput and high conversion, similar to that accomplished in Run CT-256-2. The run is extremely successful, particularly the performance of the first-stage. At the end of this reporting period (sixty-one days on stream), the F-T catalyst was still performing satisfactorily.

Detailed descriptions on the F-T catalyst loading and pretreatment are given here. However, only brief descriptions of the synthesis operation of this run are reported. The details of the synthesis operation and a summary of its performance data will be given after the completion of the run. In so doing, a scattering of performance description and data can be avoided.

a. Fischer-Tropsch Slurry Catalyst Loading and Pretreatment

Catalyst loading and pretreatment similar to those used for Run CT-256-2 were used in this run. 1,407 g of F-T catalyst I-B along with 4,572 g of spent reactor-wax were loaded. The initial catalyst loading was 20.7 wt %.

The F-T catalyst pretreatment conditions were:

H ₂ +CO flow rate, Nm ³ /hr	1.89
H ₂ /CO feed ratio, molar	0.70
Superficial feed-gas vel., cm/s	4.0
Space velocity, NL/gFe-hr	2.0
Temperature, °C	282
Pressure, MPa	1.14

The pretreatment operation was ended after ten hours when the CO conversion reached 82 mole %. Figure 4 shows the product gas volume contraction, CO and H₂+CO conversions, and CO₂ and methane concentration in the product gas during the pretreatment.

One hour after the beginning of pretreatment, 997 g of FT-200 Vestowax was loaded into the F-T reactor because the DP liquid-level indicator showed low liquid level. Four hours after the beginning of pretreatment, 1,500 mL of n-dodecane was also loaded into the slurry reactor through the slurry loading tank to wash the tank.

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

In switching from the pretreatment to the synthesis operation, the slurry reactor temperature was lowered to 260°C in steps of 3°C at a time over a thirty-seven hour period. After each temperature drop, the synthesis gas conversion first declined and then gradually increased back to the level before the temperature change. This policy of temperature reduction from the pretreatment to the synthesis condition allowed the synthesis gas conversion to stay at a higher level during this transition period.

The synthesis operation was continued at 260-262°C and 1.48 MPa for most of this run, and CO conversion was consistently maintained at about 90 mol %. Process variable studies to improve the slurry reactor performance were carried out, including operation at 2.52 MPa (350 psig) pressure and 0.6 charge H₂/CO molar ratio.

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

H ₂ +CO flow rate, Nm ³ /hr	1.23-4.52
H ₂ /CO feed ratio, molar	0.6-0.7
Superficial feed-gas vel., cm/s	1-4
Space velocity, NL/gFe-hr	1.3-4.8
Temperature, °C	260-267
Pressure, MPa	1.14-2.52
H ₂ + CO Conversion, mol %	70-86
Methane + Ethane yield, wt %	8-18

The synthesis operation was interrupted three times during this period. The first interruption was due to a false alarm at sixteen days TOS and the synthesis gas was shut off for nine hours. The second interruption was due to a small leak at the 305 cm flange (thirty days TOS) and the synthesis gas flow was restored thirty-six hours after tightening the flange. On both occasions, a slight loss in F-T catalyst activity and a slight increase in methane yield were observed. The last interruption was a leak at the bottom flange at sixty-one days TOS. The leakage could not be stopped by tightening the flange. The slurry was then unloaded and reloaded into the reactor after a new gasket was installed. After reloading, substantial deterioration of the F-T catalyst activity and substantial increase on the methane + ethane yield were observed. It was not clear if this change in the catalytic activity and selectivity were only temporary. The F-T catalyst seems to be very sensitive when exposed to the air.

c. Brief Description of Second-Stage Fixed-Bed ZSM-5 Reactor Operation

The second-stage reactor, containing the same II-B ZSM-5-class catalyst from Run CT-256-2, was put on stream one hour after the end of the F-T catalyst pretreatment. The fixed-bed inlet temperature was initially set at 343°C and adjusted as the run progressed to maintain a target i-C₄/(C₃⁻+C₄⁻) molar ratio of 0.8-1.0 in the combined product gas. The effect of the second-stage operating severity on the gasoline yield and raw liquid hydrocarbon properties was studied by varying the second-stage fixed-bed inlet temperature.

The II-B ZSM-5 catalyst was twice regenerated during this period, once at sixteen days TOS after a thirty-four day cycle and the other at forty-six days TOS after a twenty-nine day cycle. On both occasions, no significant changes in the initial catalyst activity were observed.

3. Bubble-Column Reactor Hydrodynamic Studies (1)

Hydrodynamics data of bubble-column reactor are essential for analyzing the performance of the reactor, for providing essential parameters for a slurry reactor mathematical model application and for characterizing factors of the slurry reactor scaleup. Limited work in this area was carried out using existing nonreacting bubble-columns located at Mobil's Paulsboro Laboratory. The conclusions drawn from these studies are confined by the physical limitations of the equipment available. The physical limitations include the diameter of the nonreacting columns (3.2 cm for a hot column, and 5.1 cm for a cold column), the column height (about 216 cm for both columns), and the maximum temperature of the hot column (225°C). Further studies using improved equipment are strongly recommended. However, due to limitation of funds, no experimental work of this type is planned within the framework of this contract.

There is a vast amount of bubble-column gas holdup data in the literature (e.g., a review by Shah, et al., 1982). However, most of these data are for air-water systems. The gas holdup is generally a function of liquid medium properties, bubble-column dimensions, operating conditions, type of gas distributors, and solids contents. Since none of the gas holdup correlations in the literature take all these into account, it is questionable if these data can be applied to F-T bubble-column systems. To further complicate the matter, Deckwer, et al., (1980) and Quicker and Deckwer (1981) showed that the gas bubble size in a F-T wax was significantly smaller and the gas holdup was significantly larger than those for pure hydrocarbon liquids with similar density, viscosity, and surface tension. It was therefore necessary to study bubble-column hydrodynamics in nonreactive flow models using an actual F-T slurry as the liquid medium.

Gas holdup in a bubble-column is an important parameter since it closely relates to the gas-liquid interfacial area, the residence time of the gas rising through the column, and the reactor volume required for achieving a given conversion. In general, a large gas holdup goes together with small bubble size

(1) This work was carried out by a summer employee, Mr. W. J. Cannella, a graduate student in the Department of Chemical Engineering, The University of California at Berkeley (Berkeley, California).

(Deckwer, et al., 1979). Furthermore, small bubble size implies small bubble rising velocity and larger gas-liquid interfacial area. A good gas holdup is essential in achieving a satisfactory bubble-column performance. However, too high a gas holdup would mean that a much larger reactor volume is needed to hold a given amount of the catalyst. Consequently, a high gas holdup could mean a waste of reactor volume. Based on our experience, the approximate range of desirable gas holdup is 10-35 vol %. The gas holdup is a function of the superficial gas velocity and is often very sensitive to the properties of the liquid phase.

The liquid mediums studied include FT-200 Vestowax and used slurry from the end of Run CT-256-1. The gas used was nitrogen. The effects of solid concentration, temperature, and static liquid height on gas holdup were studied in a 3.2 cm diameter hot bubble-column. The column was installed with a 15 μm stainless steel sintered plate as gas distributor and was wrapped in the outside with heating tapes to keep it hot. The effects of column diameter and static liquid height were also studied using n-hexadecane in cold bubble-columns with diameters of 3.2 and 5.1 cm. A comparison of the results with those available in the literature was also made.

Mindful of the equipment limitations mentioned in the early part of this subsection, the major conclusions obtained from the current studies are summarized in the following:

- The bubble-column gas holdup decreased strongly with increasing static liquid height. No significant effect due to temperature variation (over a 25°C variation) was observed.
- The bubble-column gas holdup increased linearly with increasing gas velocity up to about 0.4 cm/s, then quickly reached high holdup (about 60 vol %) at higher gas velocity with excessive foaming observed. Gas bubble slugging was observed at gas velocities above 1.5 cm/s.
- At solid concentrations larger than 6 wt %, the gas holdup increased with solid content.
- Using n-hexadecane as liquid medium in two cold columns, decreasing gas holdup with increasing column diameter was observed. However, the gas holdups observed there were substantially less than those observed for F-T waxes at the same gas velocity.

a. Hot Bubble-Column Studies

The relationship between gas holdup, ϵ_g , and superficial gas velocity, u_g , for FT-200 Vestowax was studied in a 3.2 cm diameter nonreacting, hot bubble-column at 200°C. The static liquid height studied was 46 cm and the results obtained are presented in Figure 5. The expanded slurry consisted of many very small gas bubbles distributed throughout the liquid and was topped by a layer of foam. The liquid was clean and it was possible to see through the column. At low superficial gas velocities ($u_g < 0.72$ cm/s) the foaming was minimal and there was a discernible boundary between the foam and non-foam liquid layers. In this regime the gas holdup appeared to vary linearly with the superficial gas velocity according to the following equation:

$$\epsilon_g = 0.30 u_g \quad (1)$$

As the velocity was further increased to about 1 cm/s, the wax began to foam excessively. The foam grew down the column as well as up and the boundary layer between the foam and the non-foam liquid could no longer be distinguished. Soon the whole column appeared to be foaming and it was no longer possible to see through the column. The gas holdup values reported included the foam and thus were very high (about 59%).

At higher velocities, the gas holdup increased slightly and then leveled off at a value of about 61%. At a velocity of about 1.5 cm/s, large gas bubbles which extended across the column diameter were observed. Operation in this regime may be highly undesirable since the gas-liquid interfacial area available for mass transfer may be greatly reduced.

Since products formed during F-T synthesis may affect the bubble-column hydrodynamics, it was necessary to repeat the study using the slurry actually formed during synthesis. A slurry containing 2.2 wt % of catalyst I-A from sixty-one days on-stream of Run CT-356-1 was used. The results are also presented in Figure 5. Qualitatively the results obtained were similar to those of the FT-200 Vestowax except that the slope of the gas holdup versus the gas velocity at the low velocities is slightly larger than that of the FT-200 Vestowax. Foaming also began to increase with increasing gas velocity, causing a large rise in gas holdup. The gas holdup then leveled off until slugging occurred.

Also depicted in Figure 5 is the gas holdup correlation developed by Deckwer, et al., (1980), as represented by following equation:

$$\epsilon_g = 0.053 u_g^{1.1} \quad (2)$$

The measured gas holdups were consistently larger than the values predicted by this correlation. However, the conditions under which the gas holdup data were obtained here may be quite different from the conditions under which the correlation was established. These conditions may include the static height, the column diameter, and the temperature.

b. Effect of Solid Concentration in Slurry

The effects of varying solids content on the gas holdup of the used slurry from Run CT-256-1 was studied. The results are presented in Figure 6 and Table 5. At low velocities (<0.4 cm/s) when there is very little foaming, the addition of solids appears to decrease the gas holdup slightly. This may be due to an increase on the apparent viscosity of the liquid. However, at higher flow rates when the foaming is excessive, the gas holdup is increased. Bikerman (1953) claims that the coalescence of foam bubbles can be prevented or retarded by solid particles immersed in the liquid. Thus, the fine solids may stabilize the foam.

The effect of solids content has also been studied by Deckwer and coworkers in a molten paraffin-wax/N₂ system under nonfoaming conditions. They observed virtually no effect on gas holdup for solids content ranging from 5.5 to 16 wt % and only a slight decrease of gas holdup (about 0.01 to 0.02) from 0 to 5.5 wt %.

Thus it appears that at least up to a solids content of about 15 wt % there is little effect on gas holdup under nonfoaming conditions, but there may be an effect under foaming conditions.

c. Effects of Temperature

The temperatures frequently used in F-T synthesis range between 200 and 300°C. Thus it is important to determine if there is any effect of temperature on gas holdup. Unfortunately, in this study, due to equipment limitation, it is impossible to raise the temperature above 225°C in the hot bubble-column. A comparison of the results obtained at this temperature and at 200°C using used slurry from Run CT-256-1 is presented in Figure 7. There seems to be no significant effect of temperature over this small range. Extrapolation to temperatures outside this range is not recommended.

The effects of temperature were also studied by Deckwer, et al., (1980). They observed no effect over a temperature range of from 143 to 285°C for a 10 cm diameter column, but did observe a decrease in gas holdup with increasing temperature for a 4 cm diameter column. They attributed this to

wall effects in the small column. Further studies on the effects of temperature and the relationship of column diameter are recommended.

d. Effect of Static Liquid Height and Column Diameter

Since the static liquid heights and column diameters of commercial reactors are expected to be larger than those used in the present hydrodynamic studies, experiments were conducted to determine what effect these parameters have on gas holdup.

The results for the used slurry from Run CT-256-1 in the hot, nonreacting bubble-column are presented in Figure 8 for static heights of 46 and 69 cm. The gas holdup was found to decrease as the liquid height increased. Similar effect was also observed by Langemann and Koelbel (1967). It was not possible to study higher static levels due to the height limitation of the nonreacting column. Further studies in taller and larger hot columns are recommended.

The effects of static liquid height and column diameter were also studied in cold flow columns using n-hexadecane. The results are presented in Tables 6 and 7. In general, the gas holdup values measured using n-hexadecane are substantially less than those measured using F-T waxes at the similar gas velocity. For example, at 0.4 cm/s gas velocity, the highest gas holdup ever observed using n-hexadecane was about 6 vol %, while values of 15-20 vol % were observed using F-T waxes. Similarly, the bubble size in n-hexadecane medium seemed to be substantially larger. There was an observed effect of both the static liquid heights and the column diameters. In general, gas holdup increases with decreasing static liquid height and column diameter. However, when the static liquid height was above 64 cm, there seemed to be little observed effect on gas holdup. When the liquid height was large enough, bubble coalescence and slugs occurred at a gas velocity higher than 1.9 cm/s.

Several studies on the effects of static liquid height and diameter on gas holdup have been presented in the literature. Deckwer, et al., (1980) observed no effect in a molten paraffin-wax/N₂ system but used relatively large liquid heights (larger than 65 cm). Likewise Yoshida and Akita (1965) observed no effect for large liquid heights (larger than 90 cm) and diameters (larger than 7.7cm). On the other hand, Langemann and Koelbel (1967) have observed a significant effect of static liquid height for a mineral oil/CO₂ system. Shulman and Molstad (1950) also observed an effect of column diameter for an air/H₂O system. Columns of 5.1 and 10.2 cm diameters gave the same results, but a column of 2.5 cm diameter gave much higher gas holdup values. In addition, foaming was observed in the 2.5 cm

diameter column and a critical velocity was reached at which the whole column seemed to be foaming.

Langemann and Koelbel (1967) suggested that there are three zones of flow which exist within a bubble-column. The first zone is near the gas distributor and is a zone of incident flow. Bubble flow patterns come to the equilibrium state which is determined by a combination of medium properties, column dimensions, and operating conditions. In this zone, the gas holdup rises, peaks, and begins to fall. In the middle zone, bubbles flow upward in an equilibrium pattern. The gas holdup tends to decrease slightly as the bubbles move up the column. The top zone is one of bubble disintegration which occurs due to the requirement of a finite contact time for bubbles to disengage from the liquid. The gas holdup rises sharply in this zone to its maximum value. The height of the last zone varies little with static liquid height. Consequently, in a short column, the average gas holdup is high because it is dominated by the last zone. Based on this analysis, one expects the average gas holdup to decrease with increasing static liquid height. In conclusion, it is imperative to study bubble-column hydrodynamics in a tall column.

4. Product Evaluation

Three raw gasoline product samples, one taken at seven days on stream from Run CT-256-2 and two taken at nine and twenty-one days on stream from Run C-256-3, were tested for existent and total gums (ASTM D381) and oxidation stability (ASTM D525). Metal deactivator at 0.5 lb per 1000 bbl. and antioxidant at 2.5 lb per 1000 bbl. were used in one portion and the antioxidant level was increased to 15 lb per 1000 bbl. in a second portion. As shown in Table 8, existent (heptane-washed) gum contents of 1 to 3 mg/100 ml were found in all samples, thus meeting the 5 mg/100 mL maximum specification of ASTM D439 for automotive gasolines. However, total residues on evaporation were very high (ranging up to 170 mg/100 mL) in several of the tests, indicating the presence of high-boiling, heptane-soluble materials. Higher antioxidant usage rates were only partially effective for reducing the total residue levels. The high-boiling materials were confirmed by subsequent ASTM D86 distillations, in which end points up to 245°C were measured (225°C is a typical end-point specification maximum for U.S. gasolines). The drastic difference on the total gums for the two samples from Run CT-256-3 may be due to operating condition differences in the second-stage reactor.

The ASTM D525 procedure provides an indication of gasoline tendencies to react with oxygen to form gum during storage. ASTM D439 specifications require 240 minutes or more for the stability period in this test; time periods of 305 to 825

minutes were obtained for these samples, indicating acceptable performance.

Standard corrosion tests and a long-term 43°C storage stability procedure have been initiated on a water-washed composite product of Run CT-256-3 to better define product qualities. Results of these tests will be reported upon completion.

5. Conclusions

The second run of the two-stage synthesis gas conversion pilot plant, designated as Run CT-256-2, was concluded after twenty-days on-stream. The highlight of the run were:

- The evaluation of the second Fischer-Tropsch catalyst, a Fe/Cu/K₂CO₃ catalyst designated as I-B, was carried out.
- The ranges of the operating conditions for the first-stage slurry Fischer-Tropsch reactor were:

Temperature, °C	257-263
Pressure, MPa	1.14-1.83
H ₂ /CO Feed Ratio, Molar	0.7
Superficial Feed-Gas Velocity, cm/s	3.2-4.1
Space Velocity, Nl/gFe-hr	1.5-3.0

The H₂+CO conversion ranged from 60 to 88 mol % and the methane + ethane yield from 9 to 15 wt % of the total hydrocarbons produced.

- A new second-stage ZSM-5 catalyst, designated as II-B, was on-stream for twenty days. It satisfactorily converted the F-T products into high octane gasoline. The ranges of the operating conditions for the second-stage fixed-bed reactor were:

Temperature, Inlet, °C	288-352
GHSV, l/hr	1,435-3,255

- After sixteen days on-stream, the bottom flange of the slurry reactor was overheated to 397°C, and the feed-gas distributor eventually plugged. This operational upset was attributed to a leakage at the bottom flange. A large loss of F-T catalyst activity (estimated to be roughly 40%) was observed. The methane + ethane yield also increased from about 10 wt % of the total hydrocarbons produced to 18-20 wt %.

The third BSU run, designated as Run CT-256-3, was initiated immediately after the operational upset of Run CT-256-2. A new batch of I-B Fe/Cu/K₂CO₃ catalyst (same as that used in Run CT-256-2) was used in the first stage reactor, and the same II-B ZSM-5 class catalyst was used in the second reactor. This run has been extremely successful and had accumulated sixty-one days on-stream by the end of this reporting period. This run is being continued. The synthesis operation was interrupted three times during this period. The first two interruptions were minor (stoppage of synthesis gas flow for nine and thirty-six hours, respectively) and resulted in slight loss in F-T catalyst activity and a slight increase in methane yield. During the third interruption, the slurry was unloaded, then reloaded after ten days. A substantial deterioration of the F-T catalyst activity and a substantial increase in the methane + ethane yield was observed.

In order to understand the hydrodynamics of bubble-column reactors, bubble-column gas holdups were measured using two existing, non-reacting columns, a 3.2 cm diameter hot column, and a 5.1 cm diameter cold column (both about 216 cm height). Using the used slurry from Run CT-256-1 in the hot column, the gas holdup was found to decrease strongly with the increasing static liquid height, and little when the slurry temperature was varied from 200°C to 225°C. The effect of varying solid concentration on the gas holdup was somewhat irregular. At low gas velocities, the gas holdup decreased slightly with increasing solid concentration. While at high gas velocities, the gas holdup increased. Similar gas holdups were observed for both the used slurry and FT-200 Vestowax in the hot column. At gas velocities higher than 1 cm/s, both mediums exhibited high gas holdup (about 60 vol %) with excessive foaming. Using n-hexadecane at room temperature in both columns, the gas holdup decreased moderately with the increasing column diameter. Further work in this area using non-reacting column of larger dimensions and higher temperatures is strongly recommended.

Product evaluations concerning stability, i.e., gum formation and oxidation, of the raw gasoline samples from Runs CT-256-2 and -3 were initiated. Existent (heptane washed) gum contents were 1-3 mg/100 ml, well within the 5 mg/100 mL specification for automotive gasolines. The oxidation stabilities, indicated by the induction period method (ASTM D525) were 305 to 725 minutes, well above the minimum specification of 240 minutes for automotive gasolines. However, total residue on evaporation (unwashed gum) were generally high (up to 170 mg/100 mL), probably due to the presence of small quantities of high-boiling, heptane-soluble hydrocarbons.

6. Future Work

- Run CT-256-3 for evaluation of the F-T catalyst I-B will be completed.
- Any modification and maintenance of the BSU will be completed.
- The evaluation of the raw gasoline product from the BSU will be continued.
- The task of scoping process design will be initiated.

V. NOMENCLATURE

GHSV Gas hourly space velocity, (mL gas (STP)/hr-mL reactor)

P Pressure, (MPa)

SV Space velocity, (NL/gFe-hr)

T Temperature, (°C)

u Superficial velocity, (cm/s)

Greek Letters

ϵ_g Gas holdup, (mL gas/mL expanded slurry)

Superscripts

i At reactor inlet

Subscripts

g Gas

VI. Literature

Bikerman, J. J., Foams; Theory and Industrial Applications, Reinhold Publishing Corp., New York, NY (1953).

Deckwer, W. D., Louisi, Y., Zaidi, A., and Ralek, M., AIChE 72nd Annual Meeting, San Francisco, (Nov. 1979).

Deckwer, W. D., Louisi, Y., Zaidi, A., and Ralek, M., I.&E.C. Proc. Des. Dev. 19, 699 (1980).

Langemann, H., and Koelbel, H., Verfahrenstechnik, 1, 5 (1967).

Quicker, G., and Deckwer, W. D., CES, 36, 1,579 (1981).

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

Shulman, H. L., and Molstad, M. C., I.&E.C. 42, 1,058 (1950).

Yoshida, F., and Akita, K., AIChE Journal, 11, 9 (1965).

TABLE 1

Major Events in Run CT-256-2
(Excluding Reactor-Wax and Slurry Inventory)

TOS, Days	Major Events
0-5.3	Pretreatment 1st-Stage: 0.7 H ₂ /CO, 1.14 MPa, 3.2-4.1 cm/s, 260-257°C 2nd-Stage: 288-324°C
5.4- 7.3	1st-Stage: 1.14-1.48 MPa, 260-263°C 2nd-Stage: 324-330°C
7.4-12.1	1st-Stage: 1.48-1.14 MPa, 4.1-3.5 cm/s, 260-263°C 2nd-Stage: 330-348°C
12.3-14.1	1st-Stage: 1.14-1.48 MPa 2nd-Stage: 348-352-346°C
15.2-16.1	1st-Stage: 1.48-1.83 MPa 2nd-Stage: 346-350°C
16.2	Upset: Slurry reactor bottom flange temperature went up
17.1	10-day shutdown: - Unloaded slurry - Replaced plugged-up distributor plate - Reloaded the same slurry
17.1-17.7	1st-Stage: 1.48 MPa, 3.4-2.8 cm/s, 263-279°C 2nd-Stage: 343°C
19.6	End of Run CT-256-2

Table 2

Major Events in Run CT-256-2
(Reactor-Wax and Slurry Inventory)

<u>TOS Days</u>	<u>Major Events</u>
-0.7	Slurry loading
0.1	Slurry sampling: 2g, from 30 cm, 23.6% solid
1.4	Wax withdrawal: 50g, 0.9% solid
4.1	Slurry sampling: 41/29.9/23.1/42g, from 30/152/305/610 cm, 17.6/16.1/14.3/9.9% solid
6.1	Wax withdrawal: 161/549/227/542/422g, 4/1.2/0.1/0.2/0.4% solid
6.2	Tried wax withdrawal from the side filter at 457 cm: Negligible filtration rate
7.1	Wax withdrawal: 642/633g, 4.7/0.2% solid
16.2	Wax withdrawal: 520/301/476/264g, 8.5/3.4/1.1/1.2% solid
17.1	Wax withdrawal: 324/548g, 0.2/0.3% solid Slurry unloading: 2,663/2,736/756g, 9.9/8.6/8.2% solid Slurry reloading: 6,100g of the same slurry plus 600g of high-solid-content waxes from earlier time; slurry solid content was 7.9%
17.5	Slurry sampling: 5/5/6.1g, from 30/152/305 cm, 10.1/10.7/9% solid
19.6	Wax withdrawal: 563/998g, 10.5% solid Slurry unloading: 4,214g End of Run CT-256-2

Table 3

Ranges of Operation Results (Run CT-256-2)

<u>First-Stage</u>	<u>Range of Results</u>	
H ₂ +CO Conv., mol %	45-86	
Methane + Ethane Yield, wt % HC	9-15	
Reactor-Wax Yield, wt % HC	1-14	
<u>Second-Stage Hydrocarbon Yield, Wt %</u>	<u>Before Alkylation</u>	<u>After Alkylation</u>
C ₁ +C ₂	9-14	9-14
C ₃ -C ₄	18-33	9-15
C ₅ -C ₁₁	49-62	59-70
C ₁₂ ⁺ (excl. reactor-wax)	1-4	1-4

Properties of Raw Liquid Hydrocarbons

Aromatics, Wt %	27-47
Acid No., mgKOH/gHC (unwashed)	0.02-0.5
Octane No., R+0	86-94
M+0	76-82

(1) Collected in ambient and chilled condensers.

TABLE 4

Effect of Pressure on Slurry F-T Reactor Performance (1)

(Run CT-256-2)

TOS, Days	12.1	14.2	15.5
Pressure, MPa	1.14	1.48	1.82
Space Velocity, NL/gFe-hr	1.84	2.34	2.84
H ₂ +CO Conv., mol %	87.6	86.9	85.9
Methane, Wt. %	9.6	8.3	7.5
Methane + Ethane Yield, Wt % HC	13.9	12.0	10.8
Exit H ₂ /CO, molar	1.07	1.30	1.31

(1) 0.7 H₂/CO, 263°C, 3.5 cm/s Superficial Feed-gas Velocity

Table 5

Effect of Solid Concentration on Gas Holdup
 (3.2 cm ID column. Gas Holdup in Vol %)

$\frac{u_g^0}{\text{cm/sec}}$	<u>Solid Content, Wt %</u>							
	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7.5</u>	<u>1</u>	<u>12.5</u>	<u>15</u>
0.14	1.3	2.3	1.9	1.9	2.1	1.5	0.9	1.0
0.24	7.0	7.5	5.6	6.1	6.1	4.4	4.4	3.2
0.46	20.5	20.3	17.9	18.0	21.1	18.8	19.3	19.0
0.60	26.3	25.3	25.7	29.2	30.7	32.0	32.2	31.9
0.72	50	51.7	50.9	52.5	52.6	54.0	54.2	50.4
0.93	60.7	59.5	58.9	59.2	58.8	59.1	61.8	65.4
1.01	60.4	59.9	57.2	60.2	58.5	62.2	66.2	67.1
1.28	59.9	60.7	60.5	59.9	58.5	62.4	69.1	69.5
1.53	58.1	51.9	59.0	59.0	58.3	62.2	(2)	(2)
2.07	56.7	56.7	58.3	57.7	54.3	62.1	(2)	(2)

(1) A used slurry from Run CT-256-1 plus catalyst I-A was used.

(2) Gas holdups were too high for the given static height and column height.

Table 6

Cold Column Gas Holdup Data Using n-Hexadecane
(3.2 cm ID Column Gas Holdup in Vol %)

<u>u_g, cm/s</u>	<u>Static Liquid Height, cm</u>					
	<u>15</u>	<u>36</u>	<u>45</u>	<u>62</u>	<u>124</u>	<u>172</u>
0.08	3.09	0.87	1.72	1.01	1.01	0.92
0.19	5.05	2.16	2.06	1.75	1.51	1.90
0.29	6.00	3.42	2.72	2.24	1.75	2.48
0.63	6.93	4.23	4.19	3.68	2.74	3.65
0.80	7.84	-	4.98	-	-	4.58
0.96	8.74	6.61	5.92	5.30	-	4.92
1.29	10.04	8.13	7.14	6.43	5.34	6.24
1.61	11.73	8.87	8.33	7.75	7.33	7.52
1.90	12.55	11.02	9.49	9.03	8.65	8.50
2.20	14.54	13.07	10.62	9.45	9.88	9.60
2.45	15.1	14.39	11.18	-	-	10.60
2.76	-	15.03	11.73	-	-	11.60

Table 7

Cold Column Gas Holdup Data Using n-Hexadecane
(5.1 cm ID Column. Gas Holdup in Vol %)

<u>u_g, cm/s</u>	<u>Static Liquid Height, cm</u>			<u>169</u>
	<u>15</u>	<u>36</u>	<u>63</u>	
0.03	1.03	0.44	0.25	-
0.07	2.04	-	-	-
0.12	3.03	0.88	0.75	1.57
0.25	4.00	-	-	-
0.38	4.43	2.16	2.21	2.29
0.64	5.88	3.21	3.16	3.35
0.86	6.80	4.24	4.22	4.39
1.08	7.69	5.04	5.24	5.41
1.29	8.57	6.22	6.13	6.07
1.47	-	-	7.01	-
1.64	-	8.13	7.87	-
1.84	-	8.68	8.71	8.76
1.97	-	9.60	9.54	-
2.29	-	10.31	10.15	-
2.60	-	11.02	10.76	-

Table 8 .

Raw Gasoline Product Evaluations

<u>Mat.</u> <u>Balances</u>	<u>Days on</u> <u>Stream</u>	<u>Additive</u> <u>Pkg. No.*</u>	<u>ASTM D381 GUMS,</u> <u>MG/100 ML</u>		<u>ASTM D525</u> <u>Oxidation</u> <u>Stab., Mins.</u>
			<u>Existent</u>	<u>Total</u> <u>(Unwashed)</u>	
CT-256-2-7	6.9	1	2	117	620
CT-256-2-7	6.9	2	1	120	725
CT-256-3-6	8.6	1	1	170	425
CT-256-3-6	8.6	2	1	142	425
CT-256-3-22	21.1	1	3	11	305
CT-256-3-22	21.1	2	1	10	355

*Additive Package No. 1 -- 0.5 lb/1000 bbl. metal deactivator +
2.5 lb/1000 bbl. antioxidant.

*Additive Package No. 2 -- 0.5 lb/1000 bbl. metal deactivator +
15 lb/1000 bbl. antioxidant

FIGURE 1

**SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD**

(RUN CT-256-2 1ST STAGE CATALYST I-B:PPTD Fe/Cu/K₂CO₃;
2ND STAGE CATALYST II-B:ZSM-5)

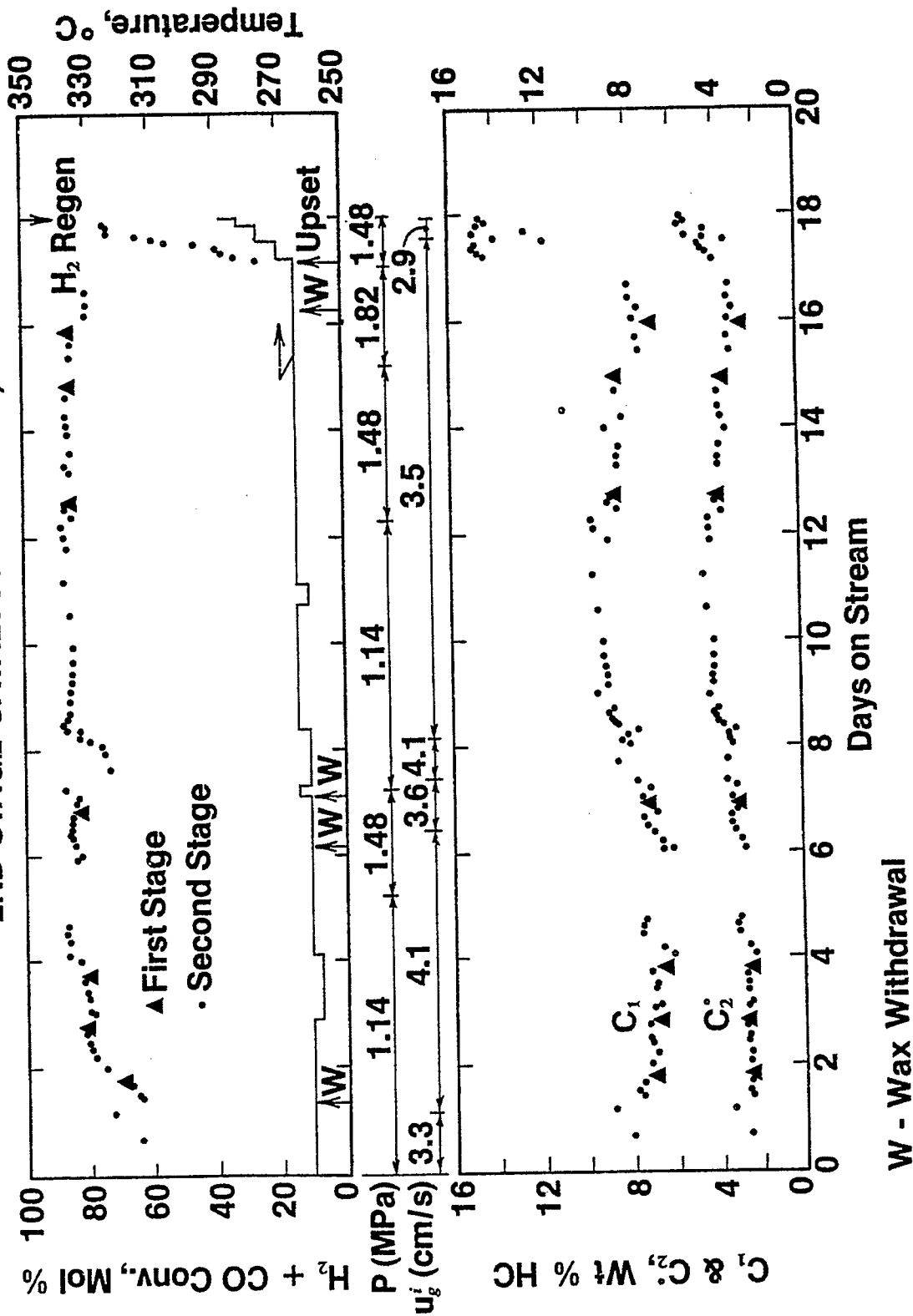


Figure 2
DISTRIBUTOR PLATE AND BOTTOM FLANGE GASKET OF THE
SLURRY REACTOR AFTER THE UNIT UPSET
(Run CT-256-2)

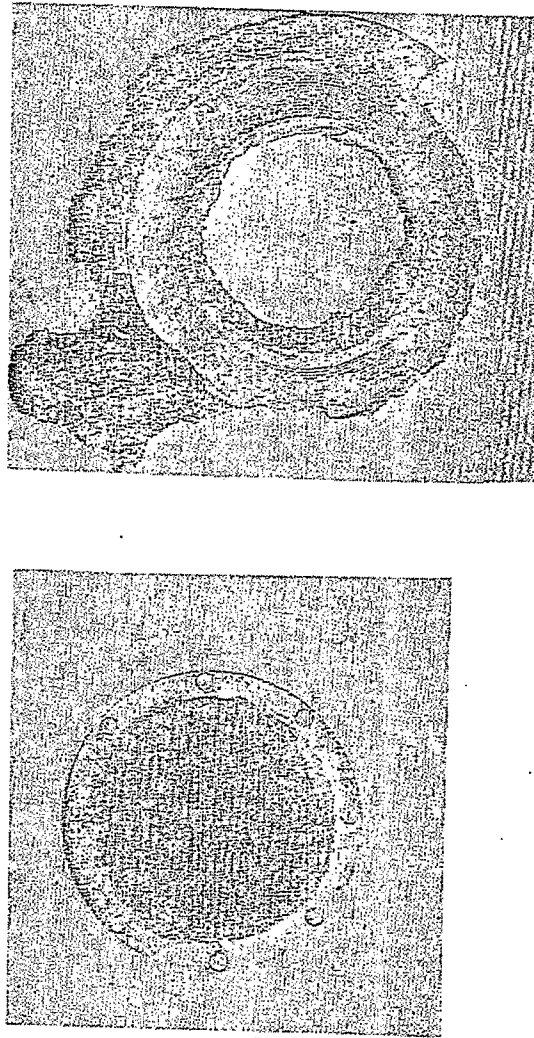
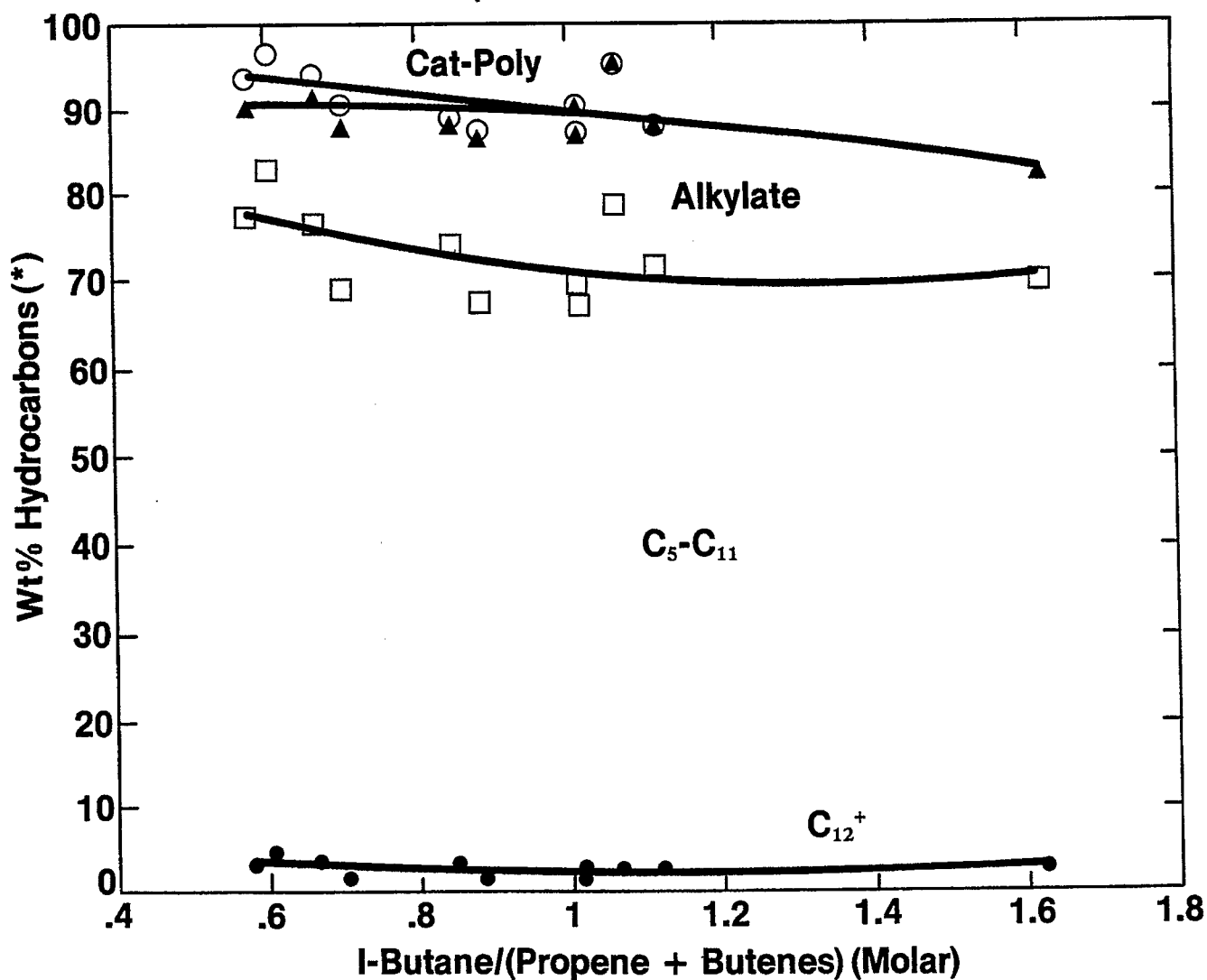


FIGURE 3
PRODUCT YIELDS VERSUS
SECOND STAGE OPERATING SEVERITY
(RUN CT-256-2)



*Excluding C₄ Paraffins in Feed and Reactor-wax

FIGURE 4

RUN CT-256-3 CATALYST PRETREATMENT

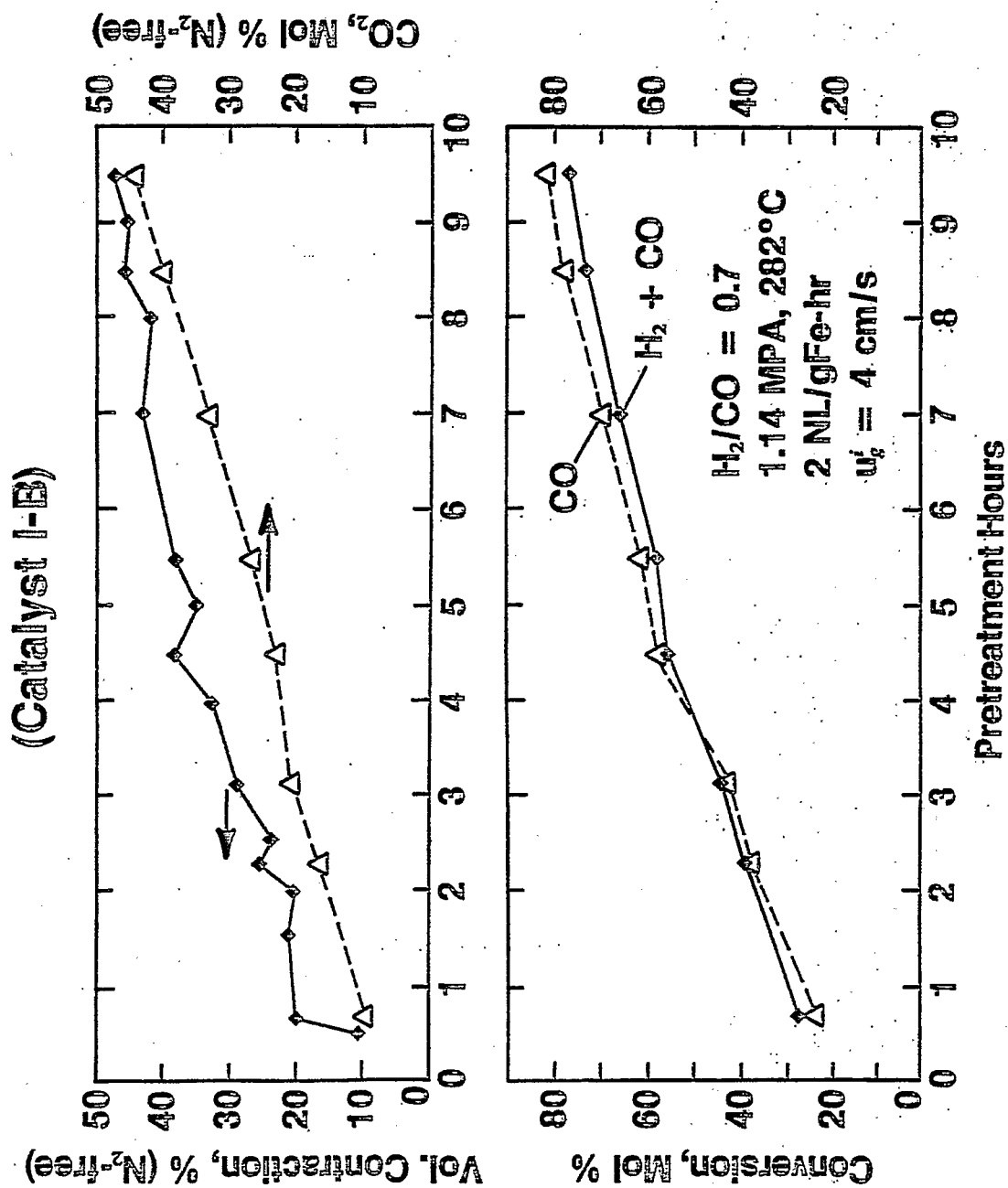


FIGURE 5

**HOT NON-REACTING
BUBBLE-COLUMN GAS HOLDUP**
(3.2 cm ID Column)

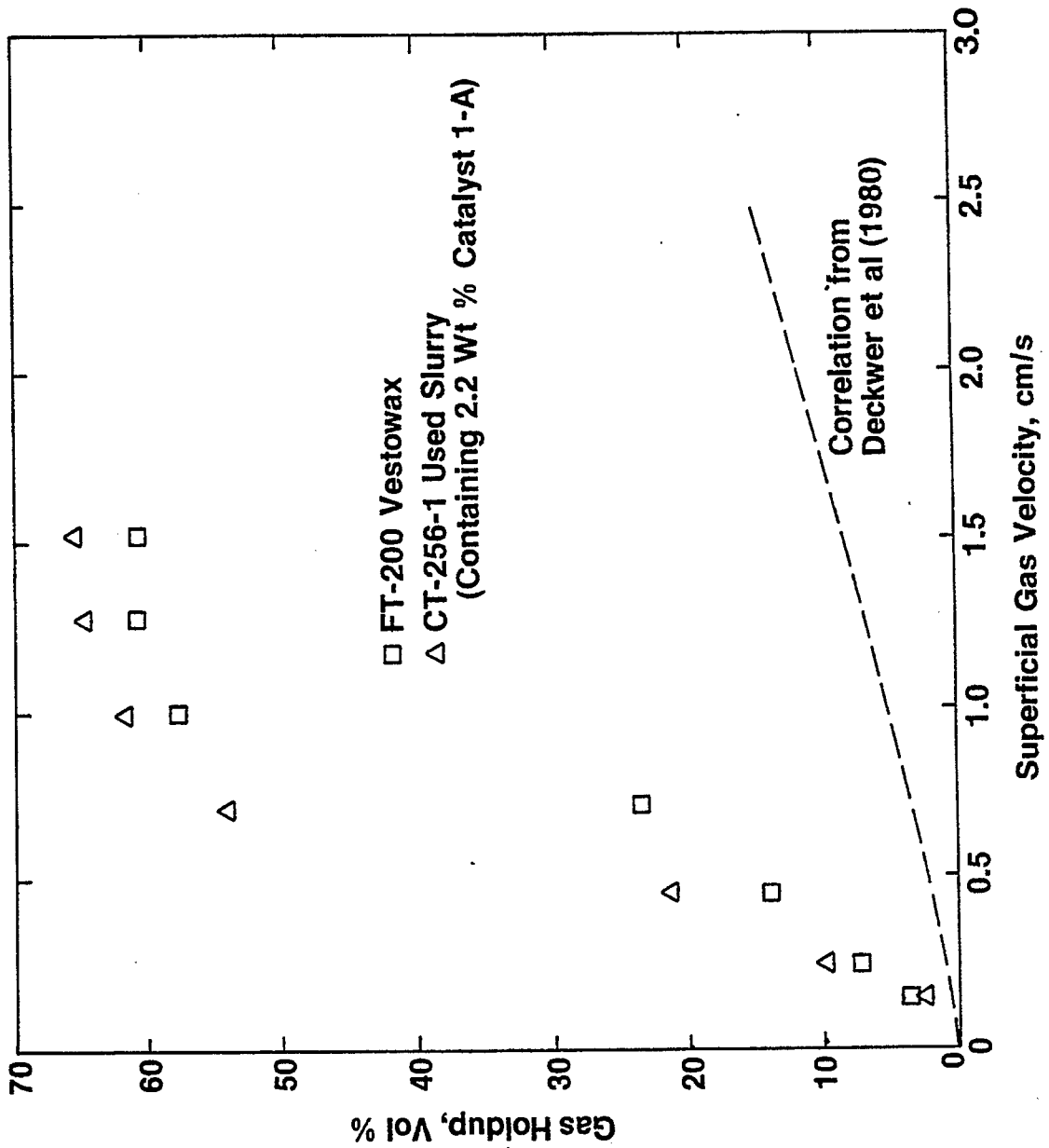


FIGURE 6

EFFECT OF SOLID CONCENTRATION
ON GAS HOLDUP

(3.2 cm ID, Hot, Non-Reacting Column)

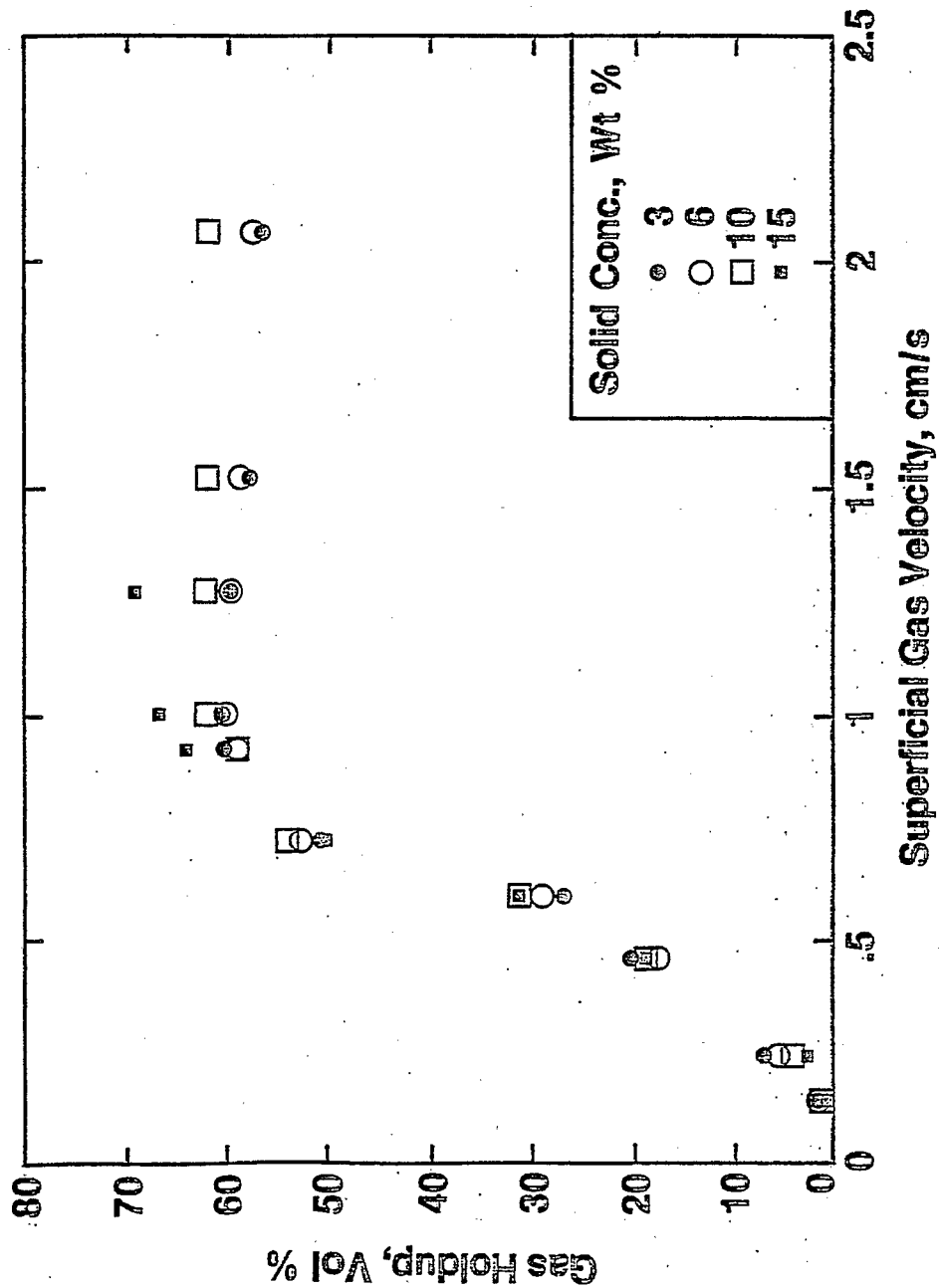


FIGURE 7

EFFECT OF TEMPERATURE ON GAS HOLDUP
(3.2 cm ID, Hot, Non-Reacting Column)

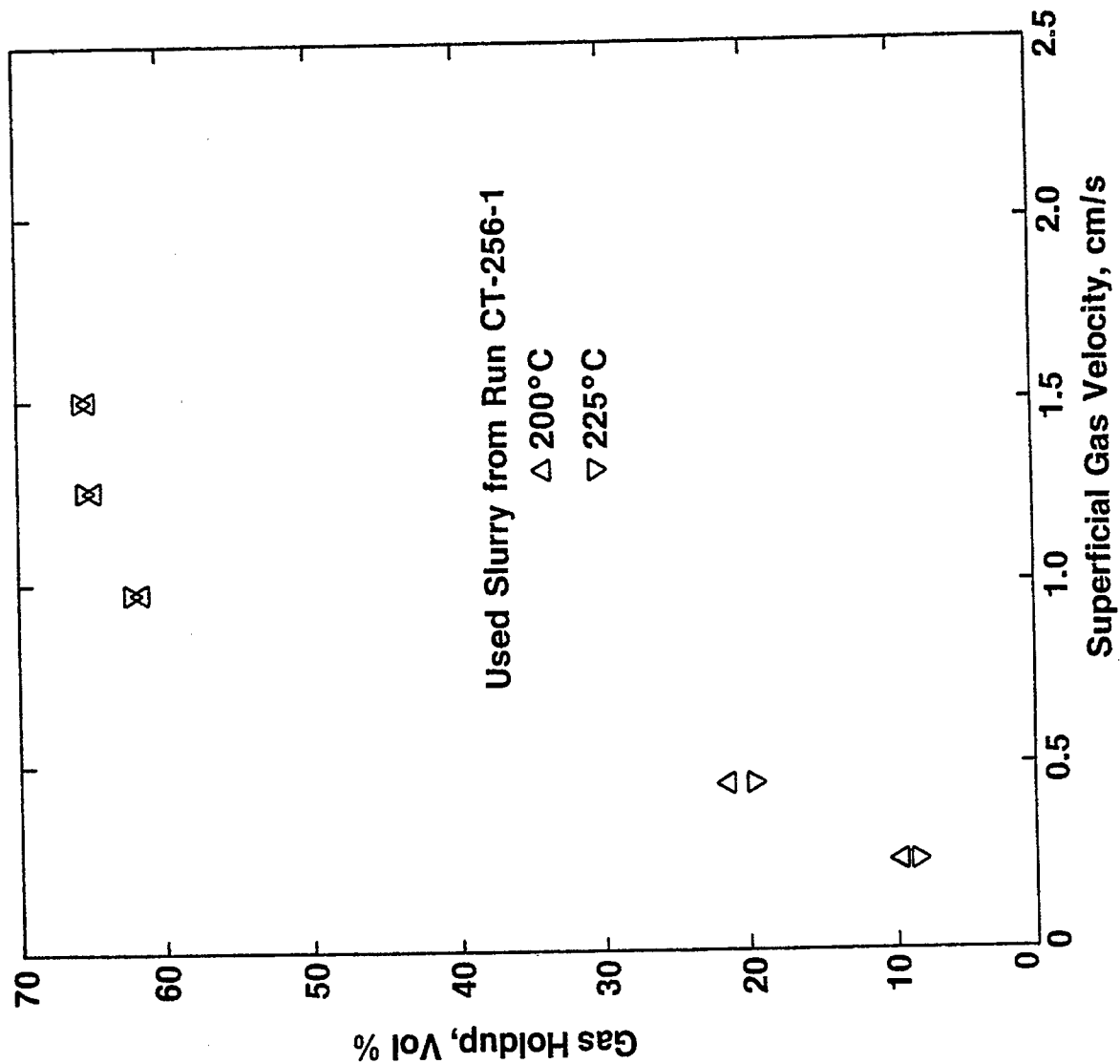
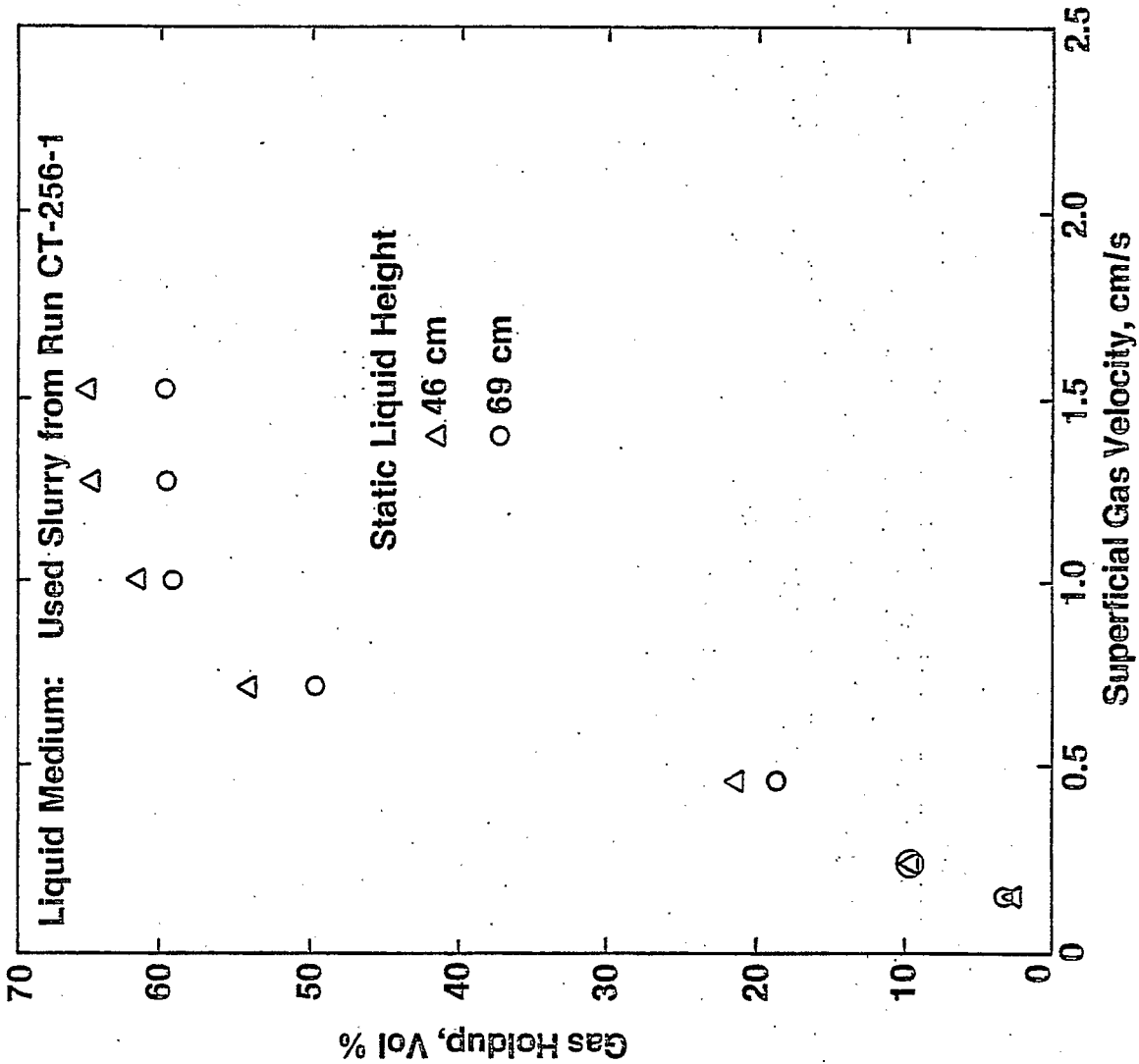


FIGURE 8

**EFFECT OF STATIC LIQUID HEIGHT
ON GAS HOLDUP**

(3.2 cm ID, Hot, Non-Reacting Column)



APPENDIX A

MATERIAL BALANCE DATA FROM CT-256

Table A-1
 First-Stage Fischer-Tropsch Bubble-Column
 Operating Conditions and Material Balances
 Based on Inter-Reactor Sample
 Run CT-256-2

(Nitrogen-Free Basis)	2-1	2-2	2-3	2-4	2-7	2-15	2-16
M.B. No.							
Days On-stream	0.9	1.9	2.9	3.9	6.9	14.8	15.8
First-Stage Conditions:							
Charge H ₂ /CO (Molar)	0.687	0.684	0.682	0.753	0.683	0.672	0.673
Temperature, °C	260	259	259	257	258	262	262
Pressure, MPa	1.136	1.136	1.136	1.136	1.473	1.480	1.825
Feed Sup. Vel., cm/s	3.269	4.139	4.059	3.999	3.612	3.429	3.444
Space Vel., NL/gFe-hr	1.461	1.914	1.906	1.878	2.281	2.208	2.705
N ₂ in Feed, Mol %	9.0	6.1	4.5	4.9	3.9	4.1	5.1
Conversions, Mol % :							
H ₂	60.22	66.53	75.83	73.67	77.32	81.44	83.89
CO	71.32	73.08	87.34	84.35	89.17	89.49	88.79
H ₂ +CO	66.80	70.42	82.67	79.77	84.36	86.25	86.82
Yields, Wt % of Products :							
Hydrocarbons (1)	17.48	16.87	21.88	18.70	20.30	19.87	19.22
CO ₂	52.91	57.85	65.53	66.67	67.86	69.27	68.68
H ₂ O (1)	0.00	0.00	0.00	0.55	0.89	0.89	1.07
H ₂	1.90	1.46	1.08	1.18	1.02	0.79	0.72
CO	27.70	23.82	11.51	12.91	9.92	9.19	10.30
Total	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	98.76	106.92	104.44	113.74	103.72	108.52	103.41
g HC/Nm ³ (H ₂ +CO) Convtd. :	211	210	225	210	202	203	186
Selectivities, Wt % of HC :							
Methane	6.70	7.13	6.33	7.35	7.24	8.55	7.93
Ethene	3.31	3.01	1.97	2.30	1.93	1.75	1.94
Ethane	2.57	2.75	2.66	3.01	3.36	3.88	3.48
Propene	8.20	8.56	7.32	8.44	8.40	9.32	8.76
Propane	1.33	1.51	1.46	1.70	1.96	2.47	2.25
Butenes	6.52	7.01	6.02	6.95	6.79	7.57	7.06
i-Butane	0.07	0.06	0.05	0.06	0.09	0.00	0.00
n-Butane	1.16	1.41	1.35	1.62	1.87	2.28	2.16
C ₅ - C ₁₁ (2)	15.10	16.48	14.08	16.51	17.76	12.05	11.68
Light Hydrocarbons (3)	20.49	17.44	21.99	17.39	19.06	18.54	19.22
Heavy Hydrocarbons (4)	20.42	25.54	30.14	28.33	27.37	31.08	33.47
Slurry Rx. Wax	13.60	8.43	6.28	5.88	3.74	1.78	1.24
Total	100	100	100	100	100	100	100

- (1) Including Oxygenates
- (2) In Gas Phase Only
- (3) Collected in Chilled and Ambient Condensers
- (4) Collected in Hot Condenser

Table A-2
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor
(Based on Inter-Reactor Sample)
Run CT-256-2

M.B. No.	2-1	2-2	2-3	2-4	2-7	2-15	2-16
Days On-straem	0.9	1.9	2.9	3.9	6.9	14.8	15.8
DIMETHYL ETHER	0.00	0.00	0.00	0.00	0.00	0.31	0.29
METHANE	6.70	7.13	6.33	7.35	7.24	8.55	7.93
ETHENE	3.31	3.01	1.97	2.30	1.93	1.75	1.94
ETHANE	2.57	2.75	2.66	3.01	3.36	3.88	3.48
PROPENE	8.20	8.56	7.32	8.44	8.40	9.32	8.76
PROPANE	1.33	1.51	1.46	1.70	1.96	2.47	2.25
I-BUTANE	0.07	0.06	0.05	0.06	0.09	0.00	0.00
1-BUTENE+2-METHYLPROPENE	6.21	6.66	5.63	6.52	6.25	6.80	6.44
N-BUTANE	1.16	1.41	1.35	1.62	1.87	2.28	2.16
TRANS-2-BUTENE	0.11	0.12	0.15	0.15	0.21	0.35	0.25
CIS-2-BUTENE	0.20	0.23	0.25	0.27	0.33	0.43	0.37
3-METHYL-1-BUTENE	0.34	0.35	0.26	0.29	0.34	0.34	0.31
I-PENTANE	0.18	0.21	0.14	0.18	0.21	0.27	0.23
1-PENTENE	4.66	5.17	4.32	5.05	4.54	4.73	4.48
2-METHYL-1-BUTENE	0.21	0.21	0.17	0.19	0.18	0.21	0.18
N-PENTANE	0.90	1.12	1.08	1.31	1.43	1.65	1.51
TRANS-2-PENTENE	0.09	0.10	0.12	0.13	0.16	0.21	0.14
CIS-2-PENTENE	0.11	0.13	0.14	0.15	0.18	0.20	0.13
2-METHYL-2-BUTENE	0.00	0.00	0.01	0.01	0.01	0.00	0.02
HEXENES + ISO-HEXANES	0.71	0.68	0.63	0.72	0.75	0.34	0.31
2-METHYLPENTANE	0.00	0.05	0.00	0.00	0.00	0.00	0.00
3-METHYLPENTANE	0.00	0.06	0.00	0.00	0.00	0.00	0.00
1-HEXENE	3.20	3.60	2.85	3.35	2.84	2.40	2.28
N-HEXANE	0.67	0.84	0.78	0.94	1.01	0.91	0.84
HEPTENES + ISO-HEPTANES	0.61	0.66	0.54	0.61	0.64	0.00	0.24
1-HEPTENE	1.71	1.86	1.42	1.69	1.40	0.57	0.63
N-HEPTANE	0.39	0.47	0.44	0.53	0.58	0.23	0.24
C8-OLEFINS + ISO-P	0.32	0.24	0.30	0.33	0.44	0.00	0.04
1-OCTENE	0.63	0.51	0.48	0.57	0.58	0.00	0.04
N-OCTANE	0.18	0.16	0.20	0.24	0.34	0.00	0.00
C9-OLEFINS + ISO-P	0.07	0.04	0.11	0.12	2.12	0.00	0.05
1-NONENE	0.11	0.04	0.10	0.11	0.00	0.00	0.00
ACETONE	0.53	0.65	0.35	0.45	0.44	0.15	0.25
I-PROPANOL	0.00	0.00	0.00	0.00	0.00	0.28	0.27
UNKNOWN LITE HYDRO-CARB LIQ (1)	20.49	17.44	21.99	17.39	19.06	18.54	19.22
UNKNOWN HVY HYDRO-CARB LIQ (2)	20.42	25.54	30.14	28.33	27.37	31.08	33.47
SLURRY REACTOR WAX	13.60	8.43	6.28	5.88	3.74	1.78	1.24

(1) Collected in Chilled and Ambient Condensers
(2) Collected in Hot Condenser

Table A-3
Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
Run CT-256-2

	(1)						
(Nitrogen-Free Basis)	2- 1	2- 2	2- 3	2- 4	2- 5	2- 6	2- 7
M.B. No.							
Days On-stream	0.9	1.9	2.9	3.9	4.9	5.8	6.9
First-Stage Conditions:							
Charge H ₂ /CO (Molar)	0.687	0.684	0.682	0.753	0.681	0.673	0.683
Temperature, °C	260	259	259	257	259	256	258
Pressure, MPa	1.136	1.136	1.136	1.136	1.136	1.480	1.473
Feed Sup. Vel., cm/s	3.260	4.095	4.064	3.985	4.120	4.031	3.617
Space Vel., NL/gFe-hr	1.461	1.914	1.906	1.878	1.934	2.506	2.281
N ₂ in Feed, Mol %	8.8	5.1	4.6	4.6	6.0	5.1	4.0
Second-Stage Conditions:							
Temp., Inlet, °C	284	284	291	295	306	322	330
Outlet, °C	333	332	333	336	343	369	376
Pressure, MPa	1.129	1.129	1.136	1.136	1.136	1.467	1.453
GHSV, hr	2450	2851	2661	2615	2573	3252	2909
Days On-stream	0.9	1.9	2.9	3.9	4.9	5.8	6.9
Conversions, Mol % :							
H ₂	59.23	64.83	75.23	76.34	79.52	78.68	77.31
CO	69.76	72.99	85.92	85.55	91.04	85.55	89.00
H ₂ +CO	65.47	69.68	81.59	81.59	86.38	82.79	84.26
Yields, Wt % of Products :							
Hydrocarbons	16.31	20.35	19.66	20.86	21.19	21.60	20.91
CO ₂	51.05	51.43	65.82	64.93	68.93	62.71	66.84
H ₂ O	1.24	0.95	0.95	0.88	0.97	1.23	1.12
H ₂	1.97	1.65	1.08	1.09	0.90	0.97	1.03
CO	29.44	25.62	12.49	12.24	8.02	13.49	10.10
Total	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	98.10	100.36	106.85	111.03	105.87	101.88	103.44
g HC/Nm ³ (H ₂ +CO) conv.:	198	239	209	223	211	218	208
Selectivities, Wt % of HC :							
Methane	7.81	5.81	7.48	6.78	7.51	5.88	7.20
Ethene	0.47	0.55	0.54	0.57	0.61	0.67	0.69
Ethane	2.74	2.06	3.02	2.72	3.27	2.81	3.43
Propene	1.44	1.94	2.11	2.29	2.46	2.78	2.45
Propane	5.20	3.04	4.52	3.72	4.40	5.07	6.38
Butenes	2.81	4.57	4.23	5.73	5.43	5.11	3.80
i-Butane	7.95	4.51	6.21	5.27	6.01	7.05	8.19
n-Butane	5.92	3.96	5.18	4.99	5.30	5.69	6.07
C ₅ - C ₁₁	49.68	61.49	57.78	59.33	56.88	58.79	55.51
C ₁₂ + (Excl. Rx. Wax)	2.28	3.63	2.65	2.71	3.00	2.34	2.53
Slurry Rx. Wax	13.60	8.43	6.28	5.88	5.13	3.81	3.74
Total	100	100	100	100	100	100	100
i-C ₄ /(C ₃ = + C ₄ =) Molar	1.63	0.61	0.85	0.58	0.67	0.77	1.12
(C ₃ /C ₃ =) Molar Ratio :	3.45	1.49	2.04	1.55	1.71	1.74	2.49
Alkylate, Wt % of HC :	9.14	8.86	11.76	10.36	11.72	13.43	13.57
Cat-Poly, Wt % of HC :	0.00	2.16	0.79	2.93	2.17	1.51	0.00
C ₅ - C ₁₁ PONA, Wt % :							
Paraffins	52.65	48.48	(2)	49.57	49.03	46.96	44.63
Olefins	8.64	26.92	(2)	23.95	27.73	23.83	19.22
Naphthenes	7.37	5.09	(2)	5.60	4.12	5.58	6.43
Aromatics	31.34	19.51	(2)	20.87	19.11	23.63	29.73

(1) All MB's adjusted for Inter-Reactor sampling except M.B. 6

(2) Not available

Table A-3 (Contd.)
 Second-Stage Fixed-Bed ZSM-5 Reactor
 Operating Conditions and Material Balances
 Run CT-256-2

(Nitrogen-Free Basis)	2- 8	2- 12	2- 13	2- 14	2- 15	2- 16	2- 17
M.B. No.							
Days On-stream	7.9	11.9	12.9	13.8	14.8	15.8	16.8
First-Stage Conditions:							
Charge H ₂ /CO (Molar)	0.679	0.679	0.679	0.671	0.672	0.673	0.675
Temperature, °C	259	261	262	262	262	262	262
Pressure, MPa	1.136	1.136	1.480	1.480	1.480	1.825	1.825
Feed Sup. Vel., cm/s	4.105	3.538	3.407	3.412	3.459	3.382	3.392
Space Vel., NL/gFe-hr	1.998	1.693	2.180	2.209	2.208	2.705	2.854
N ₂ in Feed, Mol %	6.0	7.2	4.7	3.6	4.9	3.4	3.3
Second-Stage Conditions:							
Temp., Inlet, °C	331	342	348	352	343	343	350
Outlet, °C	376	388	394	403	390	390	401
Pressure, MPa	1.136	1.136	1.480	1.480	1.480	1.825	1.825
GHSV, hr	3025	2218	2689	2819	2847	3281	3479
Days On-stream	7.9	11.9	12.9	13.8	14.8	15.8	16.8
Conversions, Mol % :							
H ₂	67.24	85.94	81.26	80.10	80.24	80.20	75.56
CO	77.06	90.13	89.97	88.56	90.48	89.27	84.11
H ₂ +CO	73.09	88.43	86.45	85.16	86.37	85.62	80.66
Yields, Wt % of Products :							
Hydrocarbons	19.80	22.62	22.82	21.16	21.62	20.43	20.13
CO ₂	58.01	67.27	66.46	67.28	68.37	67.82	63.16
H ₂ O	0.74	0.90	0.78	0.70	0.78	0.99	0.95
H ₂	1.40	0.60	0.83	0.84	0.84	0.88	1.10
CO	20.04	8.61	9.10	10.03	8.38	9.87	14.66
Total	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	108.21	108.21	104.57	108.32	107.61	103.39	103.14
g HC/Nm ³ (H ₂ +CO) conv.:	239	224	223	219	219	200	209
Selectivities, Wt % of HC :							
Methane	7.20	8.65	7.41	7.99	8.06	7.61	7.60
Ethene	0.98	0.98	0.90	0.94	0.87	0.89	0.99
Ethane	3.17	4.03	3.54	3.81	3.77	3.48	3.32
Propene	3.65	3.38	2.94	3.02	2.96	3.18	3.61
Propane	5.78	7.51	7.69	8.49	7.77	7.37	7.04
Butenes	5.94	4.97	4.10	4.16	4.42	4.90	5.88
i-Butane	7.91	8.83	8.69	9.43	8.81	8.39	8.28
n-Butane	5.92	7.15	7.05	7.53	7.26	7.09	7.03
C ₅ - C ₁₁	54.18	49.30	51.72	50.33	51.73	54.42	54.32
C ₁₂ + (Excl. Rx. Wax)	1.37	1.79	3.41	2.23	2.58	1.43	0.88
Slurry Rx. Wax	3.92	3.41	2.55	2.07	1.78	1.24	1.05
Total	100	100	100	100	100	100	100
i-C ₄ /(C ₃ = + C ₄ =) Molar	0.71	0.90	1.05	1.11	1.02	0.89	0.75
(C ₃ /C ₃ =) Molar Ratio :	1.51	2.12	2.50	2.68	2.50	2.21	1.86
Alkylate, Wt % of HC :	15.11	16.46	15.35	15.66	16.04	15.70	15.74
Cat-Poly, Wt % of HC :	2.38	0.72	0.00	0.00	0.00	0.78	2.03
C ₅ - C ₁₁ PONA, Wt % :							
Paraffins	42.57	48.55	45.28	43.97	45.89	46.41	45.46
Olefins	26.29	15.60	16.26	17.98	17.36	17.68	20.87
Naphthenes	5.88	7.47	7.80	7.61	7.19	7.05	7.44
Aromatics	25.26	28.38	30.66	30.44	29.56	28.86	26.23

Table A-4
Composition of Hydrocarbon Products from
Two-Stage Slurry P-T/ZSM-5 Syngas Conversion
Run CT-256-2

M.B. No. Days On-stream	2-1 0.9	2-2 1.9	2-3 2.9	2-4 3.9	2-5 4.9	2-6 5.9	2-7 6.9	2-8 7.9
METHANE	7.81	5.81	7.48	6.78	7.51	5.88	7.20	7.20
ETHENE	0.47	0.55	0.54	0.57	0.61	0.67	0.69	0.98
ETHANE	2.74	2.06	3.02	2.72	3.27	2.81	3.43	3.17
PROPENE	1.44	1.94	2.11	2.29	2.46	2.78	2.45	3.65
PROPANE	5.20	3.04	4.52	3.72	4.40	5.07	6.38	5.78
1-BUTANE	7.95	4.51	6.21	5.27	6.01	7.05	8.19	7.91
1-BUTENE+2-METHYLPROPENE	1.56	2.80	2.61	3.46	3.30	3.04	2.28	3.57
N-BUTANE	5.92	3.96	5.18	4.99	5.30	5.69	6.07	5.92
TRANS-2-BUTENE	0.83	1.07	0.97	1.35	1.27	1.22	0.90	1.41
CIS-2-BUTENE	0.43	0.70	0.65	0.91	0.85	0.86	0.62	0.97
3-METHYL-1-BUTENE	0.04	0.09	0.08	0.13	0.12	0.12	0.08	0.11
1-PENTANE	6.84	4.75	4.91	5.78	5.33	6.41	5.91	6.05
1-PENTENE	0.05	0.12	0.09	0.16	0.14	0.16	0.09	0.14
2-METHYL-1-BUTENE	0.32	0.85	0.62	1.11	0.94	0.85	0.50	0.80
N-PENTANE	4.05	3.76	3.62	4.88	4.25	4.60	3.90	3.94
TRANS-2-PENTENE	0.20	0.55	0.38	0.73	0.62	0.58	0.35	0.54
CIS-2-PENTENE	0.09	0.26	0.18	0.34	0.29	0.28	0.17	0.26
2-METHYL-2-BUTENE	0.16	2.58	1.70	3.19	2.67	2.18	1.30	1.97
UNKNOWN C5-MONOOLEFINS	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.02	0.03	0.03	0.04	0.03	0.05	0.03	0.06
CYCLOPENTANE	0.07	0.07	0.03	0.09	0.05	0.10	0.08	0.12
HEXENES + ISO-HEXANES	0.03	0.21	0.23	0.29	0.21	0.09	0.02	0.09
2,3-DIMETHYLBUTANE	0.15	0.12	0.06	0.17	0.11	0.15	0.17	0.13
2-METHYLPENTANE	3.02	3.35	2.28	3.88	2.95	3.43	2.80	2.57
3-METHYLPENTANE	1.11	1.10	0.69	1.29	0.95	1.30	1.12	0.99
HEXENES	0.24	1.17	0.00	0.84	1.12	0.88	0.52	0.49
1-HEXENE	0.00	0.00	0.00	0.00	0.00	0.12	0.08	0.12
N-HEXANE	1.85	2.93	1.81	3.58	2.89	2.97	2.44	2.23
2,4-DIMETHYLPENTANE	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00
METHYLCYCLOPENTANE	0.55	0.46	0.21	0.57	0.41	0.77	0.79	0.76
3,3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.02	0.02	0.00	0.02	0.02	0.03	0.03	0.02
HEPTENES + ISO-HEPTANES	0.44	1.02	0.91	1.54	0.87	0.84	0.46	0.67
1-HEPTENE	0.00	0.00	0.00	0.00	0.06	0.00	0.09	0.13
2-METHYLHEXANE	1.13	1.80	0.66	1.66	1.34	1.32	1.19	0.97
2,3-DIMETHYLPENTANE	0.16	0.13	0.01	0.15	0.08	0.15	0.18	0.14
3-METHYLHEXANE	1.02	1.46	0.47	1.34	1.05	1.15	1.08	0.87
1-CIS-3-DIMETHYL-N5	0.27	0.24	0.06	0.27	0.17	0.31	0.34	0.31
1-TRANS-3-DIMETHYL-N5	0.19	0.16	0.00	0.19	0.12	0.22	0.24	0.15
1-TRANS-2-DIMETHYL-N5	0.20	0.21	0.08	0.24	0.15	0.12	0.12	0.27
N-HEPTANE	0.73	2.24	0.80	2.25	2.00	1.68	1.51	1.49
C7-OLEFINS	0.40	1.78	0.00	1.09	1.74	1.23	0.94	0.79
METHYLCYCLOHEXANE	0.25	0.36	0.11	0.38	0.31	0.33	0.24	0.23
C8-OLEFINS + ISO-P	0.11	1.65	1.24	1.44	0.99	1.19	0.91	1.37
MONOMETHYL-ISO-C8-P	1.26	1.59	0.00	0.95	1.30	0.98	1.07	0.70
OTHER ISO-C8-P	0.15	0.13	0.00	0.13	0.09	0.13	0.15	0.11
C8-OLEFINS	0.98	3.59	0.00	1.97	3.79	2.10	1.59	1.67
C8-NAPHTHENES (N5+N6)	1.45	1.08	0.00	1.02	0.72	1.05	1.38	0.96
N-OCTANE	0.36	1.08	0.13	0.94	1.16	0.87	0.78	0.77
C9-OLEFINS + ISO-P	0.00	1.03	0.71	0.41	0.38	2.30	2.63	4.22
1-NONENE	0.00	0.00	0.00	0.17	0.00	0.00	0.00	0.00
MONOMETHYL-ISO-C9-P	0.69	0.96	0.00	0.51	0.79	0.52	0.58	0.41
OTHER ISO-C9-P	0.24	0.20	0.00	0.15	0.15	0.20	0.19	0.14
C9-OLEFINS	0.55	1.88	0.00	1.08	2.05	1.17	0.95	0.98
C9-NAPHTHENES (N5+N6)	0.66	0.54	0.00	0.53	0.40	0.35	0.35	0.37
N-NONANE	0.12	0.43	0.00	0.13	0.53	0.28	0.35	0.24
ISO-C10-P + O + N5 + N6	3.21	3.52	0.00	1.30	2.66	1.30	1.28	1.17
BENZENE	0.32	0.49	0.22	0.63	0.46	0.65	0.57	0.60
TOLUENE	1.91	0.58	0.39	2.02	1.05	2.61	2.90	2.23
ETHYLBENZENE	0.77	1.12	0.43	0.90	0.64	1.48	1.58	1.77
P-XYLENE	0.70	0.48	0.00	0.58	0.40	0.62	0.00	0.60
M-XYLENE	2.03	1.42	0.00	1.52	1.32	1.56	2.17	1.50
O-XYLENE	0.77	0.48	0.00	0.59	0.45	0.63	0.91	0.62
ISOPROPYLBENZENE	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00
N-PROPYLBENZENE	0.27	0.25	0.00	0.20	0.23	0.20	0.25	0.19
1-METHYL-3-ETHYL-BENZENE	2.99	2.27	0.00	2.17	2.11	2.26	2.94	2.14
1,3,5-TRIMETHYL-BENZENE	0.10	0.13	0.00	0.07	0.10	0.08	0.12	0.07
1-METHYL-2-ETHYLBENZENE	0.00	0.08	0.00	0.00	0.07	0.07	0.00	0.04
ISO-C4-BENZENE	0.05	0.00	0.00	0.04	0.00	0.00	0.14	0.04
SEC-C4-BENZENE	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00
1,2,4-TRIMETHYLBENZENE	1.58	1.13	0.00	1.09	0.96	1.13	1.56	1.14
1-METHYL-2-ISO-C3-BENZENE	0.07	0.07	0.00	0.03	0.05	0.06	0.05	0.04
1,3-DIETHYLBENZENE	0.78	0.81	0.00	0.57	0.72	0.58	0.00	0.52
1-METHYL-3-N-C3-BENZENE	0.14	0.27	0.00	0.15	0.25	0.19	0.70	0.14
N-C4-BENZENE	0.22	0.23	0.00	0.15	0.19	0.00	0.19	0.14
1,2,3-TRIMETHYLBENZENE	0.12	0.09	0.00	0.03	0.03	0.04	0.06	0.05
1,2-DIETHYLBENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00
1-METHYL-2-N-C3-BENZENE	0.00	0.00	0.00	0.03	0.03	0.00	0.05	0.03
C10-ALKYLBENZENES	1.17	0.96	0.00	0.70	0.79	0.70	0.92	0.67
1,2,4,5-TETRAMETHYLBENZENE	0.14	0.08	0.00	0.06	0.11	0.02	0.09	0.06
1,2,3,5-TETRAMETHYLBENZENE	0.10	0.03	0.00	0.02	0.06	0.00	0.04	0.00
1,2,3,4-TETRAMETHYLBENZENE	0.11	0.00	0.00	0.00	0.06	0.00	0.11	0.08
C11-ALKYLBENZENES	1.23	0.99	0.00	0.72	0.73	0.83	1.02	0.72
NAPHTHALENE	0.00	0.04	0.00	0.04	0.05	0.00	0.00	0.00
METHYL-NAPHTHALENES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
DIMETHYL ETHER	0.10	0.00	0.00	0.00	0.00	0.00	0.01	0.00
UNKNOWN (HC AROMATICS)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.28
UNKNOWN LITE HYDRO-CARB LIQ (1)	0.00	0.00	34.66	0.00	0.00	0.00	0.00	0.00
UNKNOWN C12+	2.28	3.64	2.65	2.71	3.00	2.34	2.53	1.37
SLURRY REACTOR WAX	13.60	8.43	6.28	5.88	5.13	3.81	3.74	3.92

(1) Collected in Chilled and Ambient Condensers

Table A-4 (Contd.)
 Composition of Hydrocarbon Products from
 Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
 Run CT-256-2

M.B. No.	2-12	2-13	2-14	2-15	2-16	2-17
Days On-stream	11.9	12.9	13.8	14.8	15.8	16.8
METHANE	8.65	7.41	7.99	8.06	7.61	7.60
ETHENE	0.98	0.90	0.94	0.87	0.89	0.99
ETHANE	4.03	3.54	3.81	3.77	3.48	3.32
PROPENE	3.38	2.94	3.02	2.96	3.18	3.61
PROPANE	7.51	7.69	8.49	7.77	7.37	7.04
1-BUTANE	8.83	8.69	9.43	8.81	8.39	8.28
1-BUTENE+2-METHYLPROPENE	2.95	2.41	2.46	2.62	2.85	3.38
N-BUTANE	7.15	7.05	7.53	7.26	7.09	7.03
TRANS-2-BUTENE	1.19	1.00	0.99	1.05	1.16	1.41
CIS-2-BUTENE	0.83	0.70	0.70	0.74	0.89	1.09
3-METHYL-1-BUTENE	0.09	0.08	0.07	0.08	0.13	0.18
1-PENTANE	6.74	6.44	6.63	6.57	6.58	6.71
1-PENTENE	0.12	0.10	0.10	0.11	0.13	0.18
2-METHYL-1-BUTENE	0.66	0.53	0.51	0.59	0.67	0.80
N-PENTANE	4.70	4.28	4.28	4.46	4.51	4.56
TRANS-2-PENTENE	0.46	0.38	0.36	0.41	0.52	0.55
CIS-2-PENTENE	0.23	0.19	0.18	0.20	0.25	0.29
2-METHYL-2-BUTENE	1.60	1.29	1.21	1.41	1.58	1.93
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.05	0.04	0.04	0.04	0.06	0.06
CYCLOPENTANE	0.21	0.24	0.24	0.18	0.18	0.18
HEXENES + ISO-HEXANES	0.10	0.02	0.03	0.02	0.04	0.03
2,3-DIMETHYLBUTANE	0.18	0.19	0.17	0.17	0.20	0.22
2-METHYLPENTANE	2.77	2.63	2.43	2.60	2.72	2.82
3-METHYLPENTANE	1.14	1.17	1.09	1.10	1.19	1.22
HEXENES	0.45	0.59	0.44	0.57	0.70	0.73
1-HEXENE	0.08	0.06	0.07	0.06	0.09	0.11
N-HEXANE	2.51	2.39	2.14	2.36	2.40	2.60
2,4-DIMETHYLPENTANE	0.01	0.01	0.01	0.00	0.01	0.01
METHYLCYCLOPENTANE	1.05	1.11	1.10	0.95	0.91	0.97
3,3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.02	0.03	0.02	0.03	0.03	0.02
HEPTENES + ISO-HEPTANES	0.46	0.35	0.32	0.39	0.41	0.71
1-HEPTENE	0.10	0.10	0.11	0.09	0.08	0.12
2-METHYLHEXANE	0.84	0.91	0.80	0.90	0.94	1.00
2,3-DIMETHYLPENTANE	0.17	0.20	0.19	0.18	0.18	0.20
3-METHYLHEXANE	0.78	0.88	0.78	0.85	0.90	0.92
1-CIS-3-DIMETHYL-N5	0.34	0.37	0.35	0.34	0.33	0.23
1-TRANS-3-DIMETHYL-N5	0.21	0.25	0.23	0.23	0.24	0.23
1-TRANS-2-DIMETHYL-N5	0.29	0.31	0.30	0.28	0.27	0.29
N-HEPTANE	1.19	1.25	1.08	1.23	1.33	1.42
C7-OLEFINS	0.64	0.73	0.56	0.76	0.92	0.96
METHYLCYCLOHEXANE	0.20	0.20	0.19	0.19	0.21	0.23
C8-OLEFINS + ISO-P	0.56	0.60	1.64	0.46	0.72	0.50
MONOMETHYL-ISO-C8-P	0.63	0.74	0.61	0.78	0.89	0.80
OTHER ISO-C8-P	0.12	0.15	0.13	0.14	0.16	0.15
C8-OLEFINS	1.10	1.11	0.91	1.34	1.73	2.42
C8-NAPHTHENES (N5+N6)	1.02	1.18	1.08	1.16	1.25	1.18
N-OCTANE	0.47	0.57	0.44	0.56	0.72	0.09
C9-OLEFINS + ISO-P	0.55	1.68	2.12	1.69	0.57	0.78
1-NONENE	0.00	0.00	0.00	0.00	0.00	0.00
MONOMETHYL-ISO-C9-P	0.34	0.36	0.30	0.40	0.46	0.44
OTHER ISO-C9-P	0.13	0.14	0.13	0.15	0.17	0.16
C9-OLEFINS	0.60	0.60	0.45	0.80	1.11	1.05
C9-NAPHTHENES (N5+N6)	0.34	0.36	0.31	0.37	0.42	0.71
N-NONANE	0.17	0.19	0.15	0.22	0.27	0.00
ISO-C10-P + O + N5 + N6	0.88	0.87	0.70	1.01	1.53	1.30
BENZENE	0.61	0.74	0.75	0.64	0.63	0.67
TOLUENE	2.56	3.18	2.59	2.67	2.67	2.26
ETHYLBENZENE	0.95	1.59	1.67	1.43	1.09	1.02
P-XYLENE	0.74	0.84	0.87	0.85	0.82	0.75
M-XYLENE	1.91	2.03	2.10	2.01	2.14	1.90
O-XYLENE	0.84	0.86	0.92	0.88	0.90	0.81
ISOPROPYLBENZENE	0.00	0.00	0.00	0.00	0.04	0.00
N-PROPYLBENZENE	0.18	0.16	0.14	0.18	0.20	0.20
1-METHYL-3-ETHYL-BENZENE	2.25	2.42	2.29	2.53	2.62	2.44
1,3,5-TRIMETHYL-BENZENE	0.06	0.06	0.06	0.06	0.07	0.07
1-METHYL-2-ETHYLBENZENE	0.00	0.05	0.05	0.02	0.00	0.00
ISO-C4-BENZENE	0.04	0.03	0.03	0.03	0.04	0.04
SEC-C4-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00
1,2,4-TRIMETHYLBENZENE	1.34	1.42	1.46	1.44	1.55	1.44
1-METHYL-2-ISO-C3-BENZENE	0.04	0.00	0.05	0.02	0.03	0.02
1,3-DIETHYLBENZENE	0.47	0.48	0.43	0.53	0.00	0.54
1-METHYL-3-N-C3-BENZENE	0.11	0.10	0.09	0.11	0.57	0.13
N-C4-BENZENE	0.13	0.12	0.00	0.13	0.14	0.13
1,2,3-TRIMETHYLBENZENE	0.09	0.03	0.03	0.04	0.05	0.04
1,2-DIETHYLBENZENE	0.00	0.00	0.06	0.00	0.13	0.00
1-METHYL-2-N-C3-BENZENE	0.00	0.00	0.00	0.03	0.04	0.03
C10-ALKYLBENZENES	0.68	0.73	0.69	0.77	0.84	0.79
1,2,4,5-TETRAMETHYLBENZENE	0.06	0.07	0.07	0.07	0.09	0.08
1,2,3,5-TETRAMETHYLBENZENE	0.04	0.00	0.00	0.00	0.00	0.04
1,2,3,4-TETRAMETHYLBENZENE	0.10	0.10	0.10	0.10	0.10	0.00
C11-ALKYLBENZENES	0.78	0.80	0.78	0.71	0.87	0.77
NAPHTHALENE	0.00	0.03	0.07	0.03	0.07	0.07
METHYL-NAPHTHALENES	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN (HC AROMATICS)	0.01	0.00	0.01	0.01	0.00	0.00
UNKNOWN C12+	1.79	3.41	2.23	2.58	1.43	0.88
SLURRY REACTOR WAX	3.41	2.55	2.07	1.78	1.24	1.05

Table A-5

Second-Stage ZSM-5 Reactor Raw Liquid Hydrocarbon⁽¹⁾ Properties
(Run CT-256-2)

Days On-Stream	3.9	6.9	8.9	10.9	15.8
Severity, $iC_4/(C_4^{=}+C_3^{=})$	0.58	1.1	1.1	-	0.72
Sp. Gr.	0.740	0.776	0.764	0.764	0.754
Acid No. (unwashed), mg KOH/g	0.16	0.12	0.49	0.35	0.016
PONA, Wt %					
P	35.0	27.3	29.3	27.4	31.1
O	19.4	13.2	12.5	13.1	15.8
N	11.9	12.4	12.3	12.2	12.8
A	33.7	47.1	45.9	47.3	40.3
Total	100.0	100.0	100.0	100.0	100.0
Octane Numbers:					
R+O	92.6	93.6	93.5	94.0	91.4
M+O	76.0	80.7	81.5	80.9	81.5
ASTM Distillation, °C					
IBP	37	38	36	36	34
50 Vol %	129	126	129	130	126
90 "	188	183	186	188	185
95 "	223	221	228	224	234
EP "	257	245	252	258	243
Loss, Vol %	2.1	1.6	2.1	1.8	2.3
Residue, Vol %	0.9	1.4	0.9	1.2	1.2

⁽¹⁾Collected from the ambient and chilled condensers. Hydrocarbon collected in the hot condenser was very small.