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

Final Report

By
J. C. W. Kuo

June 1983
Date Published

Work Performed Under Contract No. AC22-80PC30022

Mobil Research and Development Corporation
Paulsboro, New Jersey

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FINAL REPORT

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ABSTRACT

An evaluation study was conducted on a novel two-stage slurry Fischer-Tropsch/ZSM-5 process for converting low H₂/CO ratio synthesis gas, which can generally be obtained from highly efficient, advanced coal-gasification systems, into high quality gasoline. The feasibility of this two-stage technology was successfully demonstrated in a newly designed and constructed bench-scale unit (BSU), consisting of a slurry bubble column reactor followed by a fixed-bed ZSM-5 reactor.

Three Fischer-Tropsch catalysts of Fe/Cu/K₂CO₃ type were evaluated. Total hydrocarbon production as high as 815 g/gFe was achieved, which is substantially better than other results reported in the literature. Methane + ethane yields ranged from 2 to 18 wt % of total hydrocarbons produced, with reactor-wax (those heavy hydrocarbons retained in the slurry reactor under reaction conditions) yields ranging from 3 to 85 wt %. Other investigations of the first-stage operation included process variable and hydrodynamic studies.

The second-stage ZSM-5 reactor performed smoothly and demonstrated the conversion of Fischer-Tropsch products into high quality gasoline. The gasoline yields, including the alkylate and excluding the reactor-wax and light paraffins in the feed to the second-stage reactor, were as high as 87 wt %. The raw gasoline samples had satisfactory stability properties.

A conceptual process design and scoping cost estimate for a battery-limit commercial plant to produce 27,000 BPSD gasoline from clean synthesis gas was conducted. The estimated cost is \$700 million in terms of 1983 dollars at a Wyoming location.

I. 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 were 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.

Task 2 - Construction and Shakedown of Pilot Plant

The pilot plant will be constructed in MRDC Paulsboro Laboratory. The unit will be shaken down after completion.

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.

II. Summary

The Mobil Two-Stage Slurry Fischer-Tropsch/ZSM-5 Process provides a new and novel route for the conversion of coal to high quality motor fuels. The Mobil design combines the classic slurry-phase Fischer-Tropsch synthesis technology with a state-of-the-art fixed-bed ZSM-5 reactor which converts the vaporous Fischer-Tropsch products from the first-stage slurry reactor directly into high quality gasoline.

Due to the unique features of a slurry Fischer-Tropsch reactor, synthesis gas with H_2/CO molar ratios as low as 0.6 to 0.7 can be directly used, provided the Fischer-Tropsch catalyst has water-gas shift reaction activity. These low H_2/CO ratio gases can generally be obtained from the advanced coal gasification systems, such as BGC(British Gas Corporation)/Lurgi Slagger, Texaco, Shell-Koppers, and Westinghouse gasifiers. These gasifiers have high thermal efficiency and are potentially lower-cost than current one (Shinnar and Kuo, 1980). Consequently, a combination of these advanced coal gasification systems with this two-stage technology constitutes a novel and lower-cost route of converting coal to gasoline. In contrast, the methanol synthesis route stoichiometrically requires synthesis gas of at least 2/1 H_2/CO ratio. The use of a low H_2/CO ratio synthesis gas for hydrocarbon synthesis plus a simple step of upgrading the Fischer-Tropsch products into high quality gasoline in a single fixed-bed ZSM-5 reactor constitute two unique features of this two-stage technology.

The present work on the development of the two-stage process was initiated in October 1980, under DOE Contract No. DE-AC22-80PC30022. The specific objective was to develop the process in a bench-scale pilot plant consisting of a slurry Fischer-Tropsch reactor (5.1 cm ID x 762 cm high) and a fixed-bed ZSM-5 reactor in series. The scope of work encompassed design and construction of the pilot plant, evaluation of Fischer-Tropsch catalysts, process variable studies, characterization of the gasoline product, and a preliminary conceptual design and scoping economic study of a commercial plant.

The design and construction of the pilot plant was completed on schedule in December 1981. The slurry bubble-column reactor is connected at the top to a disengager which serves to prevent carryover of entrained slurry. The reactor temperature is controlled by circulating hydrocarbon oil (e.g., Mobiltherm-600) in a jacket surrounding the entire column. Individual streams of carbon monoxide and hydrogen are mixed and preheated before entering the reactor through a sintered metal distributor at the bottom. Reactor-wax which consists of heavy Fischer-Tropsch products accumulated in the slurry reactor was removed initially using filters suspended in the slurry medium

and later by on-line catalyst settling vessels. The second stage consists of two fixed-bed reactors arranged in parallel for swing operation. The reactors can be operated in both adiabatic and isothermal modes. Analysis of the combined gas product is accomplished by an on-line GC system.

The unit was put on stream in March 1982 after a brief shakedown operation. The first-stage catalyst was composed of $\text{Fe}/\text{Cu}/\text{K}_2\text{CO}_3$, while the second stage contained a ZSM-5 class catalyst. Operating conditions were selected based on prior experience and Fischer-Tropsch bubble-column mathematical model calculations. The feed H_2/CO ratio was 0.7. The startup and operation was very smooth, and conditions were varied during the run with no adverse effects. In all, five runs were achieved, ranging in length from thirteen to eight-six days. Three first-stage catalysts were evaluated and long-term stability of the slurry Fischer-Tropsch operation was demonstrated with a production of 815 gHC/gFe. Synthesis gas conversions as high as 85-91% were achieved and maintained for as long as sixty days, and methane + ethane yields as low as 1.7 wt % of hydrocarbons were observed. At low methane + ethane yields, reactor-wax yields up to 80 wt % were attained. First-stage temperatures ranged from 240 to 282°C, and the unit was operated at 1.13 to 2.52 MPa. High pressure operation reduced the methane + ethane yield substantially while greatly increasing the synthesis gas throughput. In process variable studies, the effects of 0.6 H_2/CO feed gas, as well as varying flow rates and different catalyst loadings were examined. Addition of a potassium-salt to the slurry reactor dramatically decreased the methane + ethane yield. The second stage performed well in converting the vaporous F-T products from the first-stage slurry reactor into gasoline. Temperatures in the fixed-bed reactors ranged from 288 to 466°C, and the catalyst was regenerated twice without any observable loss of initial activity.

Hydrodynamic studies were performed with hot and cold glass bubble-columns. Both Fischer-Tropsch wax and slurry, as well as n-hexadecane were used as mediums. The gas holdup varied strongly with static liquid heights, and moderately with the column diameter and solids concentration. Further work in this area is needed.

The raw gasoline collected in the cold and chilled condensers of the BSU had R+O octane numbers ranging from 82 to 98, depending on the second-stage severity. The gasoline also demonstrated satisfactory oxidation stability and corrosion protection qualities with standard additives. It also contained a small quantity of components heavier than gasoline, which could be easily removal using a conventional distillation technique.

A complex analytical scheme for defining the Fischer-Tropsch reaction products was developed. Total breakdown of the product stream was accomplished by using a variety of chromatographic techniques, along with distillation, scrubbing, and extraction. Various supporting tests, including acid number, bromine number, hydroxyl number, viscosity, and surface tension, were also employed.

Based on the process data developed, a conceptual design and scoping cost estimate of a commercial-scale plant to produce 27,000 BPSD of 10 RVP gasoline was completed. The cost estimate for the battery limit facilities at a Wyoming location is approximately \$700 million, using mid-1983 instantaneous dollars.

III. Introduction

In view of the diminishing petroleum supply in the United States, new technologies for converting coal to transportation fuels are expected to become increasingly important in the future.

In 1976, Mobil Research and Development Corporation (MRDC) announced a catalytic process for converting methanol to high octane gasoline in high yield (Meisel, et al., 1976; Wise and Silvestri, 1976). Since commercial processes for the synthesis of methanol from coal-derived synthesis gas are known, this new technology provides a viable route for the conversion of coal to gasoline. The development of the fixed-bed MTG (Methanol-to-Gasoline) process was studied under an ERDA contract, No. E(49-18)-1733 (Voltz and Wise, 1976). In 1978, under DOE Contract No. EX-76-C-01-2490, the conversion of methanol to high octane gasoline in a 4 BPD fluidized-bed pilot unit was demonstrated (Kam and Lee, 1978). Currently, a 14,000 BPD gasoline plant using fixed-bed MTG technology is being constructed in New Zealand.

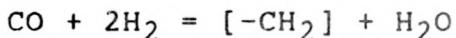
Another route of converting coal-derived synthesis gas to hydrocarbons uses the Fischer-Tropsch (F-T) reaction, which was first reported in 1923 and is named after its discoverers (Fischer and Tropsch, 1923). Excellent reviews on early F-T work have been given by Storch, et al. (1951) and by Anderson (1956). SASOL in South Africa is currently operating three commercial plants producing transportation fuels using F-T technology. Both fixed-bed tubular (Arge process) and fluidized entrained-bed (Synthol process) reactor designs are used.

Both routes mentioned above require synthesis gas of H_2/CO molar ratio greater than 2.0. In the case of methanol synthesis, this is required by stoichiometry. In the case of the conventional F-T technologies, the high H_2/CO ratio is required either for minimizing carbon formation from the carbon monoxide or avoiding formation of waxy hydrocarbons in fluidized bed systems, which causes the catalyst to lose fluidization characteristics.

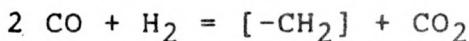
In 1978, under DOE Contract No. EF-76-C-01-2447 (Schreiner, 1978), a research guidance study was carried out on coal-to-gasoline processes via both the MTG and SASOL-type Synthol route. It was found that the predominant cost of a complete plant is associated with the gasification of the coal. Consequently, a study to identify potentially lower-cost coal gasification systems was carried out in 1978 under DOE Contract No. EF-77-C-01-2766 (Shinnar and Kuo, 1978). The majority of the advanced coal gasification systems that have high thermal-efficiency (and thus potentially lower-cost) produce low H_2/CO ratio synthesis gas (ranged from 0.35 to 1.0). This is a

direct consequence of minimum steam usage during the gasification. Of course, those low H₂/CO ratio gases can be shifted to high H₂/CO ratios and then used as feed-gases to either methanol synthesis or conventional F-T units. However, the major cost advantage from the advanced coal gasification is then negated. To maintain this advantage, a synthesis process, that can directly use a low H₂/CO ratio gas is needed.

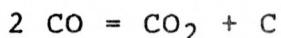
With Fe-based F-T catalysts which promote the water-gas shift reaction under synthesis conditions, the following reactions take place simultaneously (as illustrated by formation of [-CH₂] hydrocarbons):



The second reaction indicates that the Fe-based catalyst promotes "internal shift" by utilizing the water produced from the F-T reaction to make more H₂. By doing so, high single-pass synthesis gas conversion can be achieved with a low H₂/CO ratio synthesis gas. After this "internal shift" reaction, the overall F-T reaction becomes



This reaction is highly exothermic and strict temperature control is essential. A slurry reactor provides excellent reaction temperature control and prevents excessive carbon formation by the following reaction.



The rate of this undesirable reaction increases drastically with increasing temperature.

The products from F-T process, however, are highly nonselective. They include a wide range of hydrocarbons and oxygenates and require expensive refinery steps to upgrade them to marketable products.

MRDC has, however, developed a process using ZSM-5 which converts the F-T products into high-quality gasoline in a single step. In this way, the conversion of coal derived synthesis gas to gasoline can be made more attractive economically. The potential of this two-stage technology is being assessed in this study.

IV. Design of Two-Stage Bench-Scale Pilot Plant

A. Simplified Flow Diagram and Design Basis

A simplified flow diagram of the bench-scale unit is shown in Figure 1. The unit consists of four sections:

- Gas feed
- Slurry F-T reactor
- Fixed-bed ZSM-5 reactor and product recovery
- Liquid hydrocarbon product distillation

The design basis of the BSU defines the normal operating conditions and the design ranges of all major variables of the pilot plant (Table 1). At normal operating conditions, the synthesis gas feed rate is 1.87 Nm³/hr with a 0.67 H₂/CO ratio.

B. Engineering Flow, and Piping and Instrumentation Diagrams

The Engineering Flow, and Piping and Instrumentation diagrams for all sections, shown as Figures A-1 through A-4 in Appendix A, are based on the design basis defined in Table 1.

In the gas feed section (Figure A-1), the in-house H₂, and CO from a high pressure tank (13.9 MPa or 2000 psig) are filtered, purified over activated charcoal to remove any carbonyls, regulated and metered to give a simulated synthesis gas with a desired H₂/CO ratio. A desired quantity of high pressure N₂ or any other gas (e.g., methane) can also be mixed with the H₂ and CO stream. The mixed gaseous stream passes through a preheater before entering the slurry reactor. For safe handling of poisonous CO and flammable H₂ gas, solenoid valves coupled to the leak detectors are employed to shut the gases off in the event of any leak in the system.

Also shown in the diagram is an air supply for the regeneration of the second-stage reactor. Filtered, regulated, and metered air and nitrogen are fed to a compressor (E 50). The compressed mixture is then combined with the regeneration recycle gas and fed to the reactor.

Figure A-2 is the Engineering Flow, and Piping and Instrumentation diagram of the slurry F-T reactor section. The slurry reactor (5.1 cm ID x 762 cm height) consists of one 150 and two 305 cm sections of schedule 40 stainless steel pipe connected together with flange joints. The sectioning of the reactor into 305 cm and 710 cm levels offers the flexibility of design modifications, if warranted.

FIGURE 1

SIMPLIFIED FLOW DIAGRAM OF TWO-STAGE PILOT PLANT FOR SYNTHESIS GAS CONVERSION

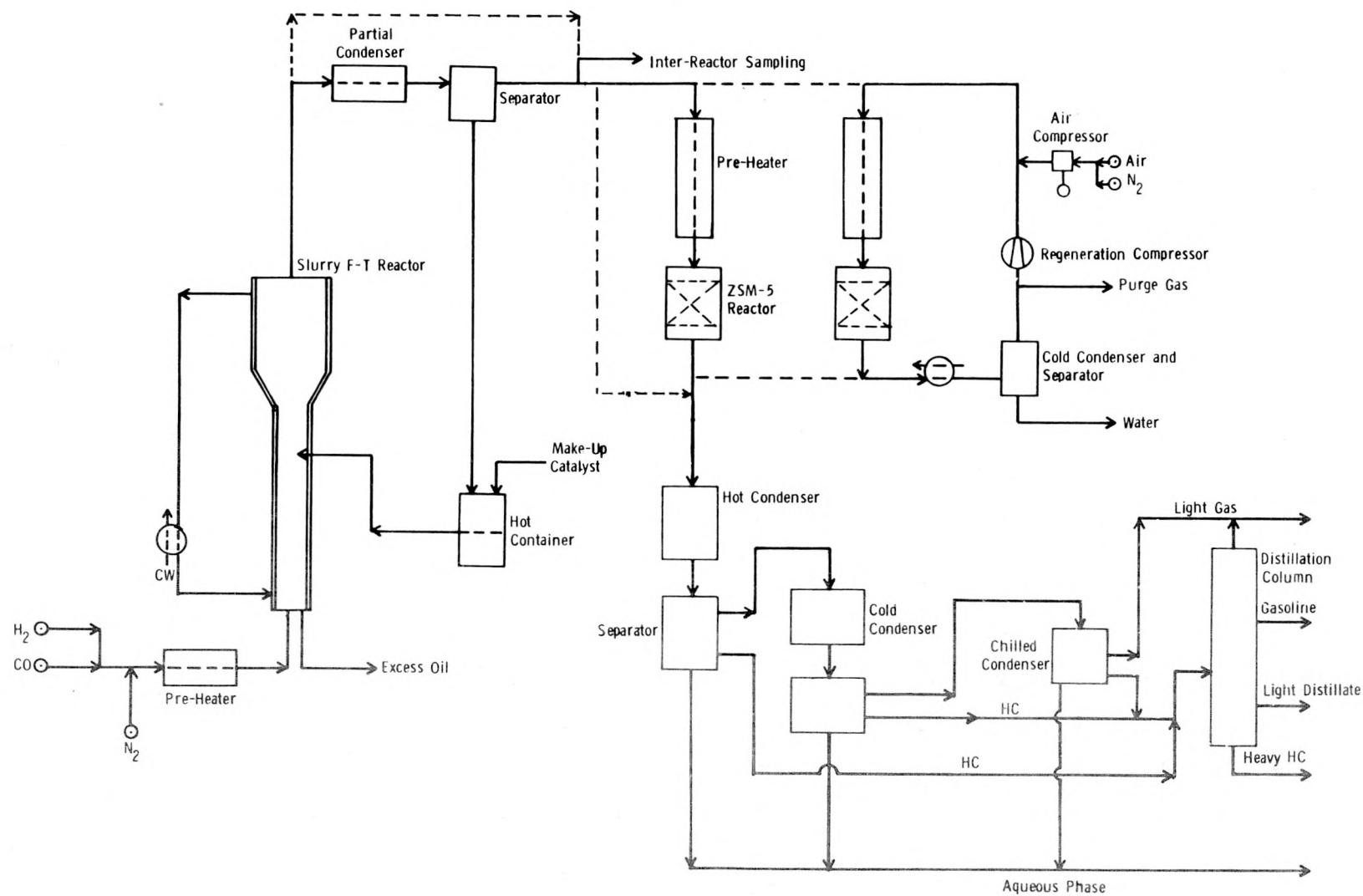


Table 1

**Design Basis of the Two-Stage Synthesis Gas
Conversion Bench-Scale Unit**

<u>I. Reactor Dimensions</u>	<u>Normal</u>	<u>Design Range</u>
Slurry F-T Catalyst Bed, cm	5.08(ID)x305(L)	5.08(ID)x305-762(L)
ZSM-5 Catalyst Bed, cm	5.08(ID)x20.3(L)	5.08(ID)x10.2-45.7(L)
<u>II. Material Balance Basis</u>		
<u>Normal Operation</u>		
Syngas Feed Rate, Nm ³ /hr	1.87	0.94-3.75
H ₂ /CO Mole Ratio	0.67	0.5-2
H ₂ +CO Conversion, Mol %	90	50-97
<u>ZSM-5 Reactor Regeneration</u>		
Air+Recycle Gas Flow Rate, Nm ³ /hr	1.39	0.70-3.21
Oxygen Concentration, Mole %	0.7-21	-
<u>III. Reactor Operation Conditions</u>		
<u>Slurry F-T Reactor</u>		
Inlet Temperature, °C	260	38-343
Exit Temperature, °C	260	216-343
Pressure, MPa	1.38	0.69-4.14
GHSV (STP), l/hr	128	64-256
Catalyst Load, g	1544	1544-3859
Reaction Heat Removal Rate, MJ/hr	4.8	1.4-10
<u>ZSM-5 Reactor</u>		
Inlet Temperature, °C	316-399	316-454
Exit Temperature, °C	379-463	316-482
Pressure, MPa	1.31	0.69-4.14
WHSV Based on Hydrocarbons, l/hr	1.5	-
Catalyst Load, g	227	114-545
<u>ZSM-5 Reactor Regeneration</u>		
Inlet Temperature, °C	316-482	316-538
Exit Temperature, °C	371-482	371-538
Pressure, MPa	2.76	1.03-4.14

Table 1 (cont'd)

IV. <u>ZSM-5 Reactor Preheater</u>	<u>Normal</u>	<u>Design Range</u>
<u>Normal Operation</u>		
Inlet Temperature, °C	260	177-343
Exit Temperature, °C	316-399	316-427
Pressure, MPa	1.31	0.69-4.14
<u>Regeneration Operation</u>		
Inlet Temperature, °C	Room	-
Exit Temperature, °C	343-482	316-538
Pressure, MPa	2.76	1.03-4.14
V. <u>Other Operation Conditions</u>		
<u>Slurry F-T Reactor Preheater</u>		
Inlet Temperature, °C	Room	-
Exit Temperature, °C	260	216-343
Pressure, MPa	1.38	0.69-4.14
<u>Partial Condenser After F-T Reactor</u>		
Inlet Temperature, °C	260	216-343
Exit Temperature, °C	260	177-343
Pressure, MPa	1.31	0.69-4.14
<u>Hot Condenser</u>		
Inlet Temperature, °C	379-463	343-482
Exit Temperature, °C	100	-
Pressure, MPa	1.31	0.69-4.14
<u>Cold Condenser</u>		
Inlet Temperature, °C	100	-
Exit Temperature, °C	Room	Room-52
Pressure, MPa	1.31	0.69-4.14
<u>Chilled Condenser</u>		
Inlet Temperature, °C	Room	Room-52
Exit Temperature, °C	0	-
Pressure, MPa	1.31	0.69-4.14
<u>Liquid Hydrocarbon Distillation Column</u>		
Pressure, MPa	0.17	0.07-0.41
Overhead Product	C_4^-	-
Bottom Product	C_4^+ C_{12}	-

The hot synthesis gas (H_2+CO) from the Feed Preheater enters the bottom zone below a distributor which is clamped between the bottom flanges. A drain is provided in the zone below the distributor to drain any slurry seeping through the distributor.

At the top, a disengaging zone (12.7 cm ID x 183 cm height) is provided to separate outgoing gases from the gas-liquid suspension. Two inclined baffles are in this zone to break up any froth formed and to minimize any liquid entrained in the gas. The product vapors leave this zone through a fine filter which prevents any catalyst carryover.

A coolant, such as Mobiltherm-600⁽¹⁾, is circulated through a jacket surrounding the reactor either to remove the heat of reaction or to add heat as may be required. The cooling jacket is divided into many sections to facilitate the attachment of pipe couplings to the reactor at different levels. These pipe couplings are used for the insertion of different probes (e.g., temperature, pressure, and liquid-level probes) and lines for the addition or withdrawal of slurry. Four sample taps are provided at 30, 152, 305 and 610 cm above the feed-gas distributor to withdraw slurry into sample bombs.

The catalyst slurry is prepared in a 26,000 cm³ Slurry Tank (E-48) and transferred to the reactor above the distributor by applying N₂-pressure in the slurry tank. The Slurry Transfer Vessel (E-49) is used to add small quantities of slurry, if needed, during the operation of the reactor.

In case of accumulation of liquid hydrocarbon products in the reactor, a small amount of the liquid can be withdrawn through a fine filter suspended at a level of approximately 213 cm. The withdrawn liquid is collected in the Spent-Wax Receiver (E-23). The fresh liquid without catalyst is stored in the Fresh-Wax Reservoir (E-22). The wax from these two tanks can be pumped into the reactor in the case of a loss of the slurry.

A partial condenser (E-8, Liquid Drop-Out Pot) is employed on the product line before the products are sent to the second-stage reactor. If a drop in slurry level occurs within the bubble-column, this condenser can be used to recover some of the heavier hydrocarbons from the F-T reactor effluent and returned to the F-T reactor.

To analyze first-stage F-T reactor products, a small side-stream can be diverted from the effluent stream. The hot and cold condensers (E-93, 94) separate this sample stream into heavy and light liquid hydrocarbons, aqueous phase, and light gases. These four streams can then be analyzed separately.

In the fixed-bed ZSM-5 reactor and product recovery

(1) A registered trade mark.

section (shown in Figure A-3), two fixed-bed adiabatic reactors (5.08 cm ID x 10-46 cm height) are used; one in normal operation and the other in regeneration. The reactor containing the coked catalyst is regenerated under pressure with a controlled supply of O₂ (0.7 - 21 mol %).

The product stream from the reactor passes through hot (100°C), cold (about 38°C), and chilled (0°C) condensers. Each condenser is followed by a separator where liquid hydrocarbons and aqueous phases are separated and subsequently collected. The uncondensed light gases containing mostly CO₂ are metered, analyzed, and finally vented off. The liquid hydrocarbon products collected from three separators are sent to a distillation column for further separation.

In the liquid hydrocarbon product distillation section (Figure A-4), the three liquid hydrocarbon streams from the hot, cold, and chilled condensers are separated into a light gas, a gasoline range product, and heavier fraction liquid products, if there are any. This separation serves two purposes:

- To make the analysis of the liquid hydrocarbon products easier.
- To obtain the proper gasoline stream for product evaluation.

The distillation column is divided into two separate sections to ease control and operation. The first section separates very heavy products (boiling above a certain temperature which can be controlled) as the bottoms. The top stream enters the second section at a desired temperature. The gasoline product is obtained as a side stream. A temperature-controlled valve monitors the withdrawal rate of the gasoline product. The top portion of the section, acting as a condenser, is maintained at 0°C by circulating chilled glycol. The reflux ratio can be adjusted by withdrawing various amounts of liquid from the top portion. The light gas from the top is combined with the light gas from the chilled condenser to be metered and analyzed. The bottoms of the second section are collected as a light distillate. Provisions are made so that this section can be completely bypassed, if necessary. In this case, light and heavy hydrocarbon liquid streams with largely overlapping hydrocarbon distributions will be obtained.

C. Detailed Engineering Design

Table 2 gives a list of thirty-nine detailed fabrication drawings for the important BSU components, such as distillation columns, preheaters, condensers, receivers, drop-out pots, and glycol flow measuring systems.

Table 2
List of Fabrication Drawings

<u>Drawing Nos.</u>	<u>Description</u>
RB-9074, 9075, 9076	Main Fractionation Column, E-43
RB-9093	Pre-fractionation Column, E-42
RB-9087	Feed Preheater, E-32
RC-4470	Hot Condenser, E-38
RC-4471	Ambient Water Condenser, E-39
RC-4472	Chilled Glycol Condenser, E-40
RC-4469	Regeneration Gas Condenser, E-35
RD-2694	Inter-reactor Sample (I.R.S.) Hot Condenser, E-93
RD-2695	I.R.S. Water Condenser, E-94
RD-2699	Heavy Fuel Oil Vent Condenser, E-100
RE-6229	Wax Drop-out Pot (Partial Condenser), E-8
RB-9095	Slurry Tank, E-48
RC-4467	Fresh Wax Reservoir, E-22
RC-4468	Spent Wax Receiver, E-23
RC-4473	Heavy Fuel Oil Reservoir, E-41
RC-4474	Two-gallon Distillate Receiver, E-44
RC-4475	One-gallon Distillate Receiver, E-45
RC-4476	Two-gallon Gasoline Receiver, E-46
RC-4477	One-gallon Gasoline Receiver, E-47
RE-6225	Slurry Sample Bombs, E-1, 2, 3, 4
RE-6236	Slurry Transfer Vessel, E-49
RD-2693	H. P. Drop-out Pot, E-26
RE-6234	Water Drop-out Pot, E-29
RE-6240	I.R.S. Hot Condenser Drop-Out Pot, E-87

Table 2 (cont'd)

<u>Drawing Nos.</u>	<u>Description</u>
RE-6241	I.R.S. Ambient Condenser Drop-out Pot, E-88
RE-6226	Chilled Drop-out Pot, E-5
RE-6227	Surge Pot, E-6
RE-6228	Surge Pot, E-7
RE-6231	Surge Pot, E-17, 18, & 19
RE-6233	Glycol Reservoir, E-24 & 25
RE-6235	Glycol Reservoir, E-30 & 31
RE-6232	Glycol Hold-up Vessel, E-20, 21, 27 & 28
RE-6230	Glycol Overflow Vessel, E-13 & 14
RE-6243	Glycol Overflow Vessel, E-15 & 16
RE-6238	Funnel, E-81, 82, 83, 84 & 96
RE-6239	Funnel, E-97
RE-6237	Gas Mixing Tube, E-55

The detailed designs of the six sections for the F-T bubble-column reactor are shown in Figures A-5 and A-6. Figure A-5 shows section 1, the top flange with a filter attachment; section 2, the disengager; and section 6, the bottom section below the distributor. Also shown in the drawing is the overall layout of the reactor. Figure A-6 shows sections 3, 4, and 5 of the reactor between 610-762 cm, 305-610 cm, and 0-305 cm levels, respectively. Both figures show cooling jackets and pipe couplings for the insertion of different probes as described in the previous subsection. Figure A-7 gives details of the fixed-bed ZSM-5 reactor. The reactor is 101.6 cm long with 5.1 cm inside diameter, with the top thirty-eight cm section acting as a preheater. The maximum catalyst bed height is fifty-eight cm (capacity - 1,100 cm³). An automated traversing thermocouple probe inserted into the thermowell at the center of the reactor records the fixed-bed temperature along the reactor.

The liquid level and gas holdup in the slurry F-T reactor are important process variables. Considerable effort was spent to evaluate methods for such measurements, i.e.:

- Axial pressure-drop measurement using pneumatic differential-pressure (DP) cells.
- Axial pressure-drop measurement using piezo-resistive pressure transducers.
- Liquid level height measurement using a floating radioactive-source.

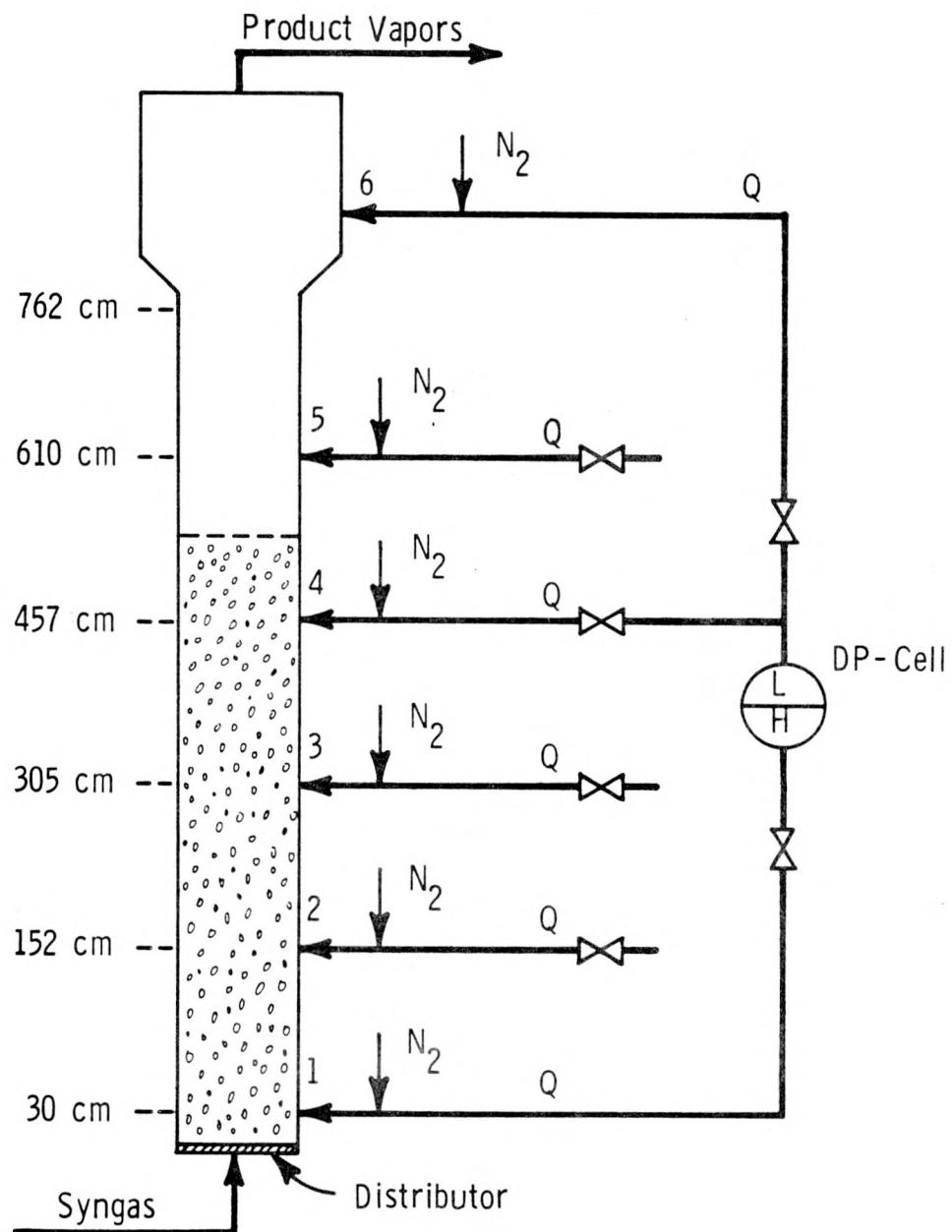
The decision was made to use the first method after thorough discussions with instrumentation experts and consultants. This method has the advantages of simplicity in both use and maintenance. The method of pressure-drop measurement using Peizo-resistive pressure transducers was ruled out because of difficulties with water-cooling to maintain the transducers at temperatures below a damaging 232°C. The method of measuring the liquid level height using a floating radioactive source in the bubble-column has been eliminated because the use of radioactive materials is cumbersome and does not give any indication of the axial profile of the gas holdup.

Figure 2 shows the schematic arrangement of a DP-cell with six N₂-purge lines along the reactor height to measure the pressure gradient. The pressure-drop between any two DP-cell lines, which gives the reactor pressure-drop between these two locations, can be measured by connecting these lines to a differential-pressure cell (DP-cell). In the figure, lines 1 and 6 are shown connected to the DP cell. Also shown is a pathway to connect lines 1 and 4 to the DP cell.

A continuous N₂-purging through the lines is necessary to keep them free of any slurry from the reactor which may plug them. Based on a laboratory experiment using hexadecane in a glass bubble-column, a purge rate of 12 cm³/min (at actual

FIGURE 2

SCHEMATIC ARRANGEMENT OF DP-CELL FOR LIQUID LEVEL MEASUREMENT



Q: DP-Cell Lines

temperature and pressure) is sufficient. To be safe, a purge rate of 30 cm³/min (actual) was used. The total N₂ purge rate was less than 4% of the flow rate of synthesis gas entering the reactor; thus, performance was not significantly affected.

Gas holdup is related to the densities of the slurry (ρ_{sl}), the expanded slurry (ρ_{esl}) and the gas (ρ_g) by the following equation:

$$\epsilon_g = (\rho_{sl} - \rho_{esl}) / (\rho_{sl} - \rho_g) \quad (1)$$

ρ_g and ρ_{sl} can be easily calculated. ρ_{esl} can be estimated from the measured pressure-drop between any two locations within the expanded slurry. For example, if the slurry level is between 457 and 610 cm levels, the pressure drop between Locations 1 and 4 can be used to estimate the average ρ_{esl} between these two locations. In general, between Locations 1 and N:

$$\rho_{esl} = 70.38 (P_N - P_1) / (z_N - z_1) \quad (2)$$

where 70.38 is the factor for converting pressure (psi) into a hydraulic head (cm of water), P_i is the pressure at location i (psi), z_i is the height of the reactor column at location i (cm), and ρ_{esl} is the average density of the expanded slurry (g/mL). An equation similar to Equation (2) can be used to calculate the average expanded slurry density between any two adjacent locations. An axial profile of the gas holdup can then be established. If the axial variation of the gas holdup is small, the density calculated from Equation (2) can be used for the whole slurry column; otherwise, the axial variation of the bed density must be taken into account. Using the same example, the liquid level in the slurry bubble-column can be calculated using the following equation:

$$z = z_4 + (z_4 - z_1) (P_6 - P_4) / (P_4 - P_1) \quad (3)$$

if the axial variation of the gas holdup is nil. With appreciable axial variation of the gas holdup, the axial profile can be taken into account to obtain a more accurate estimate of the liquid level.

Based on the information supplied by the DP-cell vendor, the absolute error of pressure drop measurements is 0.3 kPa (0.05 psi) for range of 69 kPa (10 psi). This translates to a maximum error of 3% for the average gas holdup calculation when the liquid level is above 305 cm and a maximum error of 6% in the liquid level estimate.

V. Construction, Shakedown, and Modification of Two-Stage Bench-Scale Pilot Plant

A. Unit Construction

The fabrication of the BSU components was started in March 1981. The on-site construction began in July 1981 with the erection of the steel structure to house the slurry F-T reactor. A total of 106 vessels, 607 valves, 19 pneumatic control valves, 25 pressure gauges, and 123 thermocouples were used in the BSU. The BSU construction was completed in December 1981 and was ready for shakedown. A preliminary pressure test was also carried out as part of the construction.

Two elevation-views of the 13 m high slurry reactor steel-structure can be seen in Figure A-8. The elevation "A-A" gives the view from the north; while the elevation "B-B" gives the view from the west. The slurry F-T reactor is the tall center piece in two elevation views shown in this figure. The gas-feed pre-heater (E-32) can be seen on the floor next to the slurry-reactor. The slurry-tank (E-48) and slurry transfer vessel (E-49) are placed on the first floor. The inter reactor sampling-loop components, hot (E-93), and cold (E-94) condensers, sample pots (E-87,88) and gas-meter (E-76) are mounted on the first-floor (see elevation "B-B"). Two fixed bed reactors (E-36, 37) are mounted on the outside of the first floor. The three Unistrut-frames for the sections 1,3,4 are located on the north side of the slurry-reactor structure below the fixed bed reactors (see elevation "A-A").

A photograph of the completed unit is shown in Figure 3. Figure 4 shows the completed fixed bed reactors. The top-view of the three sections can also be seen. A ground level view of the same three sections is shown in Figure 5. Some major vessels, piping, and valving are clearly shown in the figure.

All instruments have been mounted on the control panel seen in the left-bottom corner of Figure 3. On the left section of the control panel, nine Liquid-Indicator-Controllers (LICs), five Flow-Indicator-Controllers (FICs), and three Pressure-Indicator-Controllers (PICs) are located. The twenty-three Temperature-Indicator-Controllers (TICs) with eight Adiabatic-Temperature-Controllers (ATCs) are mounted on the middle and right sections of the panel. The two digital temperature indicators can display temperatures at eighty-four different locations around the unit. The important temperatures, such as those of the reactors and condensers, are recorded by the computer for permanent storage.

Any alarm condition at the unit, such as high temperature, high pressure, or gas leaks, sets off an alarm siren at the control panel and necessary actions are automatically taken. For example, in the case of excessive temperature rise in the slurry reactor, the heater for the circulating oil would be

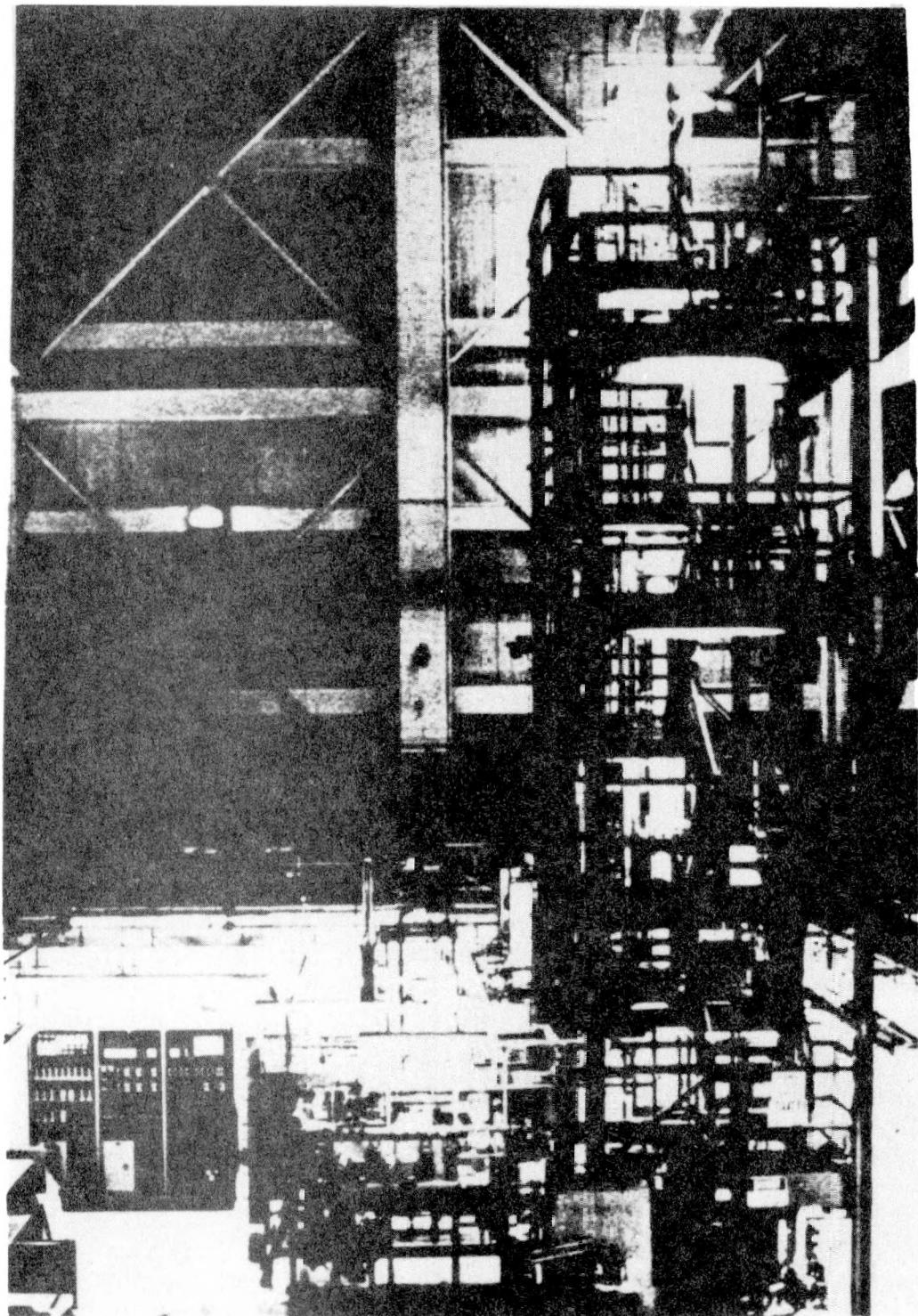


FIGURE 3

A North-west View of the Pilot Plant

- Control Panel (Left Bottom)
- Slurry Reactor "With White Insulation" (Right)
- Other Three Sections (Middle Bottom)

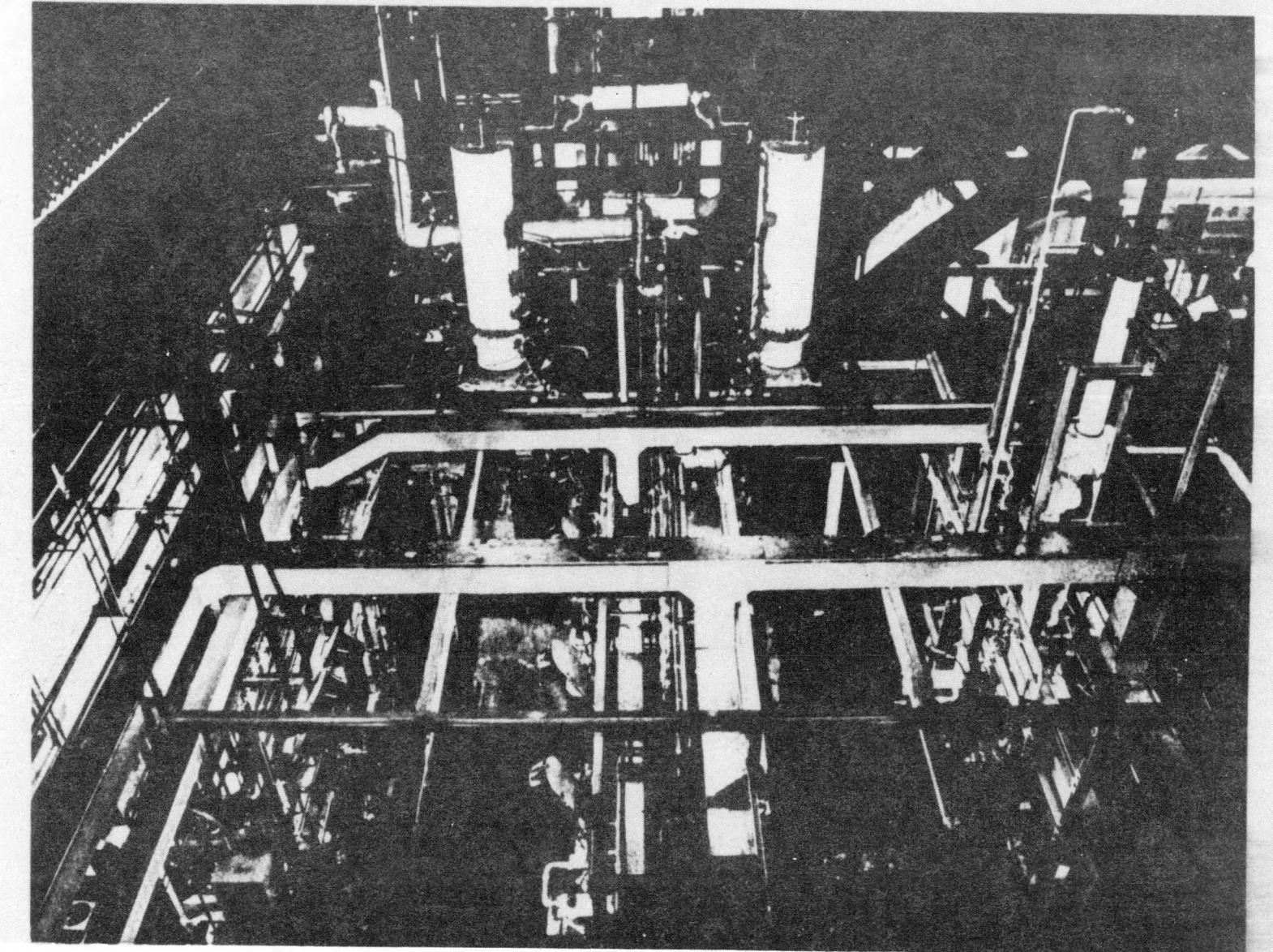


FIGURE 4

**A View of Two Fixed-Bed Reactors (Top) and
Three Sections — 1, 3, and 4 (Bottom Half)**

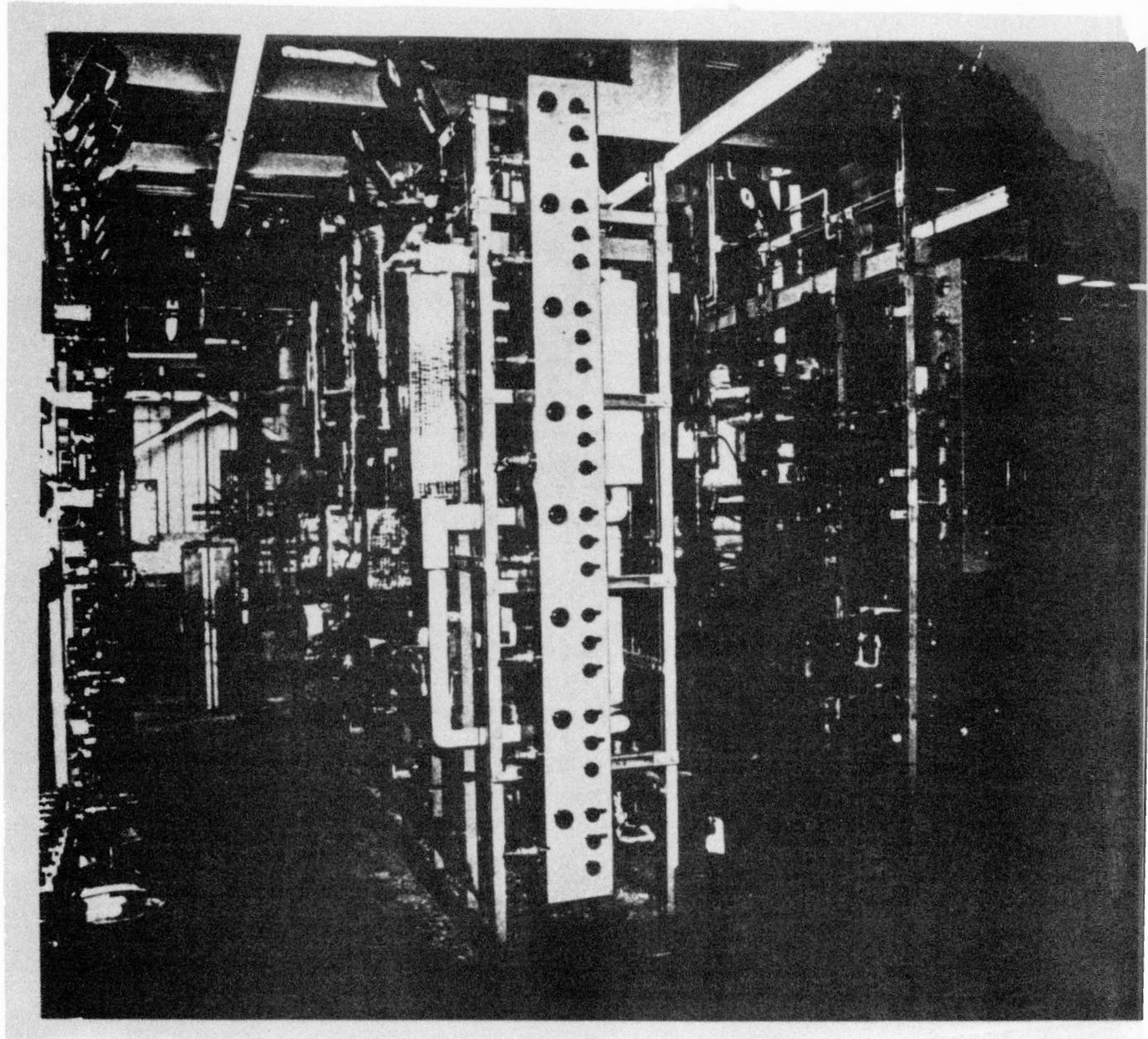


FIGURE 5

A View of Gas-Feed Section at Left,
Product Recovery Section in the Middle, and
Distillation Section at Right

turned off and the cooling water turned on. Similarly, when a H₂ or CO gas leak is detected, the alarm circuit would shut off the gas feed as well as the power to the unit.

B. Shakedown Operation

The construction of the BSU was completed on schedule and the shakedown operation was initiated in late December, 1981. The shakedown of all essential portions was completed in two months. The break-in operation of the portions of the unit that were not essential to the start-up of the reactors, such as the liquid hydrocarbon distillation section and the regeneration loop of the ZSM-5 reactors, was carried out during normal operation.

Basically, the shakedown operation included:

- Checking of all pipings and valves.
- Calibration of equipment.
- Training of operators.
- Testing of equipment.

All shakedown tasks were carried out smoothly as planned. In the following sections, the description of tasks conducted for the Gas Feed Section, the First- and Second-Stage Reactors and Product Recovery Sections, and a final BSU pressure testing, are given separately in detail.

An in-house H₂ supply was used for the BSU operation. Using a conventional gas chromatographic analysis, its purity was estimated to be 99.89 mol % with N₂ as the only impurity. The CO supply was delivered in a cylinder-trailer holding approximately 940 Nm₃ (35,000 SCF) at 13.9 MPa (2,000 psig). Its composition was analyzed using a conventional GC to be:

CO	98.12 mol %
H ₂	0.34
N ₂	1.17
CH ₄	0.37
	100.00

The in-house N₂ was also used for the BSU operation. Its purity was higher than 99.99 mol %. The compositions of these gas supplies were checked occasionally to insure their purity. Analysis of the gas composition of each new CO shipment was also mandatory.

The specific tasks that were conducted for the shakedown operation of the first- and second-stage reactors and the product recovery sections are listed below.

- Cleaned and flushed the slurry reactor, slurry loading tanks, wax-withdrawal lines and receivers, slurry sample receivers, and all associated lines with n-hexane.
- Cleaned and pressure-tested the inter-stage sampling loop with N₂.
- Flushed the fixed-bed reactors, the condensers and the separators with n-hexane.
- Pressure-tested section by section the slurry reactor and associated vessels, the two second stage fixed-bed reactors, and the product recovery section with 2.86 MPa H₂ at ambient temperature; repaired all leaks.
- Checked all steam tracings for proper operation.
- Tested the slurry-loading tanks by loading n-hexane into the cold reactor.
- Tested all temperature indicators, recorders, and controllers.
- Successfully tested the ability of the "Chromalox" oil circulation system (using Mobiltherm-600) to heat the slurry reactor up to 316°C. Also checked the "Cascade" temperature controllers (TIC-2 and -4) for maintaining a constant reactor temperature.
- Pressure-tested the slurry reactor with 2.86 MPa H₂ at 260°C to achieve less than 6.9 kPa/hr (1 psi/hr) pressure loss.
- Pressure-tested the two fixed-bed reactors with 2.86 MPa H₂ at 371°C.
- Pressure-tested condensers and separators at operating temperatures.
- Pressure-tested and ran the regeneration-recycle compressor of the second-stage reactor with N₂.
- Calibrated all level indicators and controllers.

The heating and cooling medium, Mobiltherm-600, is a high-temperature petroleum oil which is thermally stable up to 316°C. However, slight deterioration is expected at a temperature higher than 232°C due to oxidation and thermal cracking. Periodic testing of the fluid was planned to insure its proper heat-transfer characteristics. The following physical properties of this oil were obtained from Mobil's Technical Bulletin:

Sp. Gr., 15.5/15.5°C	0.97
Flash Point, °C	177
Pour Point, °C	-18
ASTM Distillation, °C	
10 vol %	338
50 vol %	371
90 vol %	404

After the shakedown operation of each section of the BSU, the whole unit was pressure-tested. The unit back-pressure controller PIC-2 was successfully checked to handle up to 2.86 MPa unit pressure with H₂ flowing through the unit at up to 4.25 Nm³/hr. During this testing, the temperatures of the first- and second-stage reactors were maintained at 260°C and 316°C, respectively. This portion of the shakedown operation was also completed with no major problems.

C. Unit Modifications

During the BSU operation, many modifications to the unit were done to correct problems which arose during the operation, or to improve the operation. Most of the modifications were carried out during unit turnaround after each run and are described below.

During the turnaround after the first run (Run CT-256-1), the following major modifications were carried out:

1. A new, smaller (1 L) catalyst slurry loading tank was constructed to replace the 19 L loading tank in the original design. The new tank was connected to the slurry reactor at 610 cm above the feed-gas distributor with a 90 cm line. The length of the connecting line was kept short to minimize catalyst loss in the line.
2. The wax withdrawal filter was replaced with a new filter of 10 µm openings. The old filter was found to have a pinhole.
3. A small, 2 µm filter was installed horizontally at 457 cm above the feed-gas distributor for testing.
4. The slurry sampling vessels E-1, 2, 3, and 4 were relocated from the ground level to the sampling points to minimize the catalyst loss and settling in the lines connecting the vessels and the reactor.
5. A new design was adopted for the N₂-purge orifices used for the DP-cell legs of the slurry reactor liquid-level measurement system. This new design had the orifice tip pointed downward instead of horizontally. A downward design may be better in keeping the slurry out of the DP-cell legs.

6. Heating tapes were installed at the originally unheated flanges located at 305, 610, and 762 cm above the feed-gas distributor. Temperature controllers TIC 24, 25, and 26 were assigned for their temperature control.
7. A new thermocouple was installed at 8 cm above the feed-gas distributor to monitor the slurry temperature close to the distributor. Also, the thermocouple at 30 cm location was found not completely inserted into the slurry reactor and was later reinserted properly.
8. The flow rate measurement of feed H₂, CO, total charge and the combined off-gas were automated.

The first two modifications were most essential to permit high catalyst loading that is required to achieve simultaneously high synthesis gas conversion and throughput. Their success was later demonstrated in the high catalyst loading operation of the second BSU run. The third modification was minor. The 2 μ m filter was shown in the later run to be impractical since the wax withdrawal rate was very low.

The fourth modification contributed to less catalyst loss and improvement in obtaining slurry samples. The fifth modification was essential for measuring the slurry level in the slurry reactor. Its operation was not successful during the second run mainly due to operators' inexperience, but it has since proven successful.

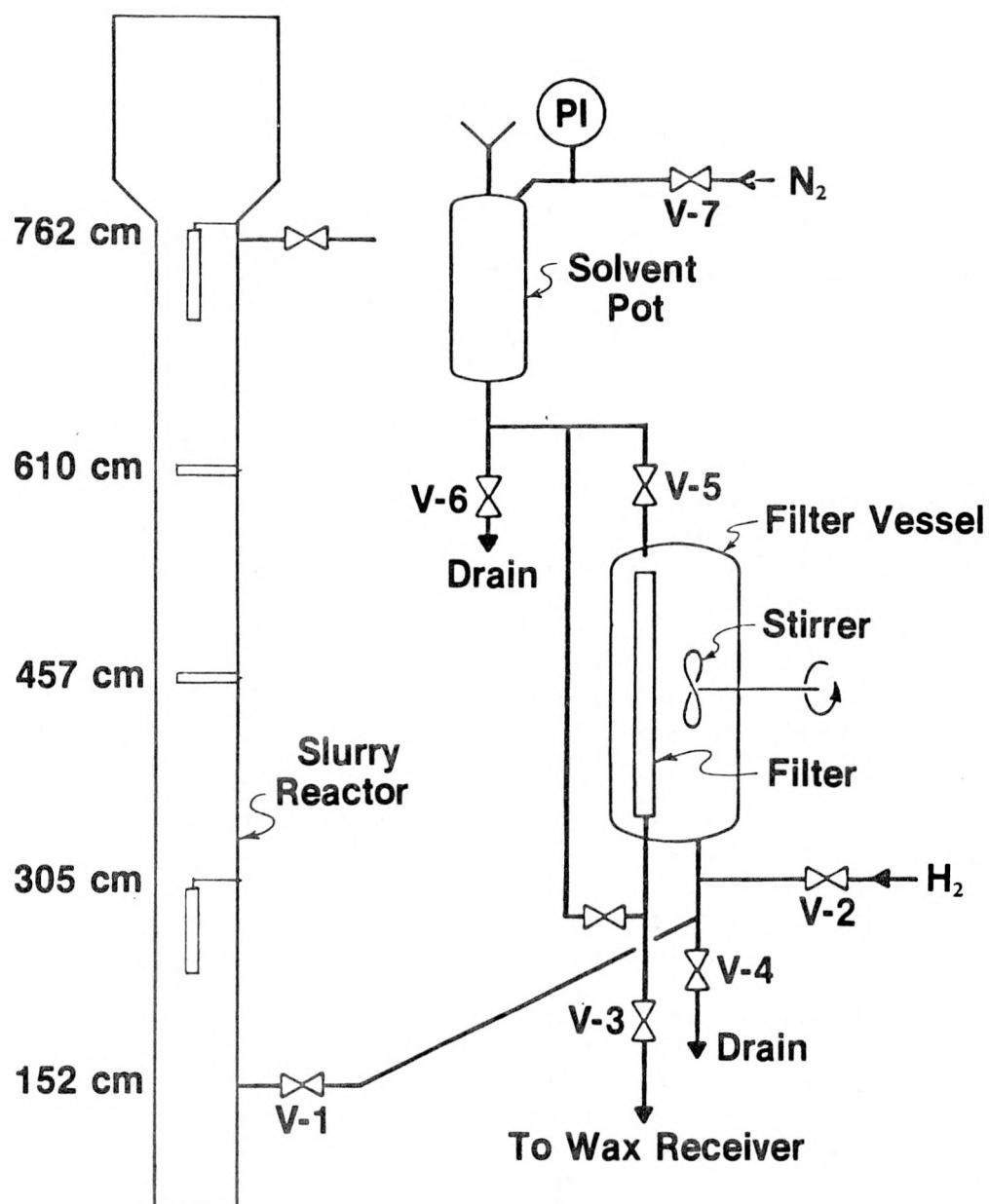
The sixth and seventh modifications were necessary for better temperature monitoring and control, and to achieve uniform reactor temperature without cold spots. The last modification was mainly for the ease of operation.

After the third run, the BSU was shut down for modifications. The major modification was addition of two external filter assemblies to withdraw reactor-wax from the first-stage reactor. The assemblies were installed to withdraw wax from 157 and 762 cm above the distributor.

A schematic of the external filter assembly is shown in Figure 6. The slurry from the reactor is brought into the filter vessel, maintained at 204-260°C, via valve V-1. The catalyst settling in the vessel is prevented by continuous agitation provided by the stirrer. The slurry can be purged with hydrogen to remove dissolved carbon monoxide, carbon dioxide, and water from the slurry. The filtered reactor-wax can be collected in the wax receiver maintained at a certain pressure depending upon the differential pressure desired across the filter. The concentrated slurry deposited in the filter vessel can be frequently flushed back into the reactor by pressuring the filter vessel through the wax receiver. If necessary, the filter vessel and filter surface can be flushed with hot solvent using the solvent pot, and the contents can then be pressurized back into

FIGURE 6

**SCHEMATIC OF THE EXTERNAL
WAX FILTER ASSEMBLY**



the reactor. The size of the filter is 1.59 cm OD x 12 cm long with 10 μm pore size filter element.

A trial operation of the filter assembly was, however, unsuccessful. The reactor-wax withdrawal rate was lower than expected and the filter element plugged after withdrawing about 200 g of reactor-wax. The solvent cleaning of the filter or the filter-blowback did not significantly improve the operation. The filter vessel was then modified to carry out separation of the catalyst from the slurry by catalyst settling and was very successful.

Other minor modifications included:

1. The 10 μm filter element at the 305 cm level of the first-stage reactor was replaced with a new element. The older element was in use for 106 days (Runs CT-256-2 and -3).
2. Another identical filter (10 μm 1.59 cm OD x 30.5 cm long) was installed inside the slurry reactor at the 762 cm level to provide additional wax withdrawal capability.
3. The 2 μm filter (1.25 cm OD x 12.7 cm long), inserted into the slurry reactor from the side tube at the 458 cm level, was replaced with a 5 μm filter to improve the filtration rate.
4. A new 10 μm (110 cm OD 2.7 cm long) was inserted into the slurry reactor from the side tube at the 610 cm level.
5. All gaskets between flanges of the first-stage reactor were replaced with new "Graphoil"⁽¹⁾ (0.3175 cm thick) gaskets. The old gaskets were made of "Bimetallic"⁽¹⁾ material and were found to split and leak during a run.
6. Ten pressure transducers were installed to record unit pressures on the datalogger computer.
7. Additional heating tape was added on the conical part of the disengager bottom and the flange at the 762 cm level of the slurry reactor. Previously only one tape was used for this section. Additional heating of this section should minimize heat loss.

(1)A registered trade mark.

VI. Operation of Two-Stage Bench-Scale Pilot Plant; Experimental Results and Discussions

A. Introduction

The major task of this contract is the development of the two-stage process in the bench-scale pilot plant. The operation began on March 17, 1982, immediately after construction and shakedown of the pilot plant. Five runs, with a total of two hundred twenty days of operation time, were carried out. The operation was smooth and uneventful except for a few occasions of mechanical upset due to leakage at the flanges of the first-stage slurry reactor, and some minor difficulty in separating the F-T reactor-wax from the catalyst slurry. Major accomplishments from the operations are summarized below.

- Evaluated three Fe/Cu/K₂CO₃ F-T catalysts. One of the catalysts (designated as I-B) accumulated an on-stream time of eighty-six days and produced 815 gHC/gFe, substantially higher than figures reported in the literature.
- Evaluated two ZSM-5 catalysts. The catalyst II-B accumulated a total on-stream time of eighty-seven days with two regenerations. No appreciable long-term aging of the catalyst was observed.
- Various process variables were studied with the slurry F-T reactor, including pressure, temperature, feed-gas superficial velocity, feed gas H₂/CO ratio, and addition of a potassium-salt.
- Operation of the second-stage fixed-bed ZSM-5 reactor at constant catalytic severity was demonstrated. A useful criterion for measuring this severity is the molar i-C₄⁼/(C₃⁼+C₄⁼) ratio in the reactor effluent gas. Daily adjustment of the reactor inlet temperature was instituted to maintain a constant severity.
- Successfully demonstrated conversion of the F-T hydrocarbon and oxygenate products in the effluent of a slurry F-T reactor into high octane gasoline by a ZSM-5 catalyst. The maximum gasoline yield of 80-90 wt % (excluding light paraffins in the feed and reactor-wax) was obtained by maintaining the severity index (i-C₄⁼/(C₃⁼+C₄⁼) ratio) between 0.8 and 1.0. The octane numbers of the raw gasoline ranged from 90 to 94 (Research clear).

- Successfully demonstrated a F-T catalyst/reactor-wax separation method using batch external catalyst settling vessels.
- Demonstrated that exposure of F-T catalyst slurry to air reduced its catalytic activity and increased the methane + ethane yield. Also, on two occasions of minor operational upsets, when the synthesis gas flow to the first-stage reactor was replaced by nitrogen for twenty-five to forty-five hours, the subsequent F-T catalyst activity reduced slightly, while the methane + ethane increased slightly.
- Demonstrated that addition of a potassium-salt in the first-stage F-T reactor resulted in rapid reduction of methane + ethane yield. However, its effect on the long-term operation of the reactor is unknown.
- Demonstrated that a methane + ethane yield of less than 5 wt % of the total hydrocarbons produced could be achieved using F-T catalyst I-B at 2.52 MPa (350 psig) and 257°C. However, reactor-wax yields were increased to 46-51 wt %.
- Discovered that a F-T catalyst (designated as I-C) could be activated without using a specific pretreatment step. Methane + ethane yield of less than 3.5 wt % was also demonstrated at reactor conditions of 240-250°C and 1.48 MPa (200 psig). Reactor-wax yields ranged from 57 to 85 wt %.

B. Run CT-256-1

1. Highlights

The first run of the BSU, CT-256-1, using Catalyst I-A (containing Fe/Cu/K₂CO₃) in the first-stage bubble-column reactor and Catalyst II-A (a ZSM-5 class catalyst) in the second-stage fixed-bed reactor was successfully concluded on May 17, 1982. The main objectives of this run were to break in the BSU, and to evaluate the F-T catalyst I-A. The total on-stream time was sixty-one days for Catalyst I-A and forty-nine days for Catalyst II-A. The unit was then shut down for modifications and maintenance in preparation for the second F-T catalyst evaluation. The major events of this run are summarized in Tables 3 and 4. Tables 5 and 6 summarize, respectively, the ranges of the process variables studies and the results from this run.

Major highlights from this run are:

Table 3

Major Events in Run CT-256-1

(Excluding Reactor-Wax and Slurry Inventory)

DOS	Major Events
0	Pretreatment
0.5	Upset: High slurry-level alarm
5-8.1	1st stage: 1.3--2.2 cm/s 260--266°C
12.6	2nd stage: Start-up
13.7-19.0	1st stage: 1.14--1.48 MPa 1.6--1.8 cm/s 266--268°C 2nd stage: 371--329°C
21.3	Upset: Steam and cooling water failure
21.7	Upset: Power failure
26.7	1st stage: 268--271°C
29.8-36.1	2nd stage: 329--302°C
36.2	Upset: Power failure
41.9-47.6	1st stage: 268--274°C 1.8--3.2 cm/s 2nd stage: 292--316°C
48.0-52.8	1st stage: 0.7--1.2--0.7 H ₂ /CO
54.8-58.0	1st stage: 268--282°C 1.3--2.2 cm/s 1.14--1.83 MPa
58.0	Charge H ₂ off. 1.8--1.0 cm/s
58.1	Charge H ₂ back on. 1.0--1.8 cm/s
58.3	Syn-gas off; N ₂ on
58.4	Syn-gas on
60.5-60.8	Hydrodynamic study
61.1	End of Run CT-256-1

Table 4

Major Events in Run CT-256-1
 (Reactor-Wax and Slurry Inventory)

DOS	Major events
-1.3	Slurry loading
-0.6	Slurry unloading: 2,041 g, 6.7% solid
0.1	Slurry sampling : 35 g, from 152 cm, 4.66% solid
1.9/3.0	Wax withdrawal : 291/440 g, 2.54% solid
4.0	Slurry sampling : 42 g, from 152 cm, 2.64% solid
6.8	Wax withdrawal : 1,624 g, 2.6% solid
6.8/18.9	Slurry sampling : 60/64 g, from 152 cm, 2.6/1.78% solid
33.9/34.7	Wax withdrawal : 1,351/626 g, 1.6% solid
34.8	Slurry sampling : 30 g, from 152 cm, 1.69% solid
	Slurry loading : 200 g cat I-A, 11.8 g Mobil base stock F-509, 1,048 g FT-200 wax
40.8	Slurry sampling : 19.2 g, from 152 cm, 1.5% solid
	Wax withdrawal : 1,026 g, 1.59% solid
	Slurry loading : 190 g cat I-A, 119 g Mobil base stock F-509, 1,000 g FT-200 wax, 1,000 g n-decane
41.8/42.7	Slurry sampling : 50/54 g, from 152 cm, 1.9% solid
43.5	Solvent loading : 1,500 g n-decane
43.8	Slurry sampling : 34 g, from 152 cm, 2.64% solid
46.9	Solvent loading : 1,500 g n-decane
47.8/55.7	Slurry sampling : 118/245 g, from 30/152 cm, 3.85/2.62% solid
	Wax withdrawal : 1,473 g, 2.54% solid
60.8	Slurry sampling : 265.2/38.7/53.8/135.1 g from 30/152/305/610 cm, 3.04/2.53/2.69/1.91% solid
	Wax withdrawal : 5,093 g, 2.22% solid
61.1	Slurry unloading: 2,660 g, 2.6% solid
	End of Run CT-256-1

Table 5

Ranges of Process Variables Studied
in Run CT-256-1

First-Stage	Range of Process Variables
Temperature, °C	260-282
Pressure, MPa	1.14-1.83
Superficial Feed-Gas Vel., cm/s	1.0-3.2
SV, NL/gFe-hr	5-18
Feed H ₂ /CO Molar Ratio	0.6-1.2
Second-Stage	
Inlet Temperature, °C	288-371
GHSV (STP), l/hr	716-2600

Table 6

Ranges of Operation Results

(Run CT-256-1)

First-Stage

Range of Results

H ₂ +CO Conv., Mol %	26-91
Methane + Ethane Yield, Wt % HC	6-20
Reactor-Wax Yield, Wt % HC	5-33

Second-Stage Hydrocarbon Yield, Wt %

	Before Alkylation	After Alkylation
C ₁ +C ₂	10-14	10-14
C ₃ -C ₄	29-44	19-40
C ₅ -C ₁₁	36-51	39-62
C ₁₂ + (excl. reactor-wax)	1-4	1-4

Properties of Raw Liquid Hydrocarbons⁽¹⁾

Aromatics, Wt %	17-81
Acid No., mgKOH/gHC	0.09-1.8
Octane No., R+0	90-98
R+3	96-101
M+0	79-85
M+3	85-93

(1) Collected in ambient and chilled condensers.

- A smooth operation of the BSU was demonstrated. Process conditions were varied over a wide range to explore the operational limit of the unit.
- An evaluation of a Fe/Cu/K₂CO₃ F-T catalyst (I-A) was completed. The results were used to compare this catalyst against other F-T catalysts which were evaluated later.
- The conversion of the F-T products into high octane gasoline over ZSM-5 catalyst was demonstrated.
- A significant reactor-wax accumulation in the F-T slurry reactor was observed. This accumulation is expected to increase greatly with decreasing methane and ethane yield.

Detailed operational data of this run are given in the next subsection.

In this first run, the catalyst loading in the slurry reactor was not sufficiently high to obtain both a high synthesis gas throughput (higher than 3 cm/s superficial feed gas velocity) and high H₂+CO conversion (higher than 85 mol %). The low catalyst loading resulted from three causes:

1. High gas holdup at the beginning of the run limited the amount of catalyst loaded into the F-T reactor.
2. Large amounts of catalyst were lost during the reactor-wax withdrawal due to a pin-hole in the wax-withdrawal filter.
3. A substantial amount of the F-T catalyst remained in the slurry loading tank and the long line between the loading tank and the reactor.

All these problems were corrected during the subsequent turnaround.

2. First-Stage Fischer-Tropsch Reactor Operation

Before loading the first-stage catalyst I-A, the slurry reactor was heated to 260°C, with N₂ preheated to 260°C at a flow rate of approximately .085 Nm³/hr (superficial gas velocity of 1 cm/s). However, the top of the reactor was maintained at 204°C to minimize wax carryover in the vapor. The second-stage fixed-bed reactor was bypassed and the effluent gas was sent directly to the hot condenser. The gas stream from the hot condenser was diverted to a wax-stripper containing a mineral

spirit to help avoid any plugging downstream from the hot condenser. The distillation section was also bypassed. The hot, cold, and chilled separators were initially filled with the mineral spirit, again to dissolve any heavy hydrocarbons coming over during the early part of the run. During this period, since little or no hydrocarbon products are formed, the vapor coming over from the slurry reactor contains mostly heavy hydrocarbons stripped from the slurry wax. These hydrocarbons may condense out as wax to plug the downstream lines. The preventive design and the cautious operation procedures adopted resulted in a smooth start-up operation of this unit.

The reactor was maintained at 0.17-0.20 MPa (10-15 psig) with flowing N_2 at 0.085 Nm^3/hr . 600 g of FT-200 Vestowax⁽¹⁾ was first loaded into the reactor through a slurry-loading tank followed by 2,775 g of slurry containing 625 g of catalyst, 750 g of Mobil F-509⁽²⁾ and 1,400 g of FT-200 wax. The loading tank and the lines were then rinsed twice with 700 g of FT-200 wax each time. The unit was then pressured to 1.14 MPa (150 psig) with N_2 bubbling at 0.935 Nm^3/hr (2.2 cm/s superficial gas velocity) in the reactor.

The unexpanded slurry level for 4,772 g of slurry (density of uniform slurry = 0.71 g/cm³) was estimated to be 311 cm. The direct observation through the 762 cm viewport indicated that the slurry level reached the lower part of the disengagement zone at 2.2 cm/s superficial gas velocity. The gas holdup at that time was more than 63 vol %, which was five times higher than that reported in the literature at the same superficial gas velocity (Deckwer, et al., 1980). This high gas holdup was probably due to a significant foaming of the FT-200 Vestowax used as the startup reactor wax. It was feared that, at the planned catalyst pretreatment gas velocity of 3.5 cm/s, the slurry level could have overflowed the top of the disengagement zone. Consequently, 2,041 g of slurry were drained from the reactor. Two samples of this slurry were taken and shown to contain 6.6 and 6.8 wt % solid based on solid content analyses. These solid contents were smaller than that of the slurry originally prepared (12.3 wt %). It was suspected that a substantial amount of the catalyst remained in the catalyst loading tanks. This suspicion was confirmed to some degree later. Based on these analyses, the amount of catalyst loaded into the reactor was 319 g instead of 625 g; the amount of the catalyst in the reactor after partial unloading was 182 g.

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

(2) A proprietary high molecular-weight parafinic base stock.

The pretreatment of the F-T catalyst I-A is reported in Figure 7. During the pretreatment, the H_2+CO conversion and the concentration of CO_2 and methane in the product combined gas are monitored very closely to avoid excessive pretreatment. The use of on-line GC analytical equipment is limited to about one analysis per hour; therefore, the exact values of the conversion and the CO_2 and methane concentrations may only be obtained once per hour. However, the total molar contraction of the product-gas stream was continuously monitored, which can be directly translated into the synthesis gas conversion as shown in Figure 7.

The pretreatment was terminated when the H_2+CO conversion reached 65 mol %. At that stage the reactor temperature was reduced to 260°C, the synthesis temperature, while keeping the same space velocity. There was no definitive criterion to judge the end of the pretreatment. Several factors such as the H_2+CO conversion, the rate of change of the conversion, the rate of change of the CO_2 and CO concentrations in the effluent gas, and the total pretreatment time could all be important. In the present case, the decision was made to terminate the pretreatment because the total pretreatment time was long in comparison to prior experience.

After the pretreatment, the material balances for the first-stage operation were obtained on a daily basis. After the second-stage reactor was in operation, the material balance for the first-stage was obtained through the inter-reactor sampling of about 10% of the total first-stage reactor effluent. A prorating factor reflecting the total mass flow of the first-stage reactor effluent was used to convert that material flow into a total material balance.

The material balance data collected in the conventional way are summarized in Table B-1 of Appendix B while those collected using the inter-reactor sampling are summarized in Table B-2. Both tables also show the process conditions for the first-stage operation. The H_2+CO conversion and methane + ethane yield data vs the time-on-stream are depicted in Figure 8. Since the methane and ethane have lower product value than the C_3 hydrocarbons and they are inert over the second-stage ZSM-5 reactor, a low yield on the methane and ethane is essential for obtaining a good process economics for this two-stage process.

The reactor-wax yields reported in Tables B-1, B-2, and B-3 (and also Tables B-7 and B-9) are those of hydrocarbons remaining in the slurry reactor under processing conditions. These values are not very accurate since the accumulated reactor-wax was withdrawn very infrequently and the reactor-wax inventory in the reactor was not monitored. The yields seemed to decrease quickly with time on-stream. The hydrocarbon yields in $gHC/Nm^3 (H_2+CO)$ converted are also reported in these tables. A

FIGURE 7

RUN CT-256-1, PRETREATMENT OF F-T CATALYST I-A
(CATALYST I-A: Ppted. Fe/Cu/ K_2CO_3)

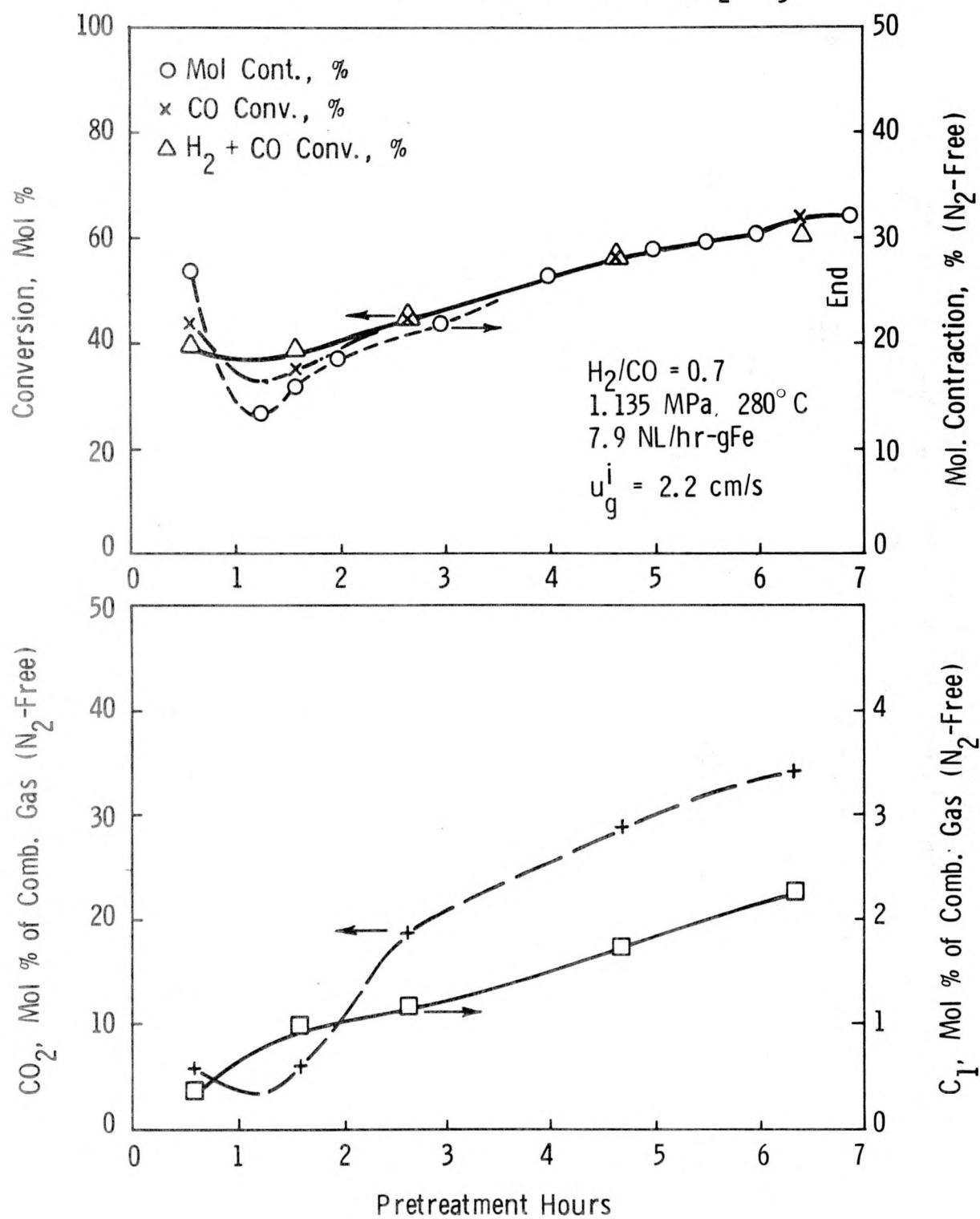
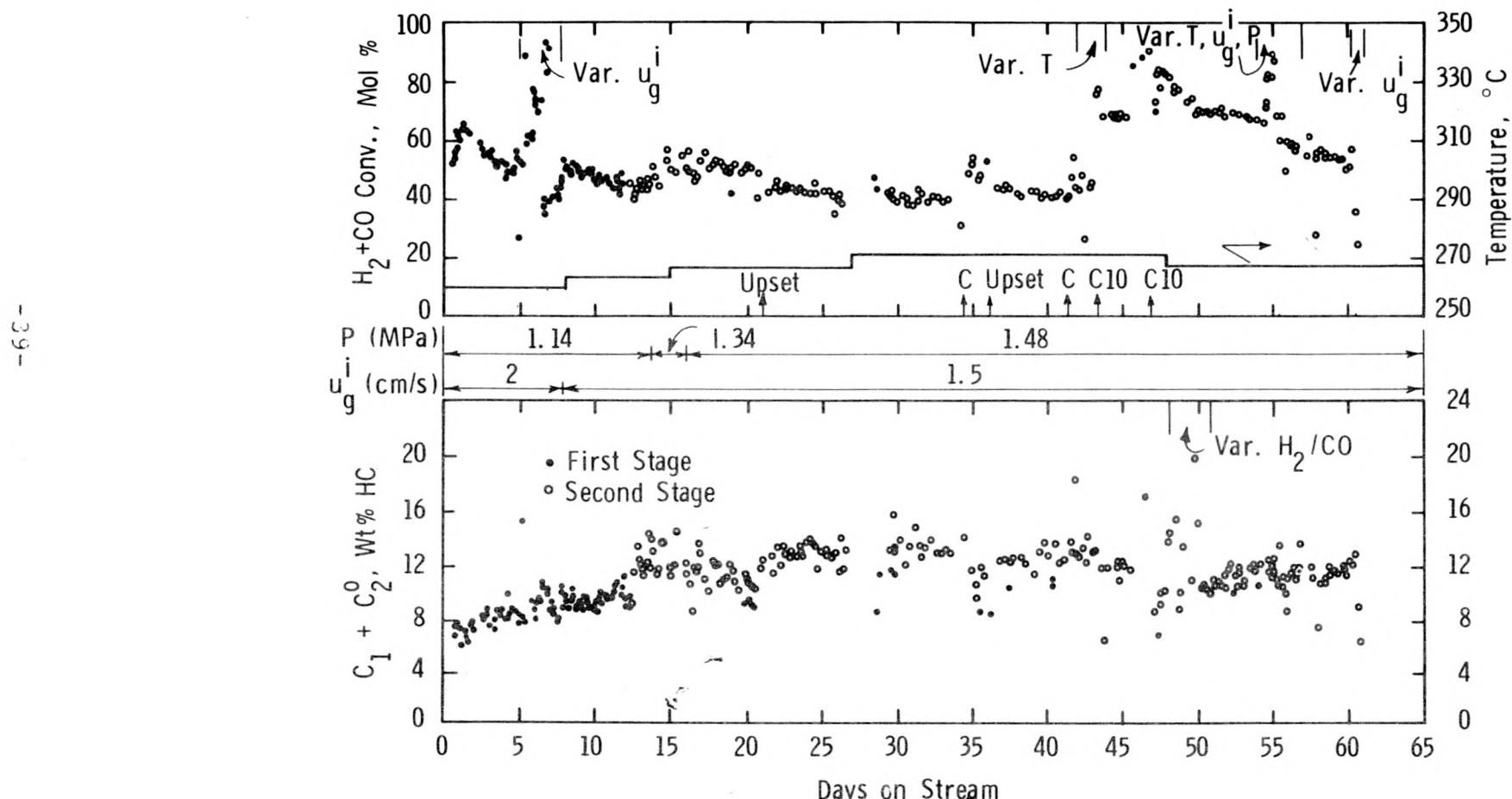


FIGURE 8

SYNTHESIS GAS CONVERSION AND METHANE + ETHANE YIELD
(Run CT-256-1, 1st-Stage Catalyst, I-A: Ppted. Fe/Cu/ K_2CO_3 ;
2nd-Stage Catalyst, II-A: ZSM-5)



theoretical yield may be estimated when the fixed H/C atomic ratio for the total hydrocarbons produced is known. For example, if the H/C ratio for the total hydrocarbons produced is 2.25, then the theoretical hydrocarbon yield is 204 gH₂C/Nm³ (H₂+CO) converted. This theoretical yield value is adopted here as a base line value. Any deviation from this yield indicates the accuracy of the material balances.

To test the operational limit of the pilot plant and to gain experience in unit operations, a wide range of process variables was studied (Table 3). For most of the time, the H₂/CO feed ratio was 0.7. Reactor temperatures of 260-271°C, pressures of 1.14-1.48 MPa and superficial feed gas velocities of 1.5 to 2 cm/s were mostly used.

In the first thirty-five HOS, there was an increase of H₂+CO conversion, probably due to the under-pretreatment of the catalyst. The first reactor-wax withdrawal was carried out at two days TOS. This wax was withdrawn through a 2 μ m-size sintered-plate filter. However, what was observed was a dark-colored slurry, which was later found to contain 2.5 wt% of catalyst. Obviously, the filter was not working properly, and it was later found to have a large hole in its filtering element. After about two DOS, the H₂+CO conversion started to decline gradually. This decline was partially due to catalyst aging, and partially to the loss of some catalyst resulting from two reactor-wax withdrawals and one slurry withdrawal between two and five DOS. Based on solid-content analyses of the three withdrawal samples, about 11% of the catalyst originally in the reactor was withdrawn. Consequently, the space velocity increased to 8.8 at five DOS from the 7.9 NL/gFe-hr used earlier.

After five DOS, variations in the feed gas velocity were studied. At a low space velocity of 4.4 NL/gFe-hr, equivalent to a superficial gas velocity of 1.3 cm/s, the conversion increased to 80%, but seemed to decline rapidly immediately afterwards. The gas velocity was brought back to 2.2 cm/s after twelve hours of operation at 1.3 cm/s gas velocity.

The methane + ethane yield demonstrated a smooth but continuous upward trend with time. It began with about 7 wt % of the total hydrocarbons produced and increased to about 11 wt % before the second-stage ZSM-5 reactor was switched on at 13 DOS.

From fifteen to thirty-five days, the H₂+CO conversion ranged from 42 to 57 mol %. There was only a small decline in the H₂+CO conversion over this period. The methane + ethane yield stayed fairly constant and averaged about 13 wt % of the total hydrocarbons produced during this period. The reactor-wax yield was estimated to be about 6 wt %.

To achieve high H_2+CO conversion at a high synthesis gas throughput, it is essential to obtain high catalyst loading in the slurry reactor. Based on solid-content analysis, the catalyst loading in the bubble-column during the period of fifteen to thirty-five DOS was very low (as low as 1.6 wt %). To increase the catalyst loading, a slurry containing 210 g of fresh catalyst was put into the slurry loading tank and injected into the reactor at thirty-five DOS. An immediate, but small increase in the H_2+CO conversion was observed. However, this increase was erased at thirty-six days when the unit was shut down for fifteen minutes due to a power failure. Another injection of a slurry containing 200 g of fresh catalyst at forty-one DOS showed practically no effect on the H_2+CO conversion. It was speculated that a substantial amount of the catalyst had remained in the slurry loading tank and the line connecting the tank and the slurry reactor. This hypothesis was consistent with the unusually low catalyst loadings measured by the solid-content analysis of the slurry samples withdrawn. Higher H_2+CO conversions (70-90 mol % from 45%) were observed after washing the slurry loading tank with 1,500 g n-decane on two occasions (at forty-three and forty-seven DOS). After the n-decane washing, the solid-content of the slurry sample increased to 3.85 wt %. This problem was corrected during the subsequent turnaround.

Table 7 summarizes the effect of the reactor temperature on the slurry reactor performance. As expected, the H_2+CO conversion went up strongly with the temperature (ranged from 268 to 282°C). However, the methane, ethane, and propane yields changed little over this range of temperature. This is contrary to what was reported by Koelbel and Ralek (1980). An activation energy for the H_2+CO conversion of 135 kJ/gMol was estimated assuming first-order kinetics without accounting for the effect of the mass-transfer resistance on the H_2+CO conversion. This value is substantially larger than values ranging from 81 to 94 kJ/gMol on Fe/Cu catalysts reported by various sources (Schlesinger, et al., 1954; Deckwer, et al., 1980). Note that if the mass-transfer resistance is taken into account, the estimated activation energy would become even larger.

The exit H_2/CO ratio increased greatly with the higher H_2+CO conversion. This trend is expected because the feed H_2/CO ratio of 0.7 is higher than the H_2/CO usage ratio.

The effect of the reactor pressure is summarized in Table 8. The experiments were run with the same superficial feed-gas velocity, and no appreciable change on the H_2+CO conversion was observed. At low pressure operation (1.14 MPa or 150 psig), a moderate increase in the methane and ethane yield was observed. No definitive trend of the exit H_2/CO ratio can be observed.

Table 7

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

(Run CT-256-1)

Temperature, °C	268	271	277	282	268
DOS	54.2	54.8	55.1	55.5	55.7
H ₂ +CO Conv., Mol %	68	72	84	91	69
Methane, Wt %	10	10	10	9	9
Methane + Ethane, Wt %	13	13	13	11	12
Exit H ₂ /CO, Molar	.79	.76	1.0	1.5	.77

(1) 0.7 H₂/CO, 1.48 MPa, 1.8 cm/s superficial feed-gas velocity
(4.9 NL/gFe-hr space velocity).

Table 8

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

(Run CT-256-1)

DOS	56.6	56.8	56.9	57.6
Pressure, MPa	1.48	1.83	1.14	1.48
SV, NL/gFe-hr	5.8	7.2	4.5	5.8
H ₂ +CO Conv., Mol %	59	58	59	56
Methane, Wt %	9	9	11	10
Methane + Ethane, Wt %	12	12	14	12
Exit H ₂ /CO, Molar	.66	.63	.88	.73

(1) 0.7 H₂/CO, 268°C, 1.8 cm/s superficial feed-gas velocity.

Table 9 summarizes the effect of the superficial feed-gas velocity on the slurry F-T reactor performance. The variation on the feed-gas velocity reflected directly on the space velocity. As expected, the H_2+CO conversion went up with decreasing space velocity. No other significant variations on the reactor performance were observed.

The last process variable studied was the feed H_2/CO ratio and the results are reported in Table 10. The effect on the H_2+CO conversion showed no definitive trend. The fact that the H_2+CO conversion at forty-eight DOS was significantly higher than that at fifty DOS further complicated the matter. The difference may be due mainly to the dynamic behavior of the system resulting from the changing H_2/CO ratio. Nevertheless, the effect on the methane and ethane yield could be clearly observed. High H_2/CO feed significantly increased the methane and ethane yield. Furthermore, when the feed H_2/CO ratios are substantially higher than the H_2/CO usage ratio (about 0.6), the exit H_2/CO ratios become very large because there is a large excess of the hydrogen. In the middle and at the end of the feed H_2/CO variable study, the ratio was restored to that at the beginning of the experiment (0.7) to check the state of the catalyst. The H_2+CO conversion changed drastically from 84 mol % to 74% and then to 72%. It is questionable if this change can be attributed to the one-day operation at the 0.6 H_2/CO feed gas.

Analyses of F-T products are very complicated and costly. There are altogether five product phases, i.e., gaseous, light hydrocarbon liquid, heavy hydrocarbon liquid, reactor-wax, and aqueous. The light and heavy hydrocarbon liquid phases were collected from the chilled and ambient condensers, and the hot condenser, respectively, and usually were combined into a single hydrocarbon liquid phase for analysis. The analyses of the gaseous phase posed no problem. The analyses of all other streams to give detailed breakdowns of the hydrocarbons and oxygenates, however, were very time-consuming and only made occasionally. The selectivities of hydrocarbon lumps given in Tables B-1 and B-2 were mainly based on the following analyses and assumptions:

- On-line GC analyses of the gaseous phases.
- "Carbon-number distribution" analyses of the liquid hydrocarbon phases using capillary-column GC technique.
- No analyses of the organic oxygenates in the aqueous and the liquid hydrocarbon phases.

The "Carbon-Number Distribution" analysis does not give PONA or oxygenate component breakdowns, but it does provide quick and consistent carbon-number breakdown for the F-T hydrocarbon

Table 9

**Effect of Superficial Feed-Gas
Velocity on Slurry F-T Reactor Performance⁽¹⁾**

(Run CT-256-1)

DOS	55.8	56.0	56.2	56.3
Superficial Feed-Gas Vel., cm/s	1.8	1.3	2.2	1.8
SV, NL/gFe-hr	5.8	3.9	7.8	5.8
H ₂ +CO Conv., Mol %	61	70	51	61
Methane, Wt %	9	8	9	9
Methane + Ethane, Wt %	12	10	12	12
Exit H ₂ /CO, Molar	.76	.76	.75	.70

(1) 0.7 H₂/CO, 268°C, 1.48 MPa.

Table 10
 Effect of Feed H₂/CO Ratio on
 Slurry F-T Reactor Performance⁽¹⁾
 (Run CT-256-1)

DOS	47.7	48.1	48.8	49.6	49.9	50.4
Feed H ₂ /CO, Molar	.7	1	.6	.7	1.2	.7
H ₂ +CO Conv., Mol %	84	85	79	74	76	72
Methane, Wt %	8	10	7	9	14	9
Methane + Ethane, Wt %	11	14	9	11	20	11
Exit H ₂ /CO, Molar	1.2	6.1	.88	.82	17	.90

(1) 268°C, 1.48 MPa, 1.8 cm/s superficial feed-gas velocity
 (4.9 NL/gFe-hr space velocity).

fraction. This analysis is very useful for monitoring the slurry F-T reactor operation.

In four balances covering DOS from two to five, detailed analyses of the C_{11}^- liquid hydrocarbon fraction and the aqueous phases were done. The C_{11}^- fractions were distilled from the liquid hydrocarbon phases. A Sep-Pak⁽¹⁾ Silica Gel Liquid Chromatography was used for the separation of the hydrocarbons and the oxygenates. Each fraction was then analyzed by gas chromatographs. The results are summarized in Tables B-3 and B-4. Table B-3 also includes those balances in which no liquid phase analyses were carried out. In those cases, only the compositions from the gaseous phase are reported. Since at the startup of this run the separators were filled with a mixture of non-F-T hydrocarbons, it took about five days for the oxygenates in the liquid hydrocarbon phases to reach a steady state, as indicated in Table B-4. The total oxygenates, mostly alcohols, reached about 5 g/100 g of the total hydrocarbon yield. For the same four balances, the aqueous phases were analyzed using a gas chromatograph and their compositions are reported in Table B-5. The yield of the oxygenates in the aqueous phases reached about 1.8 g/100 g of the total hydrocarbon yield in three days. The components were dominated by alcohols (94 wt %, mainly in C_1-C_3 alcohols) with small yields of ketones (5 wt %) and esters (<1 wt %). The method for detailed analysis of the C_{12}^+ fraction of the hydrocarbon liquid phases has been developed, but was not used in this run.

Six reactor-wax samples were analyzed for $C_{13}-C_{74}$ hydrocarbons by a GC and results are given in Table B-6. Although the carbon-number distribution in the reactor-wax was complicated by the two intermittent injections of fresh catalyst slurries at thirty-five and forty-one DOS, some definitive trends of the shifting of the carbon-number distribution during the run can be observed:

- Large reduction of $C_{26}-C_{28}$ (from about 20 wt % to about 10 wt %).
- Large increase of $C_{29}-C_{32}$ (from about 9 wt % to about 19 wt %).
- Moderate reduction of $C_{34}-C_{36}$ (from about 27 wt % to 18-20 wt %).
- Large increase of $C_{44}-C_{63}$ (from about 10 wt % to 18-22 wt %).

(1) A registered trade mark.

It was not possible to determine if the distribution reached an equilibrium at fifty-six DOS. Further investigation will be needed.

Based on a hypothesis of a single parameter of chain-growth probability, the carbon-number distribution of the F-T products may be described by the well-known Schulz-Flory distribution (Flory, 1967) represented by the following equation:

$$\log (M_I/I) = \log (\ln^2 \alpha') + I \log \alpha' \quad (4)$$

A Schulz-Flory type carbon-number distribution plot based on the material balance at fifty-two DOS is given in Figure 9. An α value, representing the chain-growth probability, of 0.70 is estimated from the plot for the hydrocarbons excluding the reactor-wax. The distribution, however, shows large deviation from the Schulz-Flory distribution when the reactor-wax is included. This phenomena may be due to the fact that in a slurry system large molecules can re-absorb onto active catalyst sites, allowing for further chain growth. The approximate reactor-wax yield at fifty-two DOS was estimated to be about 6 wt % of the total hydrocarbon produced.

The operation of this run was voluntarily terminated after sixty-one DOS. After the shutdown, the catalyst slurry was drained from the reactor. Slurry samples were taken for solid-content analysis and an attempt was made to account for the catalyst inventory. The 605 g of the catalyst initially loaded into the slurry loading tank plus the 390 g added during the run gave a total of 995 g added into loading tank. However, the solid analysis of the slurry sample unloaded after the end of the run gave only sixty-nine g of the catalyst. Later rinsing of the slurry loading tank and the slurry reactor gave another 125 g. Analysis of the solid-content of all the slurries withdrawn during the run gave 429 g. Altogether, 372 g of the catalyst could not be accounted for because of the difficulties discussed above.

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

The second-stage reactor, containing a ZSM-5 class catalyst, designated II-A, was smoothly brought on-stream under the following conditions:

Inlet Temperature, °C	371
Reactor Pressure,	Cascaded
GHSV (STP), l/hr	880

The second-stage reactors were designed for an adiabatic operation. The conversion of the F-T products over ZSM-5 is moderately exothermic as shown by the temperature profiles given in Figure 10 for different inlet temperatures. The slight

FIGURE 9
SCHULZ-FLORY DISTRIBUTIONS FOR
FIRST-STAGE F-T PRODUCTS
(Run CT-256-1, 52 DOS)

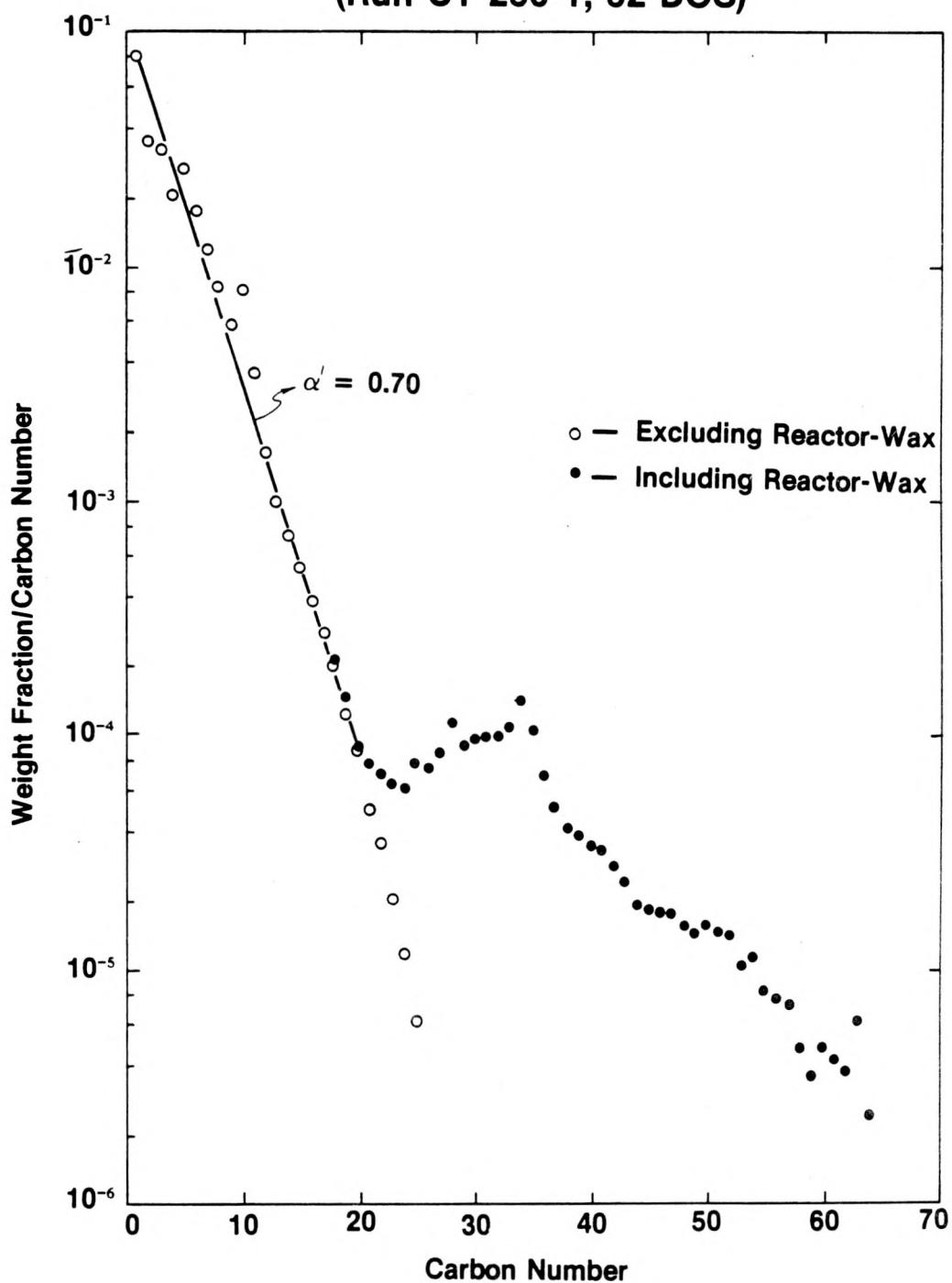
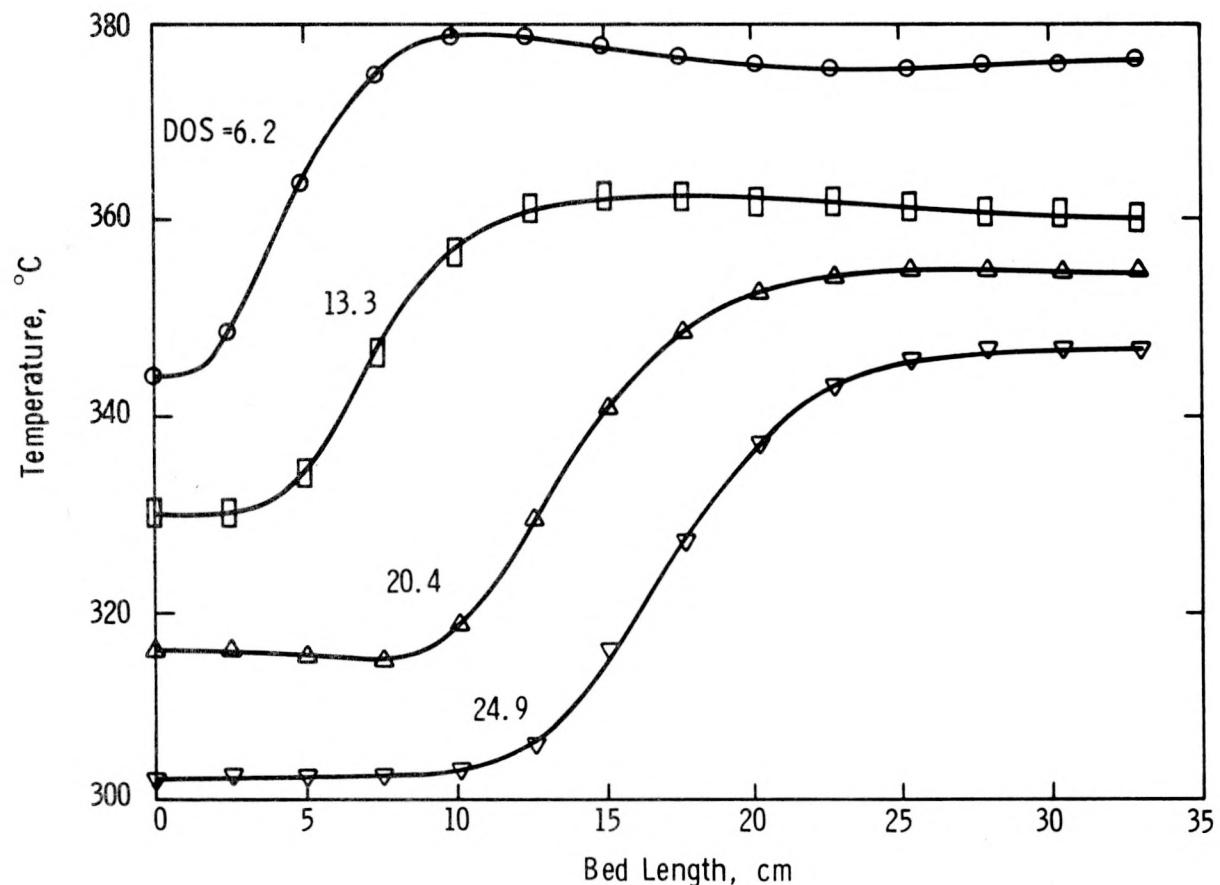


FIGURE 10
SECOND-STAGE FIXED-BED ZSM-5 REACTOR TEMPERATURE PROFILES
(Run CT-256-1)



decline of the temperature near the end of the catalyst bed probably indicated an imperfect adjustment of the zoned heaters in simulating an adiabatic operation.

Material balances were performed almost daily as summarized in Table B-7 of Appendix B. The properties of the raw liquid products collected from the ambient and chilled condensers are summarized in Table B-8, while detailed hydrocarbon compositions are given in Table B-9. Two types of material balance information are included in Table B-7; one obtained without inter-reactor sampling and the other with inter-reactor sampling.

In this trial run, the initial reactor inlet temperature was set arbitrarily at 371°C, which resulted in a very high severity. This high severity reflected in a high conversion of the light olefins, and large formation of propane, butanes and aromatics. This yield trend means a low C₅⁺ and alkylate yields. Therefore, to increase the gasoline yield (including the alkylate), it was imperative to lower the second-stage ZSM-5 catalyst severity. This was achieved by lowering the reactor inlet temperature to 329°C over a six-day period. The inlet temperature was further reduced to 302°C after another seventeen days. However, for a majority of the time, the severity of the second-stage operation was very high. This was mainly caused by the unexpected low gas throughput in the first-stage reactor resulting from the low catalyst loading problem.

One useful criterion to measure the severity of the second-stage operation is the molar i-C₄⁼/(C₃⁼ + C₄⁼) ratio. A high severity operation indicates high conversion of propene and butenes and large formation of i-butanes which gives a high ratio of i-C₄⁼/(C₃⁼ + C₄⁼). In addition, a value of unity of this ratio indicates theoretically the best alkylate yield by the alkylation of the propene and butenes with the i-butanes produced. A ratio of unity, therefore, usually coincides with a high total gasoline yield. From Table B-7, this ratio was above 1.39 at all times and above 3.0 most of the time.

The operability of the second-stage reactor was very satisfactory. However, its severity must be optimized in order to maximize gasoline yield.

The raw gasoline collected in the chilled and ambient condensers contained small amounts of acids based on acid number analyses. Those acids, however, can be removed by simple water washing. In one instance, twenty g of a raw gasoline sample with an acid number of 0.19 mgKOH/g was washed twice with fifty g of distilled water. The acid number was reduced to zero after the washings.

4. Second-Stage ZSM-5 Catalyst Regeneration

The second-stage ZSM-5 catalyst, though only moderately deactivated after forty-nine DOS, was oxidatively regenerated to check out the regeneration facilities of the BSU. These facilities include a regeneration recycle compressor, make-up air compressor and regeneration product GC system.

For safety reasons, the reactor to be regenerated was first physically isolated from the rest of the BSU by disconnecting the piping between them. The reactor was then connected with the regeneration circuit and the whole circuit was purged and pressured by nitrogen to 1.14 MPa. A nitrogen flow rate of 6.1 Nm³/kg catalyst-hr was maintained by the recycle compressor. The reactor was then heated up to 343°C and 0.079 Nm³/hr make-up air was then introduced. The maximum catalyst bed temperature was maintained at or below 485°C by adjusting the reactor inlet temperature and the make-up air flow rate.

The O₂-concentration at the reactor exit was continuously monitored during the course of regeneration using an electrochemical oxygen analyzer. The exit O₂-concentration was maintained at less than 1 mol % by adjusting the make-up air flow rate when the reactor inlet temperature was less than 466°C. At the end of regeneration, the reactor exit O₂-concentration was allowed to increase to 7 mol %. At that time, the axial catalyst bed temperature was practically uniform at about 483°C. The total regeneration took about fourteen hours and the total product water collected during that period was 6.3 g. After regeneration, the activity of ZSM-5 was restored.

C. Run CT-256-2

1. Highlights

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 smoothly started up on June 24, 1982. The major events of this run are summarized in Tables 11 and 12, while the operational results are summarized in Table 13. 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 of 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.

Table 11

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

<u>DOS</u>	<u>Major Events</u>
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
2.3-14.1	1st-Stage: 1.14-1.48 MPa 2nd-Stage: 348-352-346°C
5.2-16.1	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
7.1-17.7	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 12

Major Events in Run CT-256-2

(Reactor-Wax and Slurry Inventory)

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

Table 13
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

Second-Stage Hydrocarbon Yield, Wt %

	<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⁽¹⁾

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.

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	1.4-2.7
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
SV, NL/gFe-hr	1.5-2.9
H ₂ +CO Conversion, mol %	45-86
Methane + Ethane Yield, wt % HC	9-15

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

Temperature Inlet, °C	284-350
GHSV (STP), 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.

2. First-Stage Fischer-Tropsch Reactor Operation

The procedure for loading the catalyst slurry into the first-stage reactor was basically the same as that used for Run CT-256-1 except for the following improvements:

- The startup slurry was prepared using 4,000 g of spent reactor-wax (containing about 0.5 wt % solid), 895 g of FT-200 Vestowax, and 1,375 g I-B catalyst in 791 g Mobil base stock F-509. The initial catalyst loading was 19.5 wt %.
- The slurry was loaded into the reactor through a new 1 L size loading tank, followed by washing with 500 cm³ of n-decane. During washing, a portable stirrer was inserted into the tank to agitate the slurry to ensure a good washing.

The static slurry level, not including the washing n-decane, was estimated to be 427 cm. Reactor slurry samples withdrawn later showed that high catalyst loading was indeed achieved.

During run CT-256-1, the gas holdup in the F-T column in the latter part of the run was substantially lower than that at the beginning of the run. The reactor-wax produced by the F-T reactions might be the major contributor to this lower gas holdup. Since a moderate gas holdup is essential for achieving high catalyst loading in the reactor, spent wax from the first run was used in this run. Right after loading, with a nitrogen flow at 4 cm/s, the expanded slurry level was between the 610 and 762 cm viewports. The gas holdup was estimated to be approximately 35 vol % which is substantially less than the initial gas holdup (63 vol %) observed in the last run.

The pretreatment conditions for the F-T catalyst I-B were:

H_2+CO Flow Rate, Nm^3/hr	1.84
H_2/CO Feed Ratio, molar	0.70
Superficial Feed-Gas Vel., cm/s	4.0
SV, NL/gFe-hr	2.0
Temperature, $^{\circ}C$	280
Pressure, MPa	1.14

These conditions were similar to those used in the last run except for the low space velocity, which resulted directly from the high catalyst loading achieved in this run.

The course of pretreatment was carefully monitored by measuring the product gas volume contraction, H_2 and CO conversion, and CO_2 and methane concentration in the product gas. All these quantities increased with time-on-stream as shown in Figure 11. The pretreatment was terminated after eleven hours when CO conversion reached 82 mol %.

Figure 12 depicts the H_2+CO conversion and methane and ethane yield versus time on-stream. The material balances were performed daily and results are summarized in Table C-1 of Appendix C. Table C-2 gives the detailed hydrocarbon product compositions.

The synthesis operation was commenced at $260^{\circ}C$, 1.14 MPa (150 psig) and 3.2 cm/s. The initial H_2+CO conversion was 45 mol % and gradually increased to about 73 mol % after about one DOS. This increase in conversion was attributed to continual activation of the F-T catalyst. To take advantage of this continual increase of the catalyst activity, 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 DOS.

FIGURE 11

RUN CT-256-2 FISCHER-TROPSCH CATALYST PRETREATMENT
(CATALYST I-B)

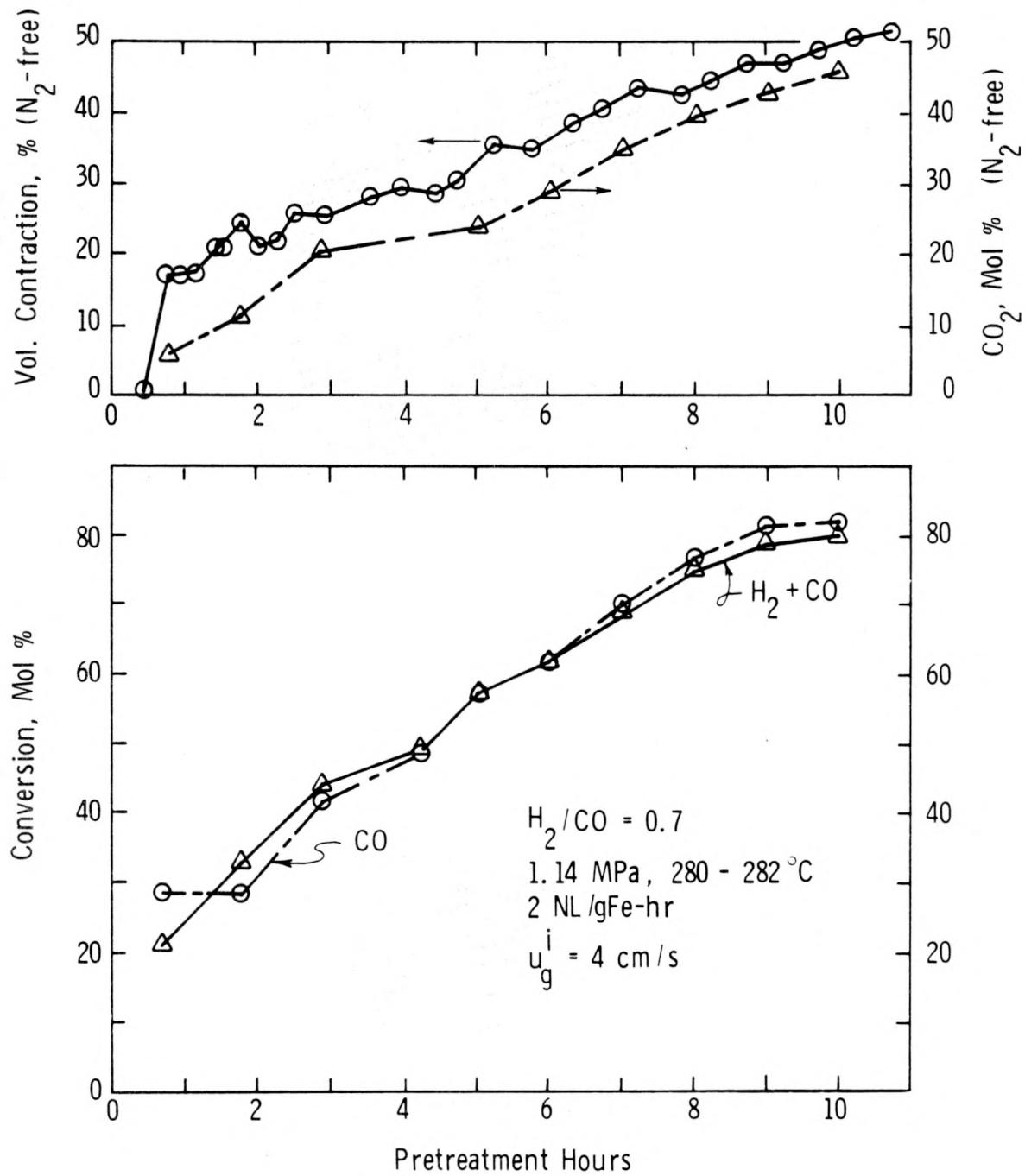
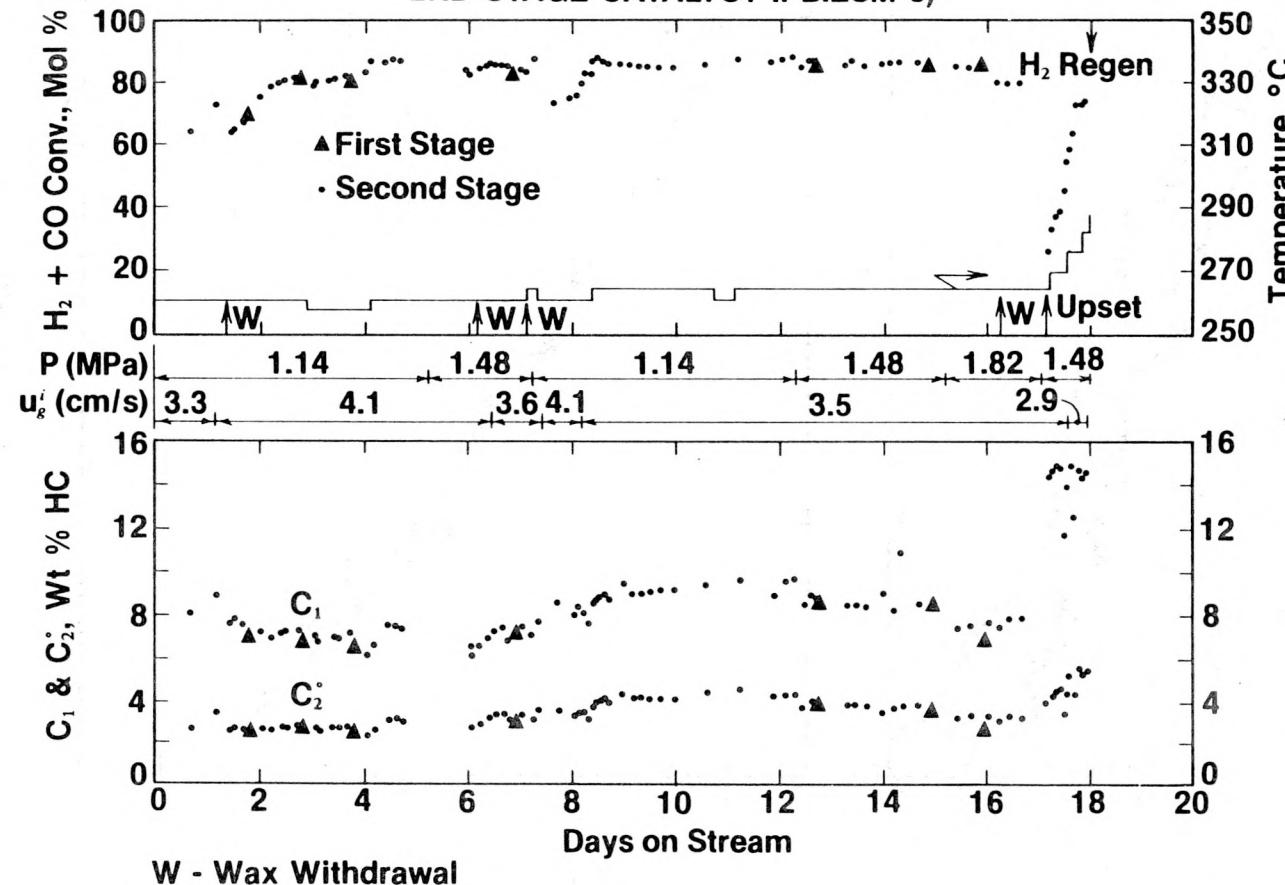


FIGURE 12

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)



From five to seven DOS, 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 accumulated in the slurry reactor. Three reactor-wax withdrawals through the filter located at the 305 cm level gave a total of 3,225 g reactor-wax to maintain a 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 DOS. The H_2+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 DOS, the feed-gas superficial velocity was lowered to 3.4 cm/s. The H_2+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 variation required to reach the same H_2+CO conversion as 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, a stable catalyst activity was observed during the next seven days.

From twelve to fifteen DOS, 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 H_2+CO conversion was very stable at 86 mol % for a seven-day period (eight to fifteen DOS) with slurry reactor conditions at 1.14-1.48 MPa, 262°C and 3.4 cm/s.

To further increase the synthesis gas throughput, the slurry reactor pressure was increased at fifteen DOS 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 H_2+CO conversion decreased slightly to about 85 mol %. Table 14 summarizes the effect of reactor pressure on the slurry reactor performance. The major effect is the decreasing methane + ethane yield with increasing pressure.

Table 14

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

(Run CT-256-2)

DOS	12.1	14.2	15.5
Pressure, MPa	1.14	1.48	1.82
SV, 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 %	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

At sixteen DOS, 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 g. Following the wax withdrawal, the H_2+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 DOS, 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 13 is a photograph of the feed-gas distributor and bottom-flange gasket removed from the slurry reactor after the upset.

It is speculated 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 the distributor.

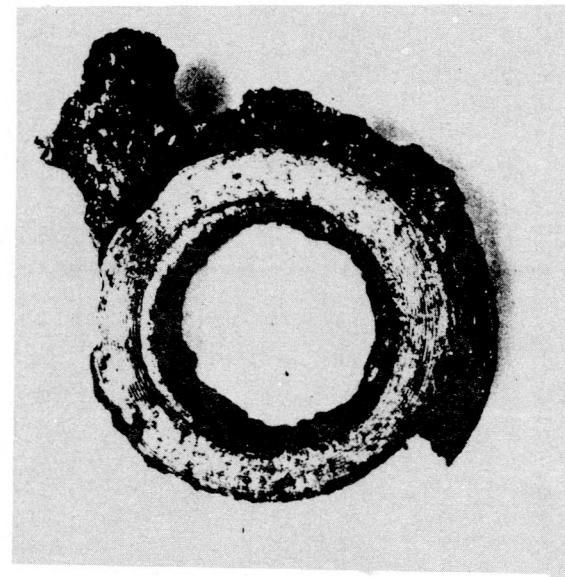
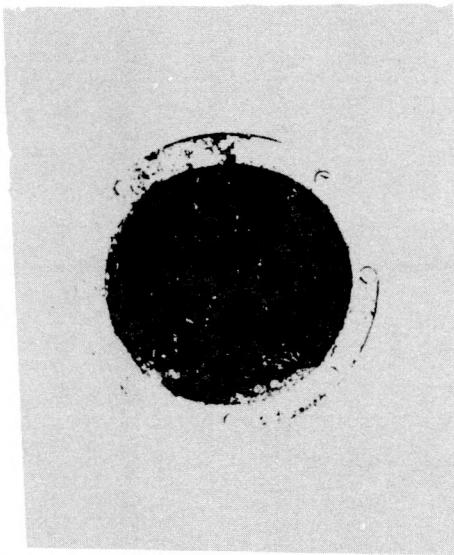
After a downtime of ten days, the slurry was reloaded and the slurry reactor restarted at 263°C, 1.48 MPa and 3.4 cm/s. The H_2+CO conversion was only 25 mol % and the methane + ethane yield was as high as 18 wt % of total hydrocarbons produced. The catalyst was obviously damaged during the operational upset. This damage could be attributed to several factors during the upset:

- Coking of the F-T catalyst 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 CO_2 and H_2O 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 H_2+CO conversion was only 75 mol % with a methane + ethane yield of about 21 wt %.

FIGURE 13

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



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

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

A second-stage reactor, containing 215 g of II-B ZSM-5 catalyst, was brought into operation two hours after the beginning of the synthesis operation. The material balances for the run are summarized in Table C-3 of Appendix C. Table C-4 gives the detailed product hydrocarbon compositions.

Also, catalytic severity of the second-stage operation was guided by the $i\text{-C}_4/(C_3^= + C_4^=)$ 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 5.3°C per day to compensate for the second-stage catalyst aging. This temperature policy was found to be adequate for the run.

Figure 14 shows the effect of second-stage operating severity, expressed as the $i\text{-C}_4/(C_3^= + C_4^=)$ molar ratio in the product, on the gasoline yield. On this plot, the alkylate yield is estimated by alkylating first the $C_4^=$ and then $C_3^=$ 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 C_4^- 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 $i\text{-C}_4/(C_3^= + C_4^=)$ molar ratio of 0.6 to 1.2. The corresponding raw liquid hydrocarbon R+O octanes were 89 to 92.

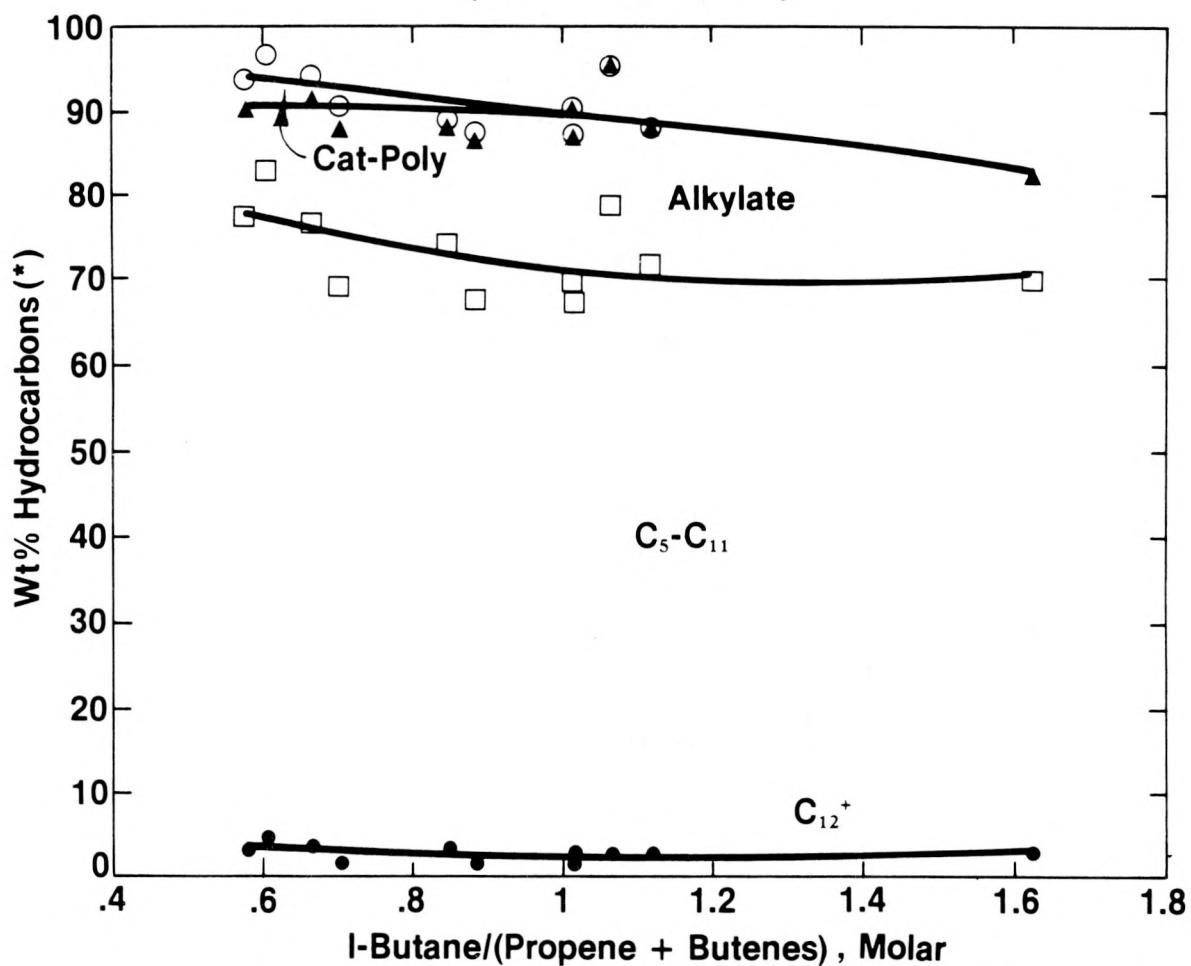
D. Run CT-256-3

1. Highlights

The third BSU run, designated as Run CT-256-3, using Catalyst I-B (containing $\text{Fe}/\text{Cu}/\text{K}_2\text{CO}_3$) in the first-stage bubble-column F-T reactor and Catalyst II-B (a ZSM-5 class catalyst) in the second-stage fixed-bed reactor, was smoothly started up on July 27, 1982. The major objectives were to evaluate the performance of the F-T catalyst I-B over an extended period of time and then to perform process variable studies. The major events and operational results of this run are summarized in Tables 15 and 16, respectively.

FIGURE 14

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



*Excluding C₄ Paraffins in Feed and Reactor-wax

Table 15

Major Events in Run CT-256-3

(Excluding Reactor-Wax and Slurry Inventory)

<u>DOS</u>	<u>Major Events</u>
-0.4-0.0	Pretreatment: 1st-Stage: 282°C; 1.14 MPa; 4.2 cm/s.
0.0-8.0	Syntheses started: 1st-Stage: 282-260°C, 1.48 MPa; 4.2-3.7 cm/s.
8.0-16.0	2nd-Stage on: 329-385°C.
16.3-17.9	2nd-Stage regeneration Upset: Unit under nitrogen nine hrs.
18.0-29.4	1st-Stage: 260-261°C; 3.7-3.5 cm/s. 2nd-Stage: 343-304-346°C.
29.7	Upset: Leak at 305 cm level flange; unit under nitrogen purge 36.5 hrs.
29.7-45.9	1st-Stage: 3.45-3.0 cm/s. 2nd-Stage: 346-466°C.
46.5-47.8	2nd-Stage regeneration
50.0-59.7	1st-Stage: 261-266°C. 2nd-Stage: 304-318°C.
59.8-60.8	1.48-2.17 MPa Upset: Leak at 0 cm level flange. Slurry unloaded, then reloaded after fifty hrs.
60.9-67.9	1st-Stage: 267°C; 1.48 MPa; 3.1-2.5 cm/s. H ₂ /CO in feed: 0.7-0.6 2nd-Stage: 323-349°C.
67.9-80.0	1st-Stage: 1.48-2.5 MPa: 2.5-3.7-1.0-2.8-2.5 cm/s. 2nd-Stage: 349-408°C.
80.8	Addition of a potassium-salt.
81.3-85.9	Hydrodynamic upset 1st-Stage: 2.51-1.48-2.51 MPa. 2nd-Stage: 408 → 426°C.
86.0	End of Run CT-256-3

Table 16
Ranges of Operation Results (Run CT-256-3)

<u>First Stage</u>	<u>Range of Results</u>
H ₂ +CO Conv., Mol %	54-93
Methane + Ethane Yield, Wt % HC	6-18
Reactor-Wax Yield, Wt % HC	3-13

Second-Stage Hydrocarbon Yield, Wt %

	<u>Before Alkylation</u>	<u>After Alkylation</u>
C ₁ +C ₂	9-20	9-20
C ₃ -C ₄	14-38	12-28
C ₅ -C ₁₁	32-55	46-68
C ₁₂ + (excl. reactor-wax)	1-9	1-9

Properties of Raw Liquid Hydrocarbons⁽¹⁾

Aromatics, Wt %	12-41
Acid No., mgKOH/gHC (unwashed)	0.04-0.4
Octane No., R+0	82-94
M+0	74-84

⁽¹⁾ Collected in ambient and chilled condensers.

Major highlights of this run were:

- Smooth operation of the slurry F-T reactor with high catalyst loading (20.7 wt % initially), high synthesis gas throughput, and high conversion was demonstrated over a period of eighty-six days.

The ranges of the first-stage slurry F-T reactor operating conditions and performance were:

H ₂ +CO Flow Rate, Nm ³ /hr	1.0-2.6
Temperature, °C	259-267
Pressure, MPa	1.13-2.51
H ₂ /CO Feed Molar Ratio	0.6-1.0
Superficial Feed-Gas Velocity, cm/s	1.2-4.4
SV, NL/gFe-hr	1.3-3.4
Catalyst Loading, wt % (nominal)	11-21
H ₂ +CO Conversion, mol %	54-93
Methane + Ethane Yield, wt % HC	6-18
Hydrocarbon Production, gHC/gFe	815

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

Temperature, Inlet, °C	288-466
GHSV (STP), l/hr	1,350-4,580

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

- There were two small and one large interruptions in the Fischer-Tropsch synthesis operation. A slight loss in Fischer-Tropsch catalyst activity and a slight increase in methane yield were observed during the small interruptions. The major interruption took place at sixty-one DOS due to a leak at the bottom flange of the slurry reactor. The slurry was unloaded and reloaded into the reactor after a new gasket was installed. Substantial deterioration of the catalyst activity and substantial increase in the methane + ethane yield were observed. The F-T catalyst seems to be very sensitive to exposure to the air.
- The reactor-wax yield increased significantly with decreasing methane + ethane yield.
- A H₂/CO feed ratio of 0.6 (instead of 0.7) was used for twenty-six days with no significant effect on the F-T catalyst stability. Lower methane + ethane yield was observed during this time. The H₂/CO usage ratio is very close to 0.6 as indicated by the fact the exit

H_2/CO ratio remained at nearly 0.6 over a wide range of conversion. The usage of the synthesis gas is better at 0.6 feed-gas H_2/CO ratio.

- Higher operating pressure with constant superficial feed-gas velocity in the slurry F-T reactor resulted in a slightly lower H_2+CO conversion, but a significantly lower methane + ethane yield (from 11 wt % to 9% when pressure increased from 1.48 MPa to 2.51 MPa). The oxygenate yield also increased significantly over the same pressure range.
- Addition of a potassium-salt to the slurry reactor drastically decreased the methane + ethane yield from 13 wt % to 8%. Unfortunately, no conclusions on synthesis gas conversion and catalyst stability could be drawn.
- The gas holdup data in the slurry bubble-column were estimated using a system of DP-cell legs. There was no significant change of gas holdup profiles in the first seventy-five DOS. Catalyst concentration profiles along the bubble-column were also measured and found to follow profiles predicted by a published mathematical model on slurry settling.
- A "hydrodynamic upset" of the slurry reactor occurred at eighty-two DOS, probably due to catalyst settling, resulting in a low H_2+CO conversion and a 5°C lower temperature at the upper portion of the reactor. The upset disappeared after eight hours of high gas velocity operation, but reappeared after the velocity was lowered.
- A second-stage ZSM-5 reactor operating severity index, expressed as the $i-C_4/(C_3^= + C_4^=)$ molar ratio in the product, of 0.5-1.0 gave maximum gasoline yield. Higher pressure operation had no significant effect on the second-stage operation and yield. Peak research octane numbers of 90-94 were obtained for the raw gasoline at severity indexes of 0.3-2.0.

2. First-Stage Fischer-Tropsch Reactor Operation

Catalyst loading and pretreatment similar to those in 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
SV, 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 15 shows the product gas volume contraction, CO and H_2+CO conversions, and CO_2 and methane concentration in the product gas during the pretreatment.

Immediately after the catalyst pretreatment, the slurry reactor temperature was lowered to 260°C in steps of 3°C over a thirty-seven hour period. With each drop in temperature, the conversion first declined, then gradually increased back to the original conversion level. This policy of temperature reduction kept the conversion high during this transition period. The pressure was increased to 1.48 MPa at this time, establishing the conditions which were used for the majority of the run. This brought the carbon monoxide conversion to about 90%, the target.

Figure 16 shows the conversion and methane and ethane selectivities, as well as the temperature pressure, and superficial gas velocity for the entire run. The range of synthesis conditions and performance of the first stage F-T reactor were:

H_2+CO Flow Rate, Nm^3/hr	1.0-2.6
H_2/CO Feed Ratio, Molar	0.6-1.0
Superficial Feed-Gas Vel., cm/s	1.2-4.4
SV, NL/gFe-hr	1.3-3.4
Temperature, °C	259-267
Pressure, MPa	1.13-2.51
H_2+CO Conversion, mol %	54-93
Methane + Ethane Yield, wt %	6-18

The run can be roughly divided into two parts. In the first part, a long-term aging study on the Catalyst I-B was carried out. After the long-term stability of the synthesis operation was well established, a period of process variable studies was commenced at sixty-one DOS. The process variables examined include:

- Superficial feed-gas velocity
- Reactor pressure
- Feed H_2/CO ratio

FIGURE 15

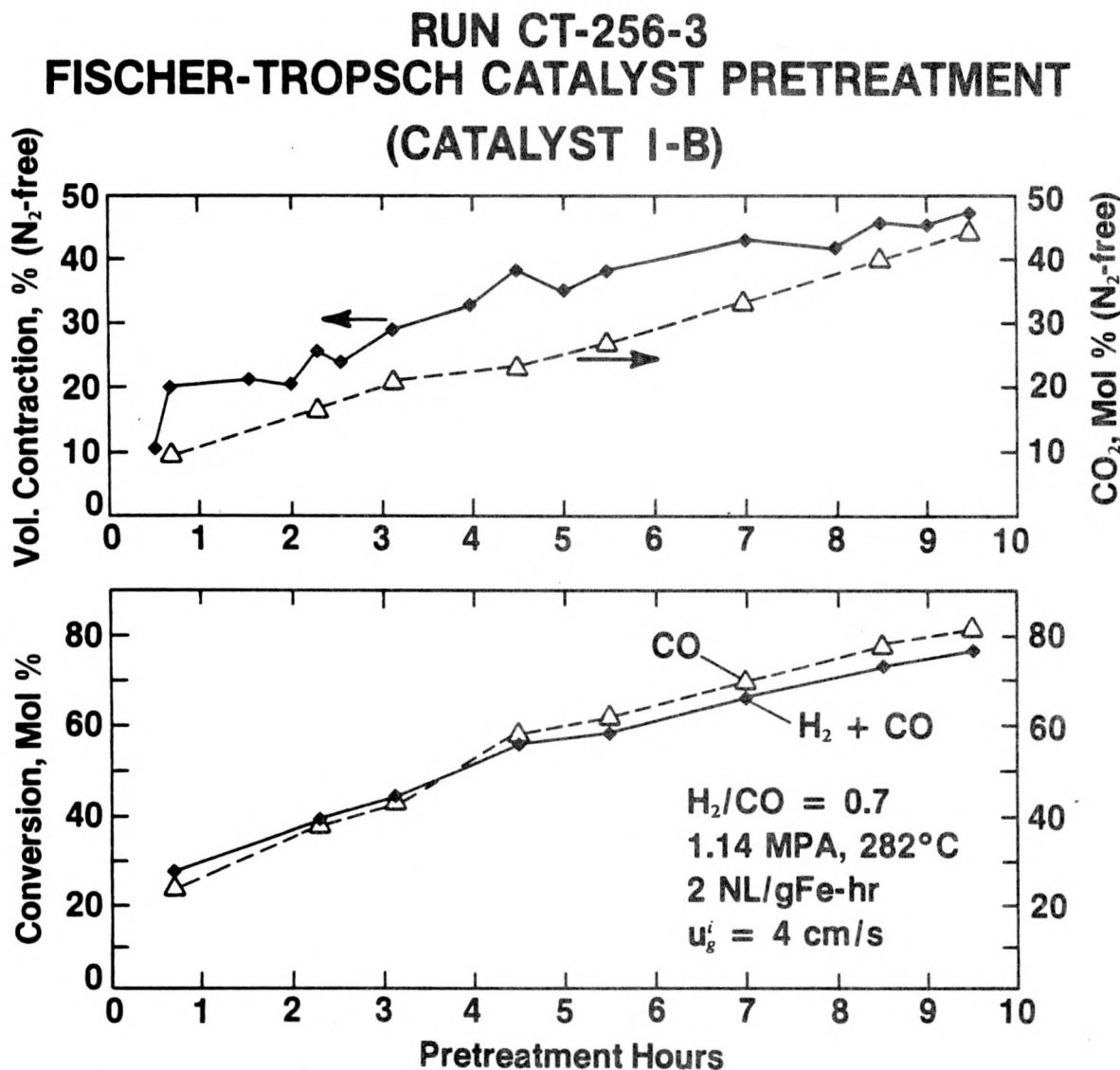
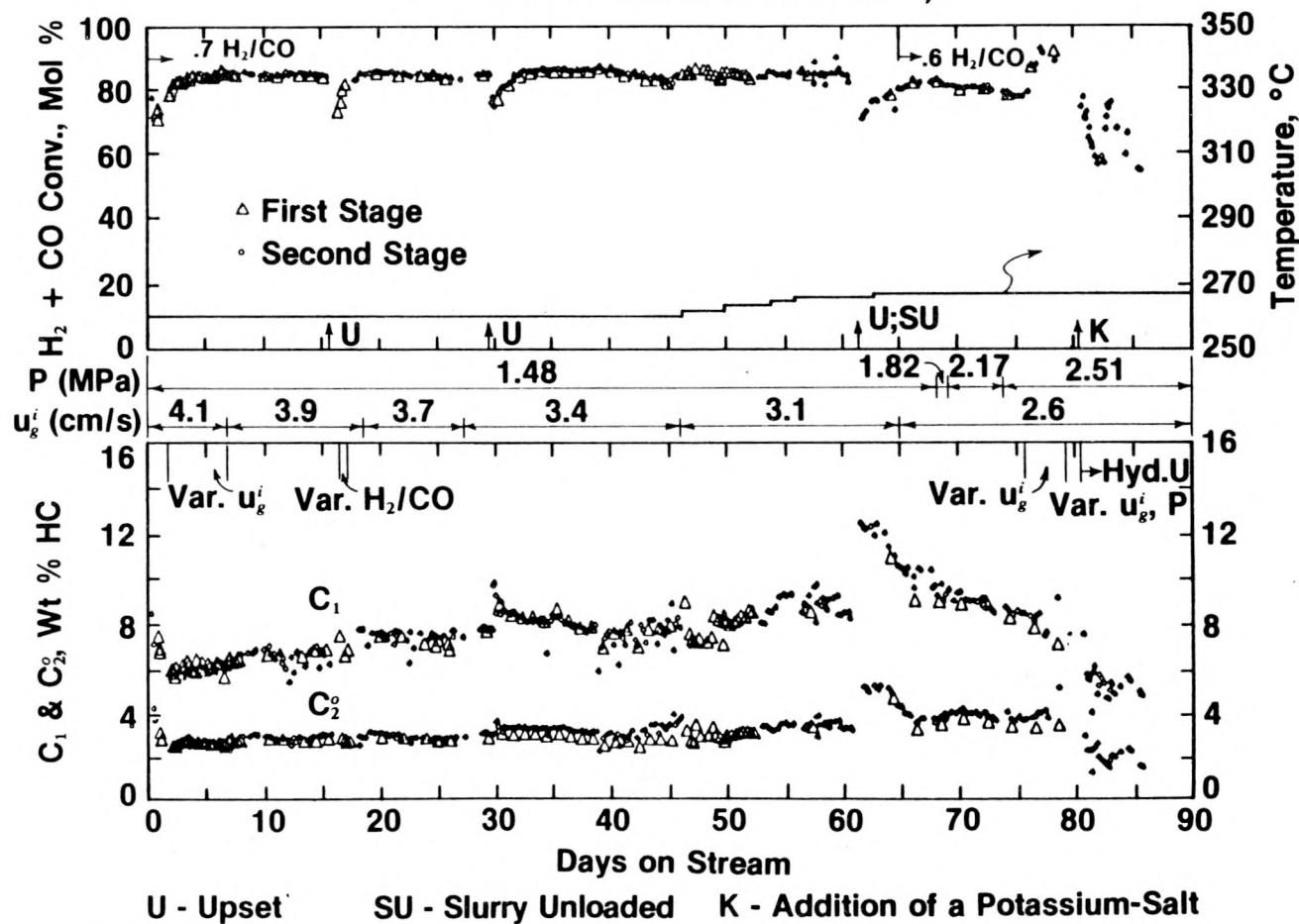


FIGURE 16

SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD

(RUN CT-256-3, 1ST-STAGE CATALYST I-B:PPTD Fe/Cu/K₂CO₃;
2ND-STAGE CATALYST II-B:ZSM-5)



- Addition of a potassium-salt

The synthesis operation was interrupted three times during the run. The first interruption was due to a false alarm and lasted nine hours, during which time the unit was purged with nitrogen. The second interruption was caused by a small slurry leak at the 305 cm flange. Tightening the flange stopped the leak, and synthesis gas flow was restored after thirty-six hours. Both of these interruptions caused a slight decrease in conversion and a corresponding increase in methane + ethane selectivity. This type of behavior has been observed before. The third interruption was another slurry leak, this time at the bottom flange. The leak could not be stopped by merely tightening the flange, so the slurry had to be removed while the gasket was replaced. The slurry was then reloaded after fifty hours and synthesis continued. The result was a substantial increase in the methane + ethane selectivity (from 13 to 19 wt %) and a substantial decrease in H_2+CO conversion (from 87 to 70%). Conversion increased for the next five-day period to 80%, aided by a 2°C temperature increase. It demonstrated that exposure to air is detrimental to catalyst performance.

At eighty-one DOS, an amount of potassium-salt was added to the slurry reactor through the catalyst slurry loading pot in an effort to lower the methane + ethane yield. It is clear from Figure 16 that the methane + ethane selectivity dropped from 13 to 8 wt % with little change on synthesis gas conversion. Unfortunately, however, an unexpected upset which occurred about twelve hours after the potassium-salt addition negated any improvement that addition of the potassium-salt might have imparted to the H_2+CO conversion. Addition of a potassium salt to a slurry F-T reactor has been previously reported by Koelbel and Ackermann (1951) and Koelbel and Ralek (1980).

This "Hydrodynamic Upset" took place following a sensitivity study of the superficial gas velocity. The velocity had been brought down as low as 1.1 cm/s for the study, after which it was reestablished at 2.6 cm/s. The potassium-salt was then added, and the conversion then dropped rapidly from over 80% to 55%, while the reactor temperature above the 305 cm level was 5°C lower than that below 305 cm. It was suspected that the catalyst had settled during the low-velocity operation. Therefore, at eighty-two DOS, the reactor pressure was dropped in stages to 1.48 MPa (200 psig) in order to increase the linear superficial gas velocity in the slurry reactor. This higher gas velocity reestablished uniform reactor temperature after three days. At that time, the synthesis gas conversion also rose to 78%. The superficial feed-gas velocity at this point was 4.2 cm/s. However, when the pressure was increased back to 2.51 MPa (350 psig) the next day, the temperature discrepancies returned with conversion slowly dropping back to the 55% level.

At this time, it was decided to terminate the run. The total accumulative hydrocarbon production for the run was 815 gHC/gFe, a new record.

Material balances were performed daily. Tables D-1 and D-2 summarize the operating conditions and results for this run. Detailed analytical breakdowns of the first-stage products were also performed. Table D-3 shows the composition of the hydrocarbon products produced by the Fischer-Tropsch catalyst for several balances. The oxygenated products were broken down separately and are displayed in Table D-4. In addition, the oxygenates contained in the aqueous phase were analyzed, as shown in Table D-5. The reactor-wax, which was removed by filtration, was broken down on the basis of carbon number. Table D-6 tabulates the results of these studies, while Figures 17 and 18 are graphical representations of some of these distributions. It is interesting to note that between six and twenty-one DOS the distribution had reached a steady-state at 1.48 MPa reactor pressure with peak carbon numbers of 27-28 and similar average carbon numbers. The initial wax medium obviously contained some heavier components as indicated by a peak carbon number of 35 at six DOS. At higher reactor pressures (2.17 MPa and higher), however, slightly heavier hydrocarbons are retained in the slurry reactor as shown in Figure 18. The shift is small with a peak carbon number about 30-31 and an average carbon-numbers of about 28-29.

Reactor-wax was removed regularly to keep the level in the slurry reactor at 610-670 cm. DP-cell readings were used to determine the slurry inventory in the reactor at any given time. A cumulative reactor-wax production curve (Figure 19) is very smooth up to sixty-one DOS as indicated by the least-squares-fitted curve. The reactor-wax production rate at any given time was estimated using the corresponding slope of the curve. In this way, the reactor-wax yields as a percentage of the total hydrocarbon yield were calculated and included in Tables D-1 and D-2. The reactor-wax production data between sixty-one and seventy-four DOS were out-of-line because the major operational upset occurred at sixty-one DOS. During that time, the slurry was unloaded from and reloaded into the reactor. The reactor-wax yields up to sixty-one DOS are plotted against the methane + ethane selectivities in Figure 20. It confirms that at lower methane + ethane yields, the reactor-wax yield increases significantly.

Inclusion of all hydrocarbons and oxygenates from a total material balance allows the construction of a Schultz-Flory type plot (Flory, 1967), as shown in Figure 21. There is a distinct change in the slope (α) of the distribution (probability of chain growth) from 0.79 to 0.88 at carbon number twenty-two, coinciding approximately with the inclusion of the reactor-wax. This trend resembles that of a similar plot given for Run

FIGURE 17
REACTOR-WAX CARBON-NUMBER DISTRIBUTION
(Run CT-256-3)

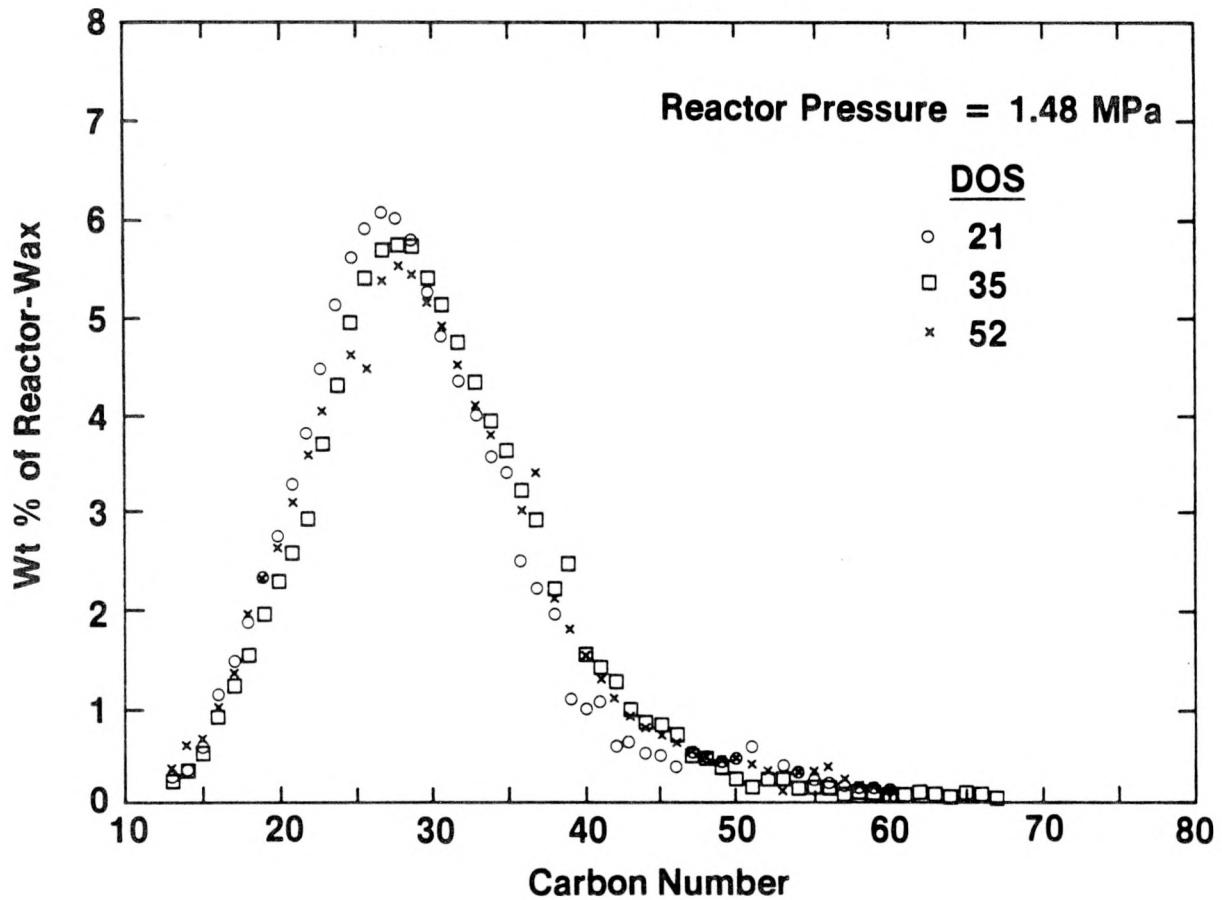


FIGURE 18

EFFECT OF REACTOR PRESSURE ON
REACTOR-WAX CARBON-NUMBER DISTRIBUTION
(Run CT-256-3)

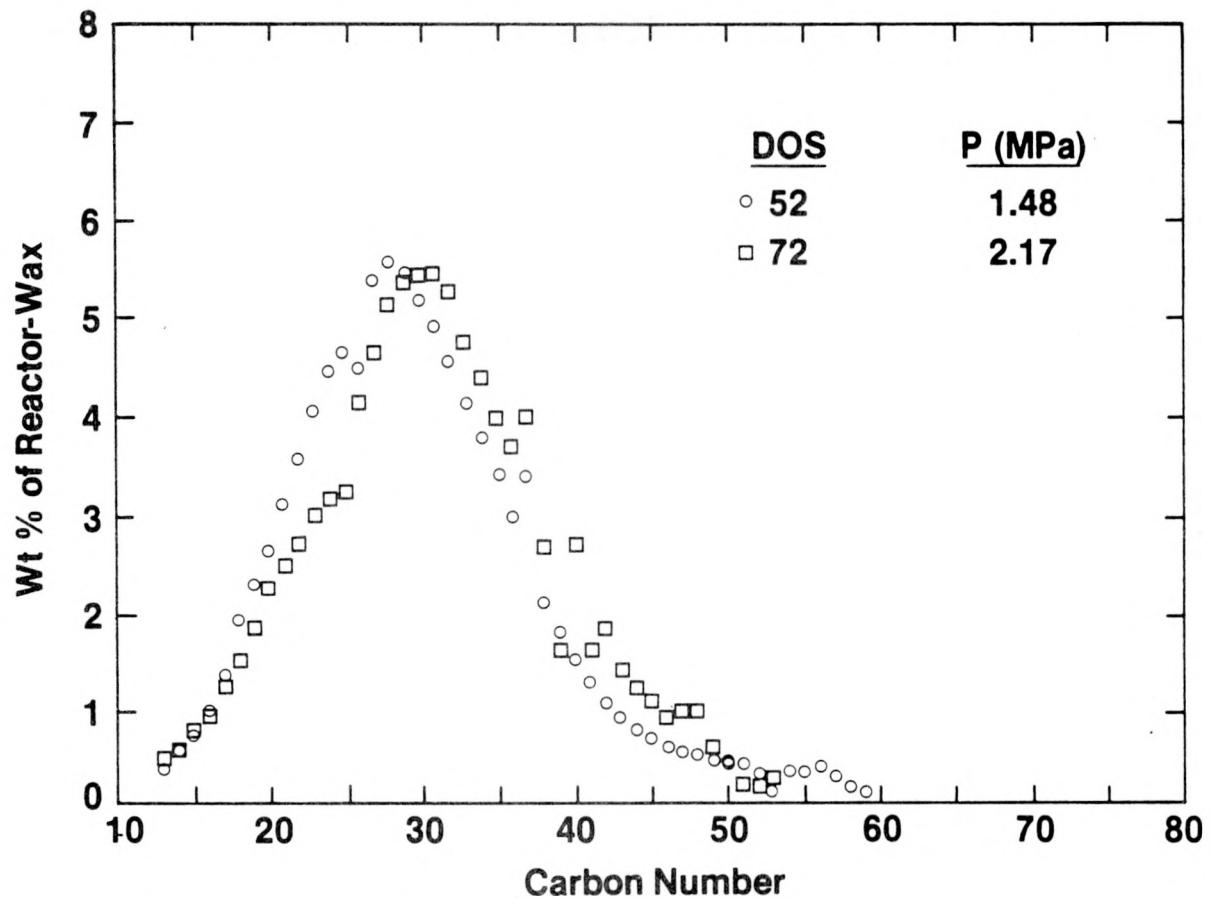
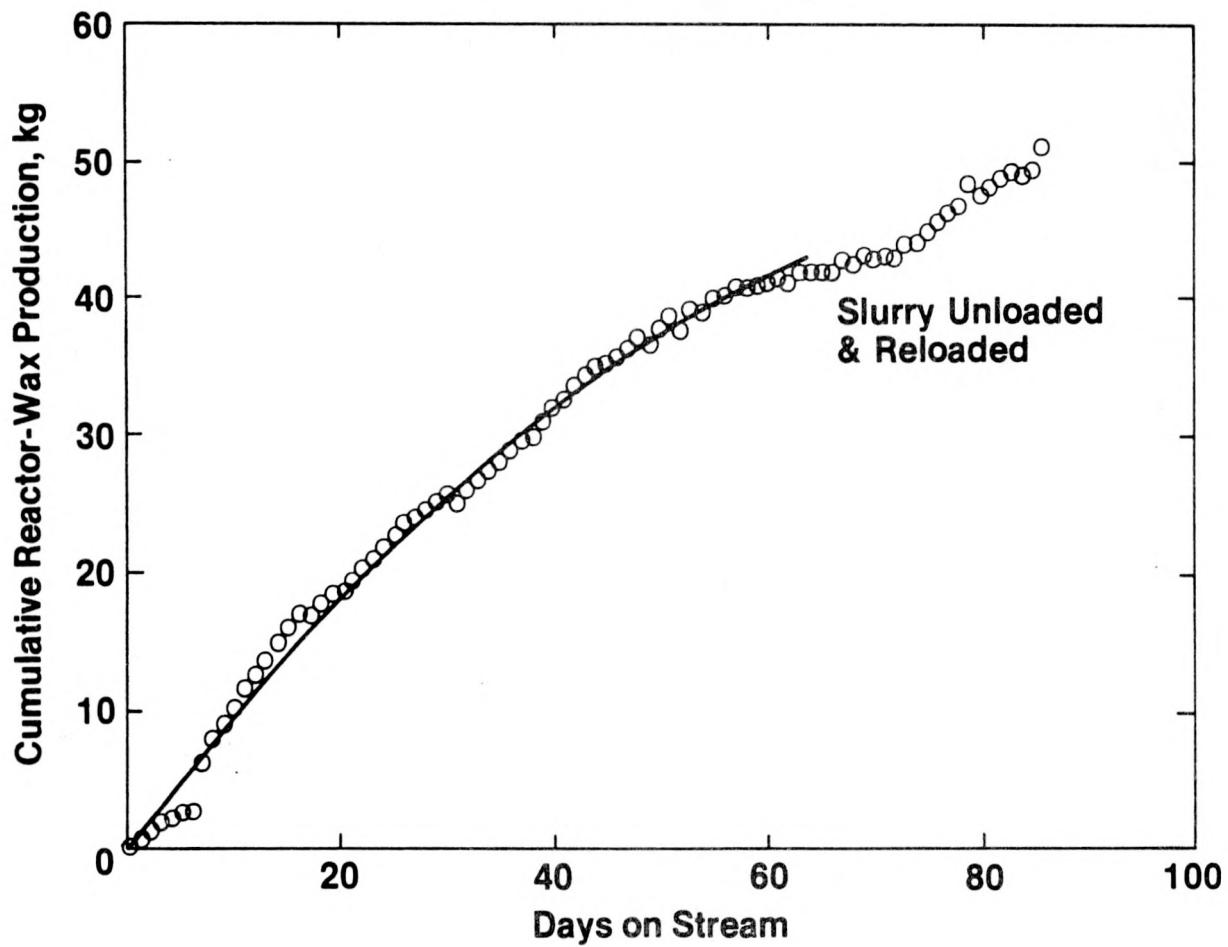


FIGURE 19

**CUMULATIVE REACTOR-WAX PRODUCTION
FROM FIRST-STAGE
FISCHER-TROPSCH REACTOR**

(Run CT-256-3)



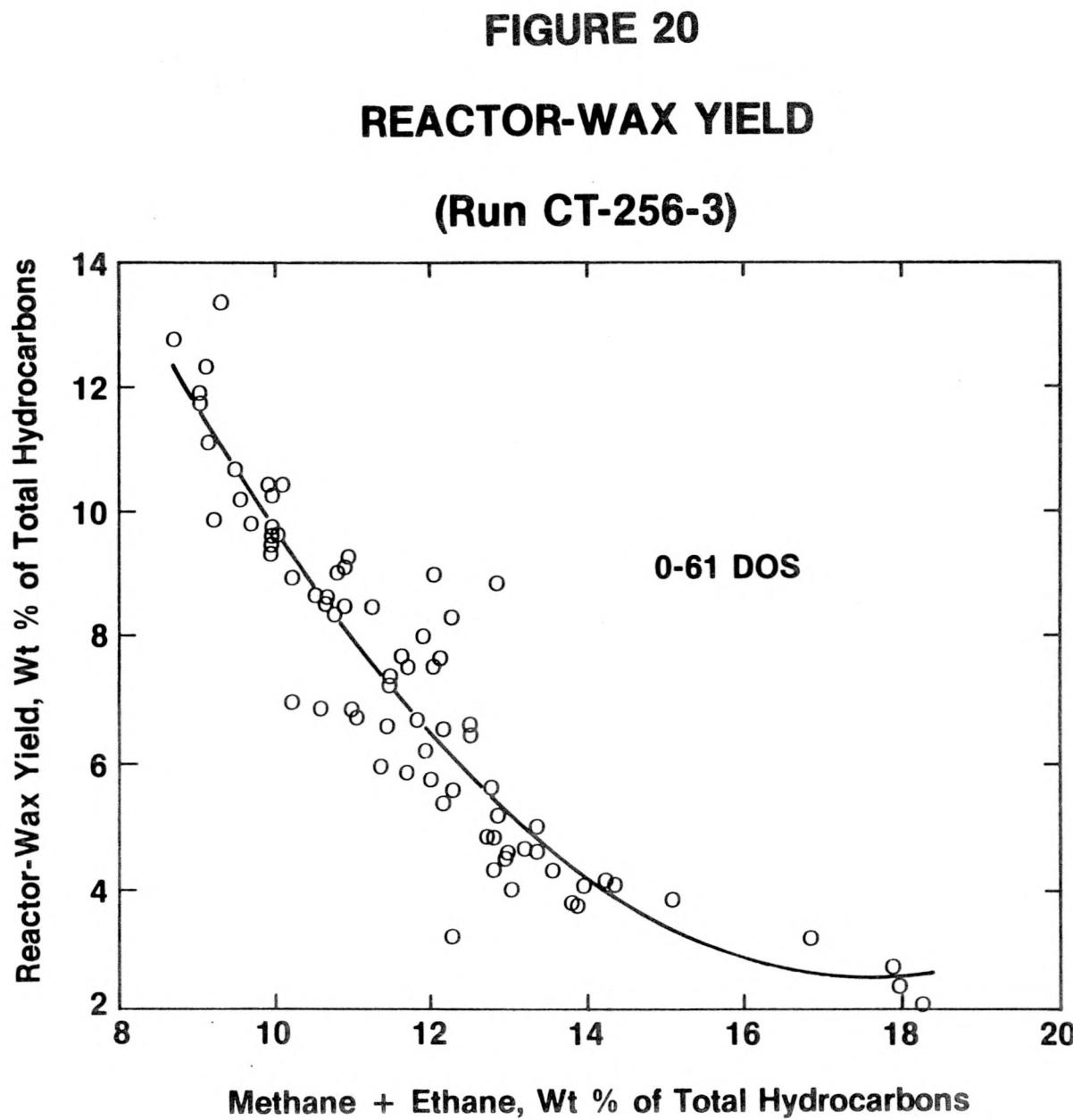
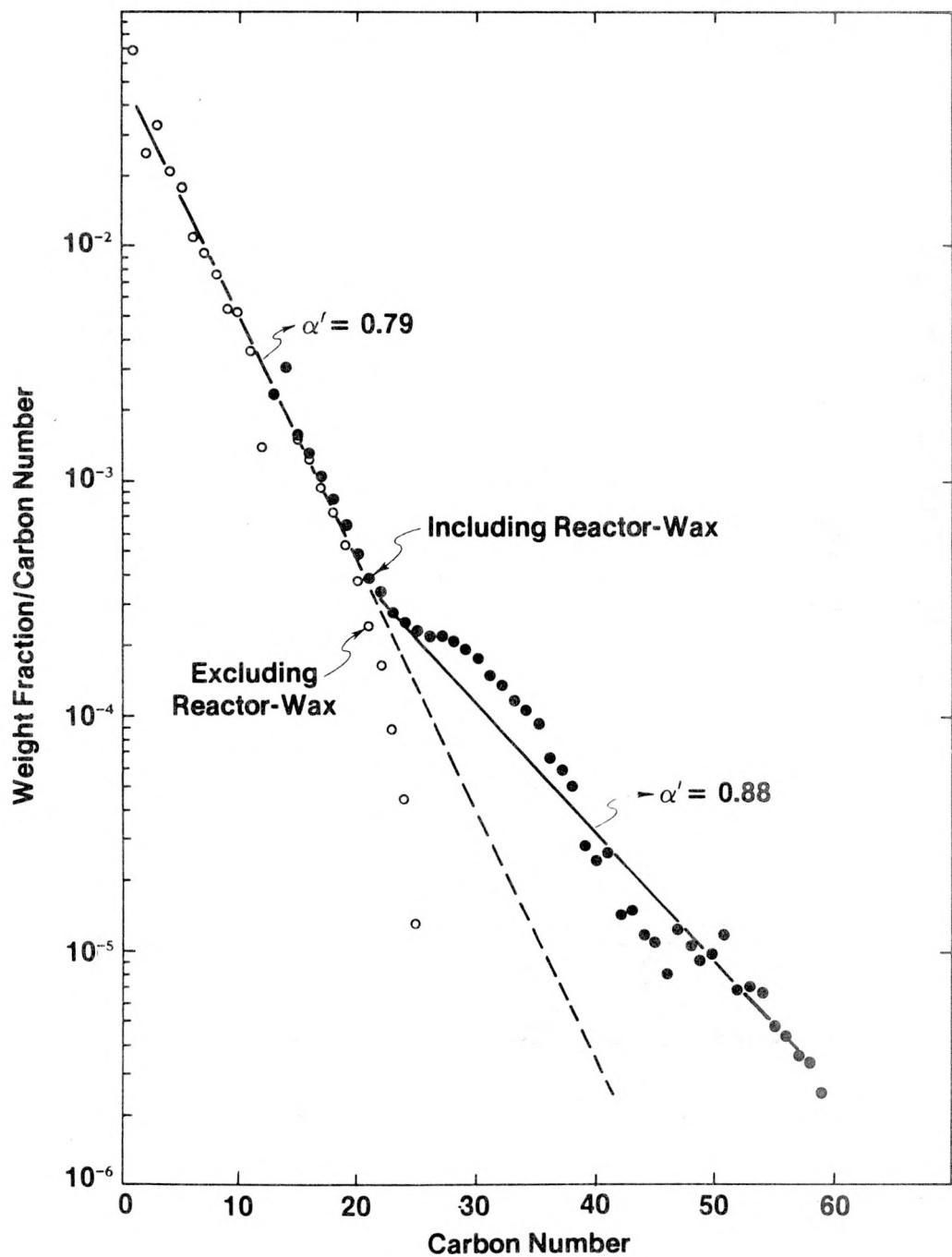


FIGURE 21
SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE
FISCHER-TROPSCH PRODUCTS
(Run CT-256-3, 11.5 DOS
Reactor-Wax Yield — 9.5 wt %)



CT-256-1 shown in Figure 9. As explained earlier, this phenomena may be due to the fact that in a slurry system large molecules can re-absorb themselves onto active catalyst sites, allowing for further chain growth.

As the superficial gas velocity is lowered, the residence time of the synthesis gas is increased, which should increase synthesis gas conversion (Table 17). In addition the methane yield goes down slightly.

In another study, the H_2/CO ratio in the feed gas was changed from 0.7 to 0.6 to observe its effect on slurry reactor performance. This was done at sixty-five DOS and continued until the end of the run. At the time of the switch, however, the catalyst was in the process of recovering from the third upset, which had occurred at sixty-one DOS. Following an upset such as this, the conversion is initially low, then climbs steadily to a point slightly lower than that before the upset. Similarly, the methane + ethane selectivity is initially high, but then declines gradually to a level somewhat above the previous one. This seems to correspond to a "reactivation" of the catalyst. Looking at Figure 16, this same trend is evident following the upset, but it appears that the methane + ethane selectivity declines to the same level as before the upset. It is logical to conclude that the lower H_2/CO ratio in the feed enabled this to occur. By decreasing the amount of available hydrogen, the yields of hydrogen-rich components, such as methane and ethane, were decreased.

Also interesting is the effect of the feed H_2/CO ratio on the H_2/CO ratio in the exit gas shown in Figure 22. Data from the whole run are used to construct this plot. Consequently, they include wide ranges of operational variables and result in a large spread of the data. The lines shown on the figure are least-squares-fitted. Here it is seen that a feed ratio of 0.6 causes the exit ratio to remain nearly same ratio over a wide range of conversions. At 0.7 H_2/CO feed ratio, however, an excess of hydrogen appears at all times, particularly at the higher conversions. This figure indicates that the H_2/CO usage ratio is very close to 0.6. When a feed H_2/CO ratio higher than the usage ratio is used, the excess hydrogen is reflected as higher H_2/CO in the exit gas. The exit H_2/CO ratio increases with increasing synthesis gas conversion because the water-gas shift reaction favors the formation of hydrogen according to thermodynamic equilibrium. It appears, then, that there are distinct advantages to operate the synthesis at a feed H_2/CO ratio close to the usage ratio, i.e., lower methane + ethane yield and better usage of the synthesis gas. However, the long-term effects on catalyst aging have yet to be determined. Also, note that most of the 0.6 H_2/CO data were taken at higher pressure.

Table 17

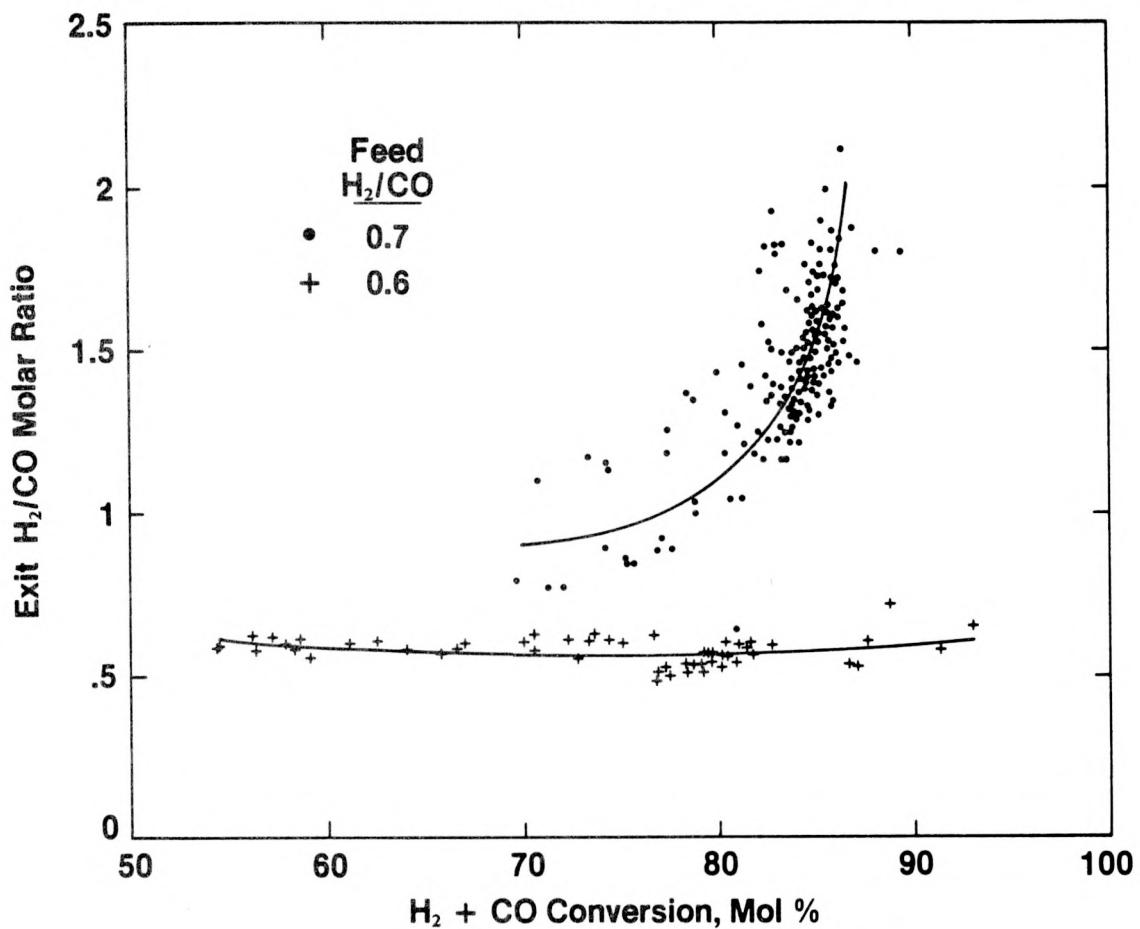
**Effect of Superficial Feed-Gas Velocity on Slurry
Fischer-Tropsch Reactor Performance (1)**

(Run CT-256-3)

DOS	75.4	76.5	77.4
Gas Superficial Velocity, cm/s	2.5	2.1	1.6
SV, NL/gFe-hr	3.12	2.53	1.95
H ₂ +CO Conv., Mol %	77.1	87.2	93.1
Methane, Wt % HC	8.8	8.5	7.8
Methane + Ethane, Wt % HC	12.7	12.6	12.2

(1) 0.6 H₂/CO, 267°C, 2.51 MPa

FIGURE 22
**EXIT H_2/CO RATIO OF FIRST-STAGE
SLURRY FISCHER-TROPSCH REACTOR**
(Run CT-256-3)



Pressure effects were studied at a feed H₂/CO ratio of 0.6 and a temperature of 267°C. As the pressure was changed, the synthesis gas flow rate was altered so that the same superficial feed-gas velocity was maintained at 2.6 cm/s. Table 18 shows the results of this process variable study. The pressure was varied from 1.48 to 2.51 MPa (200 to 350 psig) over an eight-day period. It is seen that the methane and ethane yields decrease as the pressure is raised. This is due to the higher probability of the chain-growth under higher pressure. The effect on synthesis gas conversion, though, is less clear. The conversion drops slightly with increasing pressure although the superficial feed-gas velocity is maintained constant. The 2% drop in conversion between 2.17 and 2.51 MPa may be mainly due to experimental data scattering. However, the space velocities were greatly increased due to higher pressure operation. This increase in the space velocity is more than sufficient to compensate for the slightly lower conversion at the same feed-gas velocity. Of course, the other major advantage is the significant drop in the methane yield.

The effect of pressure on the yield of oxygenated products was also noted, as shown in Table 19. This shows that as the pressure is increased, so is the oxygenate yield. The magnitude of the increase is not clear from this table, however, because the other process variables were also changed (H₂/CO ratio, superficial velocity, and temperature).

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

The second-stage reactor, containing 215 g of II-B ZSM-5 catalyst, was brought on-stream one hour after the end of the F-T catalyst pretreatment. The material balances performed over the sixty-seven days of second-stage operation are summarized in Table D-7 of Appendix D. The properties of the raw liquid hydrocarbons collected from the ambient and chilled condensers are reported in Table D-8, while Table D-9 gives the detailed product hydrocarbon compositions.

Also, as mentioned in previous runs, the severity of the second-stage operation was guided by the i-C₄/(C₃⁼+C₄⁼) molar ratio (the severity index) in the combined gas stream after the second-stage reactor. To achieve a severity index of 0.8-1.0, the initial inlet temperature of the second-stage reactor was set to 343°C. This cycle was started in Run CT-256-2 (see Subsection VI.C.2.) In this run, the catalyst was regenerated twice with no apparent loss of activity. During the twenty-eight day second cycle and the unfinished thirty day third cycle operation, the second-stage inlet temperature had to be increased at about 5.3 °C/day to maintain the target severity. The fixed-bed inlet temperature and the temperature rise across the catalyst bed are reported in Figure 23.

Table 18

**Effect of Pressure on Slurry Fischer-Tropsch
Reactor Performance (1)**

(Run CT-256-3)

DOS	66.8	68.8	72.4	74.8
Pressure, MPa	1.48	1.82	2.17	2.51
SV, NL/gFe-hr	1.95	2.32	2.77	3.12
H ₂ +CO Conv., Mol %	81.2	81.7	79.5	77.5
Methane, Wt % HC	10.8	10.1	9.4	8.7
Methane + Ethane, Wt % HC	14.8	14.4	13.6	12.6

(1) 0.6 H₂/CO, 267°C, 2.6 cm/s superficial feed-gas velocity.

Table 19

**Effect of Pressure on Oxygenates Yield from
First-Stage Fischer-Tropsch Reactor**

(Run CT-256-3)

DOS	50.6	74.5
Pressure, MPa	1.48	2.51
Temperature, °C	263	267
Feed H ₂ /CO, Molar	0.7	0.6
Superficial Feed-Gas Velocity, cm/s	3.1	2.6
SV, NL/gFe-hr	2.18	3.15
H ₂ +CO Conversion, Mol %	85.2	77.5
Oxygenates, Wt % of HC	8.6	12.0

FIGURE 23

SECOND-STAGE FIXED-BED ZSM-5 REACTOR
INLET AND OUTLET TEMPERATURES

(Run CT-256-3)

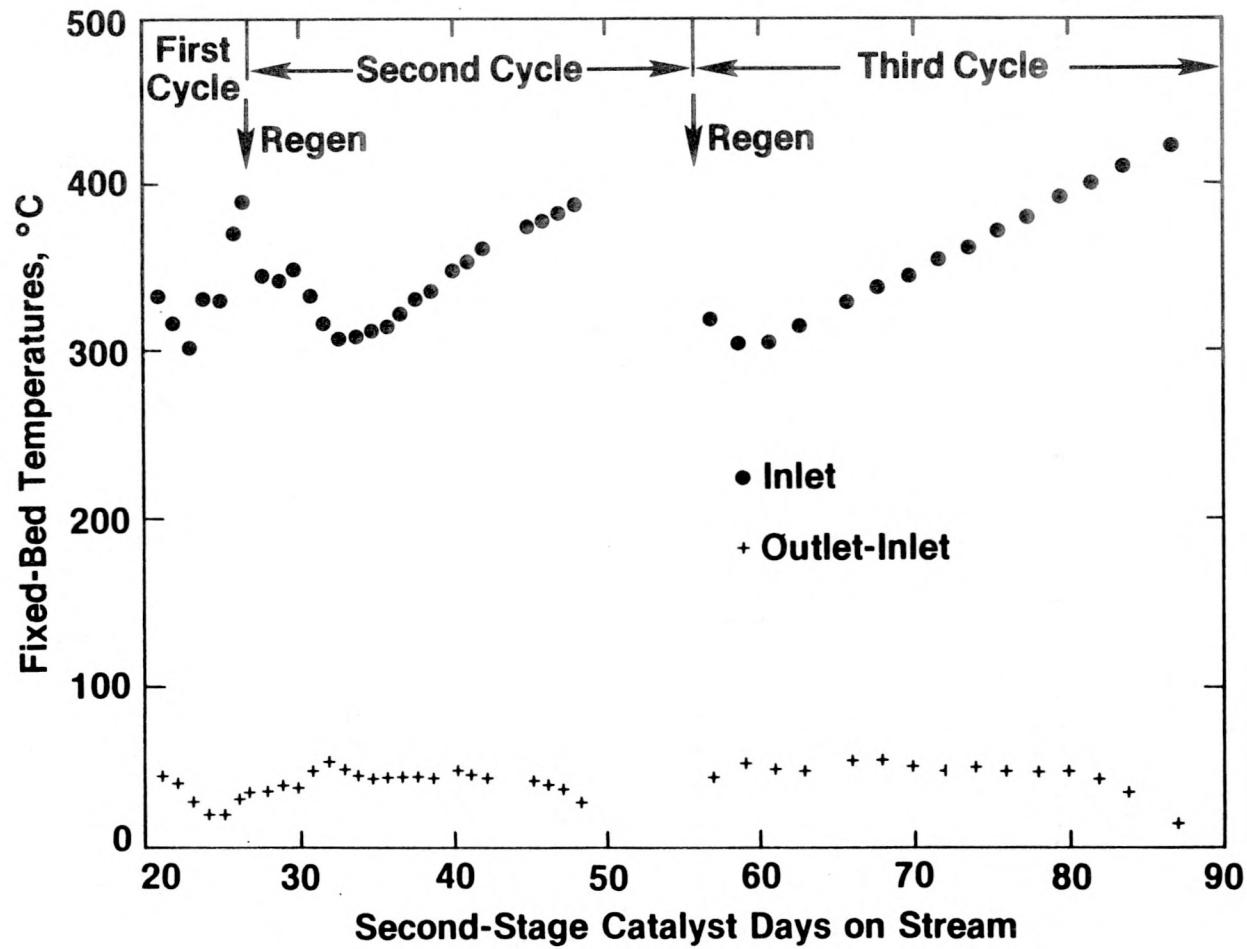


Figure 24 shows the effect of second-stage operating severity index on the hydrocarbon yield. As mentioned earlier, the alkylate yield is estimated by alkylating first butenes and then propylene with i-butanes. If there is an excess of light olefins, they are converted to "Cat-Poly gasoline" using conventional catalytic polymerization process. In making this plot the product yields are normalized excluding the reactor-wax and C_4^- paraffins carried over from the first-stage reactor. Peak C_5^+ gasoline yields of 85-90 wt % could be achieved at severity index of 0.5-1. High pressure operation (2.51 MPa versus 1.48 MPa) had no significant effect on the second-stage operation and yield.

Figure 25 shows the Research Octane Number and the aromatic and olefin content of the raw liquid hydrocarbon product collected in the cold and chilled condensers as a function of the second-stage operating severity index. Peak octane number of 90-94 is obtained for severity indexes of 0.3-2.0. The corresponding aromatics content is 30-50 wt % and olefins content is 5-25 wt %. Too high aromatics content is equivalent to high severity or reduced gasoline yield. Too low aromatics content, however, also results in a low gasoline yield. Hence, optimal gasoline yield is restricted to a severity index of 0.5-1.0. Motor octane number for the raw liquid hydrocarbon products are summarized in Table D-8.

Another indication of the second-stage catalyst performance is the acid number of the raw liquid hydrocarbon products, also reported in Table D-8. Acid numbers of 0.04-0.4 show the ability of the ZSM-5 catalyst to convert organic acids. For comparison, first-stage F-T liquid hydrocarbon products have acid number of 1.1-3.0. Finally, the ASTM distillation properties of the raw hydrocarbon products did not vary much with catalyst aging or changing operating severity (Table D-8).

E. Run CT-256-4

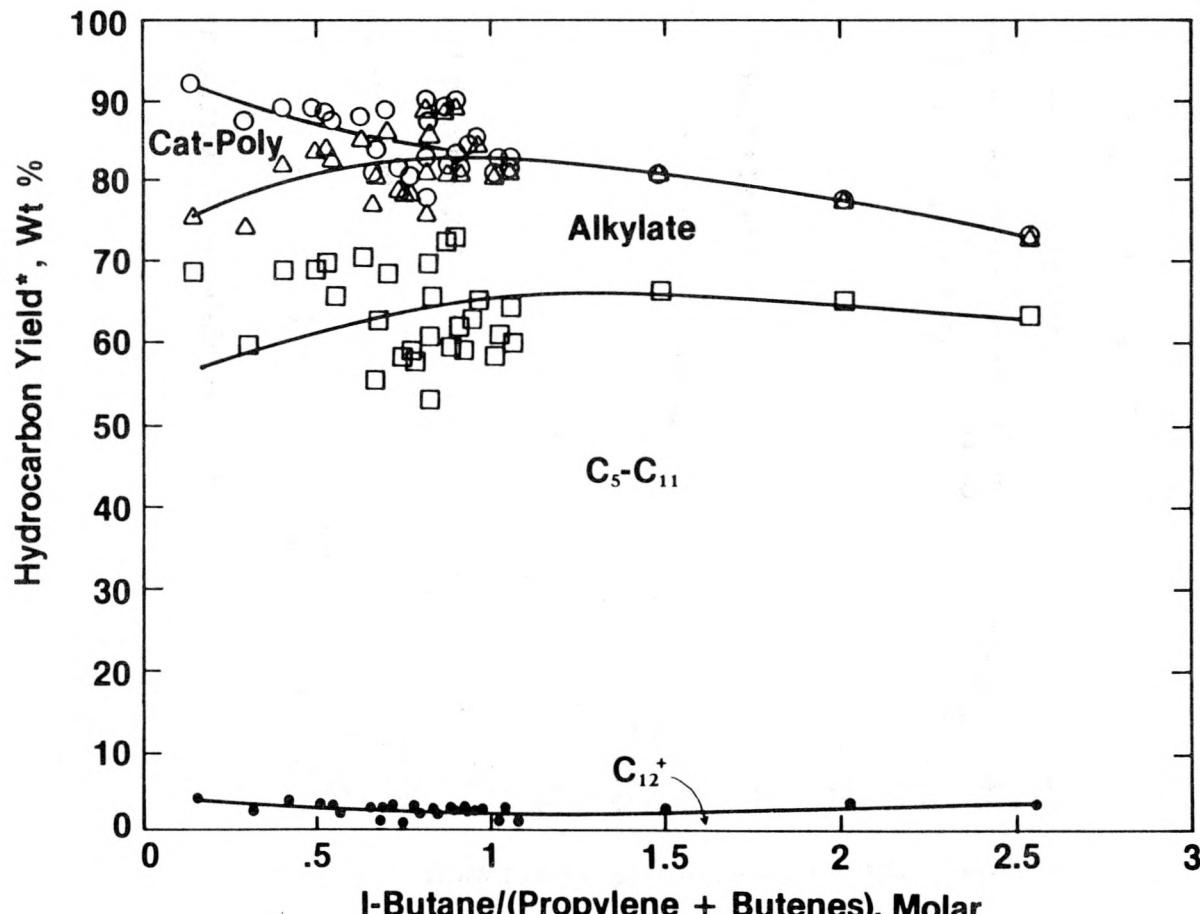
1. Highlights

The fourth BSU run, designated as Run CT-256-4, using the same gasoline-mode F-T catalyst I-B used in Run CT-256-3, was smoothly started up on January 10, 1983 and was concluded after thirty-seven DOS. The major objective was to operate the same gasoline-mode catalyst under higher pressure and slightly lower temperature to reduce methane + ethane yield. Another objective of this run was to test different reactor-wax withdrawal systems. The major events and ranges of process variables and operating results of this run are summarized in Tables 20 and 21, respectively.

FIGURE 24

PRODUCT YIELDS VERSUS
SECOND-STAGE OPERATING SEVERITY

(Run CT-256-3)



*Excluding C₄ paraffins in feed and reactor-wax

FIGURE 25

**SECOND-STAGE
RAW LIQUID HYDROCARBON PROPERTIES**

(Run CT-256-3)

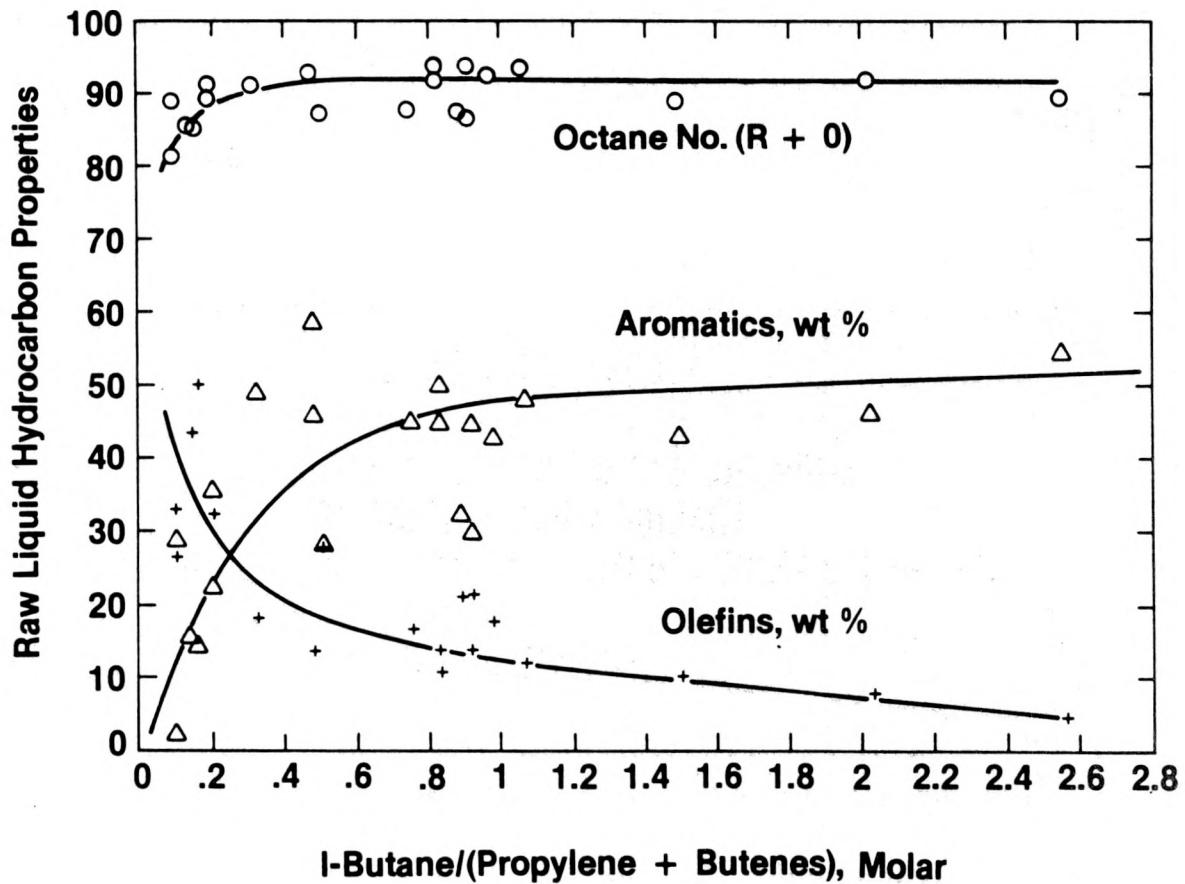


Table 20

Major Events in Run CT-256-4

<u>DOS</u>	<u>Major Events</u>
-0.4 - 0	Pretreatment
0 - 0.5	280---->260°C; 5 cm/s; 1.56 NL/gFe-hr
0.5 - 2.7	1.14---->2.52 MPa; 257°C; 4 cm/s
2.7 - 6.6	2.52 MPa; 257°C; 3 cm/s; 3 - 6.5 NL/gFe-hr
6.6 - 34.8	2.52 MPa; 257°C; 2 cm/s
29.8	493 g fresh catalyst added
34.8 - 36.7	2.52---->1.48 MPa; 257-260°C; 2 cm/s
36.7	End of Run CT-256-4

Table 21

Ranges of Process Variables & Operating Results
(Run CT-256-4)

<u>First-Stage Process Variable</u>	<u>Range</u>
Temperature, °C	257 - 280
Pressure, MPa	1.14 - 2.52
Superficial Feed-Gas Velocity; cm/s	2 - 5
SV, NL/gFe-hr	1.2 - 6.5
Catalyst Loading (Nominal), Wt %	4.4 - 22.2

Operation Results

H ₂ + CO Conversion, Mol %	17 - 75
Methane + Ethane Yield, Wt % HC	3.5 - 5
Reactor-Wax Yield, Wt % HC	46 - 51

Major highlights of this run were.

- Methane + ethane yield of less than 5 wt % of hydrocarbons produced was obtained throughout the run.

The ranges of the first-stage slurry F-T reactor operating conditions and performance were:

H ₂ +CO Flow Rate, Nm ³ /hr	1.18-3.43
Temperature, °C	257- 280
Pressure, MPa	1.14-2.52
H ₂ /CO Feed Molar Ratio	0.7
Superficial Feed-Gas Velocity, cm/s	2-5
SV, NL/gFe-hr	1.2- 6.5
Catalyst Loading, wt % (nominal)	4.4-22.2
H ₂ +CO Conversion, mol %	17- 75
Methane + Ethane Yield, wt % HC	3.5-5
Reactor-wax Yield, wt % HC	46-51

- A high reactor-wax yield (46-51 wt % of the total hydrocarbons produced) was observed, which was consistent with the low methane + ethane yield. With this mode of operation, reactor-wax upgrading to liquid fuels becomes essential.
- During the first sixteen days of operation, about 55% of initial catalyst load was lost via reactor-wax withdrawals through filters. An external catalyst settling method was successful in recovering withdrawn catalyst from the slurry, but significant deactivation of the catalyst occurred, probably due to exposure to air.
- An on-line catalyst settling method was successfully tested. The external filter assembly at the 762 cm location was converted to a slurry settling vessel and was used to remove 300-400 g/hr of reactor-wax containing less than 0.2 wt % catalyst.
- A batch of fresh catalyst was added to the slurry reactor to make up for the lost catalyst. The fresh catalyst, however, did not seem to activate at the synthesis conditions.
- The reactor-wax obtained after seventeen DOS was heavier and more viscous than that produced in Run CT-256-3. This was probably due to operation at higher pressure and slightly lower temperature.

- The acid numbers of the F-T hydrocarbon liquid and aqueous phase were substantially higher (10-32, and 35-109 mgKOH/g, respectively) than those from Run CT-256-3 (1-3, and 2-7 mgKOH/g, respectively). The oxygenate contents are also expected to be higher.

The second-stage ZSM-5 reactor was not operated during this run since the first-stage operation was not steady. This was due to continuous catalyst loss at the early part of the run. Also, high H_2+CO conversion and high synthesis gas throughput could not be achieved during the latter part of the run.

2. First-Stage Fischer-Tropsch Reactor Operation

Due to higher catalyst loading the pretreatment conditions were slightly different from those used in Run CT-256-3. 2,000 g of F-T catalyst I-B in 1,100 g Mobil F-509 was loaded along with 5,900 g of spent reactor-wax from previous run. The initial catalyst loading was 22.2 wt %. To avoid pretreating this catalyst at too low a space velocity, a high feed-gas superficial velocity of 5 cm/s was used.

The F-T catalyst pretreatment conditions were:

H_2+CO Flow Rate, Nm^3/hr	2.16
H_2/CO Feed Ratio, Molar	0.70
Superficial Feed-Gas Velocity, cm/s	5.00
Temperature, $^{\circ}C$	280
Pressure, MPa	1.14

The pretreatment was ended after ten hours, the same number of hours as in Run CT-256-3. The CO conversion at this time was 77 mol %. This conversion was somewhat lower than what was expected from the high catalyst loading. It may be due to the high superficial gas velocity employed. Figure 26 shows the product gas volume contraction, CO and H_2+CO conversion, and CO_2 concentration in the product gas during the pretreatment.

In switching from the pretreatment to the synthesis operation, the slurry reactor temperature was lowered to 260 $^{\circ}C$ in steps of 3 $^{\circ}C$ at a time over a twelve hour period. The conversion continuously dropped during this period due to lower temperature. The synthesis gas flow rate was also adjusted to reach 4 cm/s superficial velocity at 260 $^{\circ}C$. The catalyst was continuously activated during this period and consequently the conversion increased from 41% at twelve HOS to 75% at thirty-six HOS. Figure 27 gives the H_2+CO conversion, methane and ethane yields, and space velocity during the synthesis operation. Figure 28 gives the cumulative reactor-wax production during this run.

FIGURE 26
RUN CT-256-4
FISCHER-TROPSCH CATALYST PRETREATMENT
(CATALYST I-B)

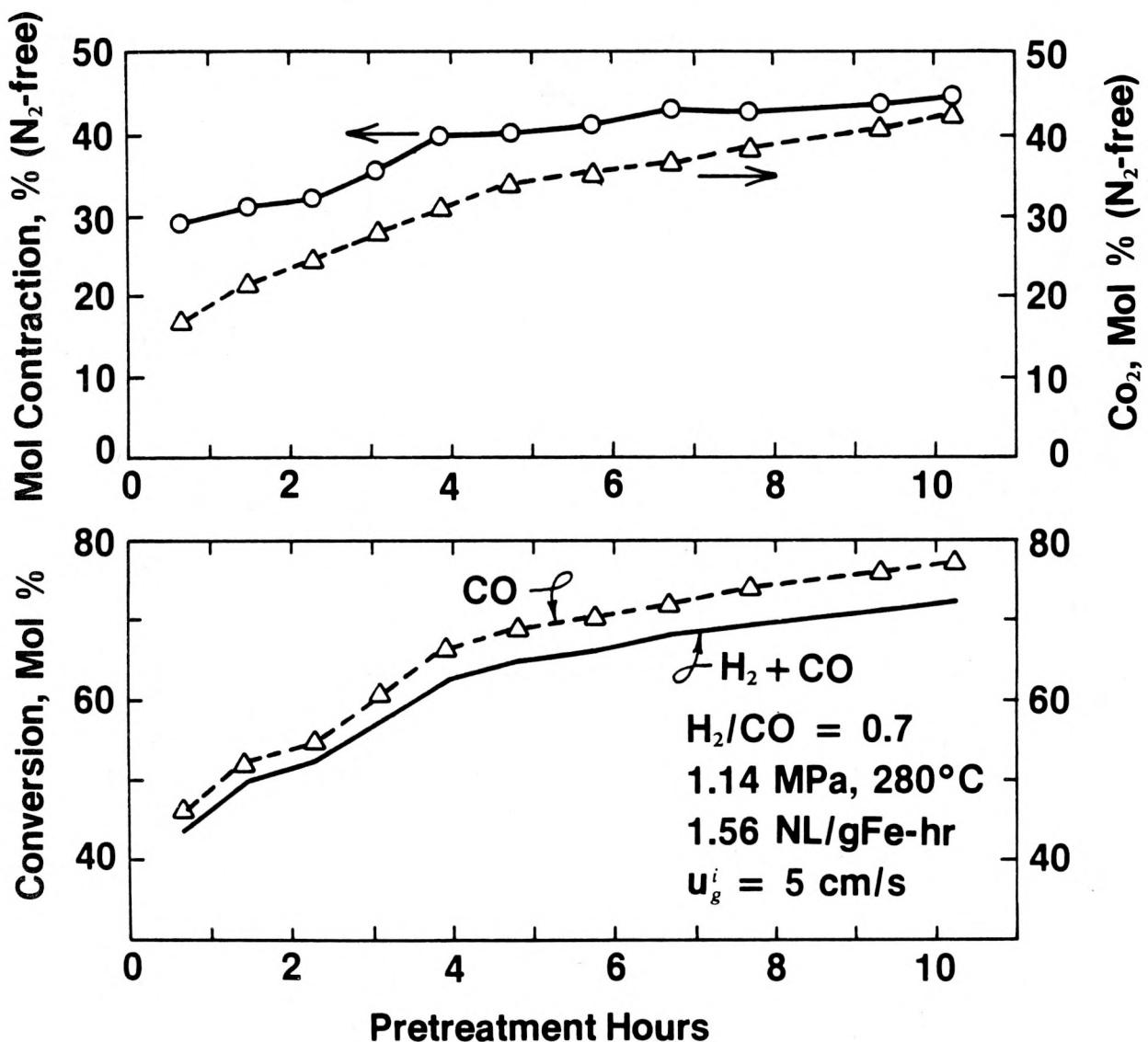
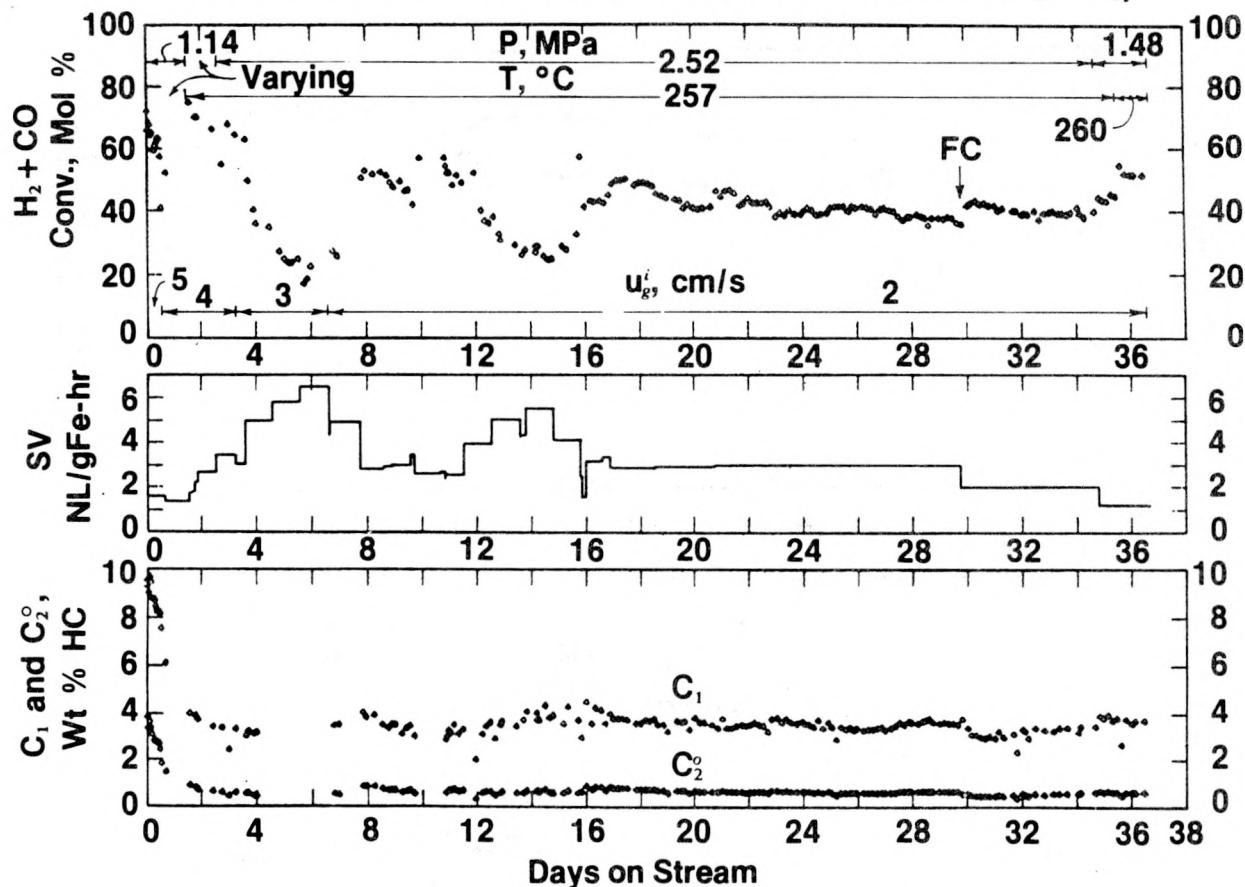


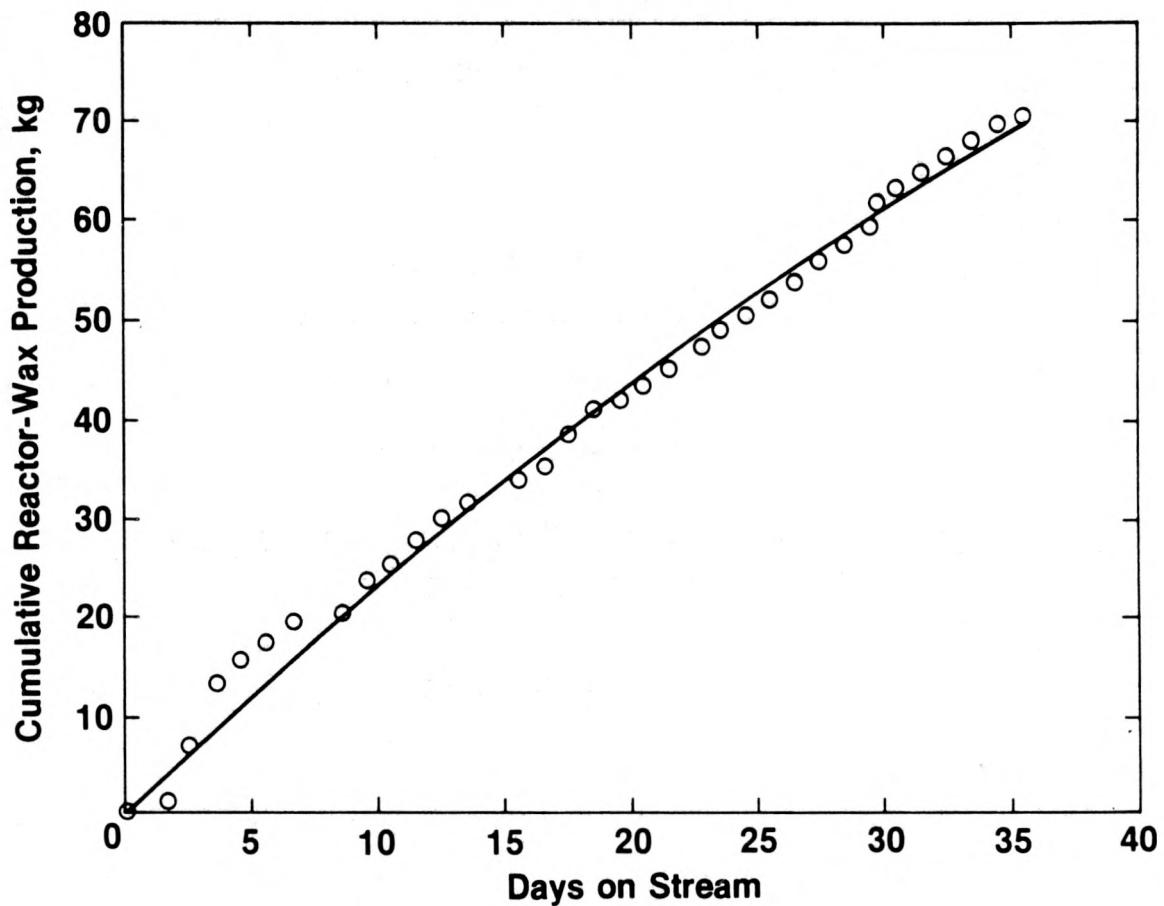
FIGURE 27
SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD

(RUN CT-256-4;
1ST-STAGE CATALYST I-B: PPTD Fe/Cu/K₂CO₃)



FC: Fresh catalyst added

FIGURE 28
CUMULATIVE REACTOR-WAX PRODUCTION
FROM FIRST-STAGE
FISCHER-TROPSCH REACTOR
(RUN CT-256-4)



Over the next twenty hours, the reactor pressure was raised to 2.52 MPa (350 psig). The H_2+CO conversion dropped from 75 to 55 mol % during this period, mainly due to catalyst loss which occurred during the reactor-wax withdrawal using the filters. The reactor-wax yield at this time was about 51 wt % of the total hydrocarbons produced. Later analysis showed that the reactor-wax contained as high as 5 wt % of catalyst. The space velocity hence increased as indicated in Figure 27.

The superficial velocity was then lowered to 3 cm/s at three DOS to increase the H_2+CO conversion to 62 mol %. The conversion, however, as seen in Figure 27, kept decreasing due to continuous catalyst loss via reactor-wax withdrawals. The lower catalyst inventory in the reactor was confirmed later by slurry samples taken. Using the catalyst content analyses of slurry samples and the total liquid height obtained from DP-cell readings, the catalyst in the reactor was estimated to be 891 g; a total catalyst loss of 55% from the initial loading. The space velocity shown in Figure 27 was based on estimated catalyst inventories in the slurry reactor. The catalyst inventories were periodically checked by taking slurry samples from the taps.

At seven DOS the feed-gas superficial velocity was further lowered to 2 cm/s to compensate for further catalyst loss. An attempt was then made to reload some of the lost catalyst into the reactor after a concentrated slurry was obtained by settling the withdrawn reactor-wax in an oven (149-178°C) over magnets for six to eight hours. By doing so the space velocity was maintained nearly constant during seven to eleven DOS. The H_2+CO conversion of 42-50 mol %, however, was substantially lower than the high conversion achieved at an earlier period of the run at an equivalent space velocity. This indicated that the catalyst was substantially damaged during the settling operation when it was exposed to air. This was consistent with what was observed during the major operational upset in Run CT-256-3. Catalyst loss due to reactor-wax withdrawal continued up to seventeen DOS. Further addition of the lost catalyst during fifteen to seventeen DOS increased the H_2+CO conversion.

At that time, a new test of the slurry loading tank as an on-line batch catalyst settling vessel was carried out. This was done by replacing the loading funnel with a dip-tube positioned about two-thirds the way into the loading tank. A batch of slurry was brought into the loading tank, maintained at 232°C (450°F), and allowed to settle for one hour with magnets beneath the tank. The reactor-wax withdrawn through the dip-tube contained only 0.2-0.3 wt % of catalyst. The concentrated slurry at the bottom of the tank was pushed back into the reactor using high pressure nitrogen. However, some slurry always stayed in the tank and some was lost through the vent-line of the tank. The latter catalyst loss was not accounted for.

Due to the success of the catalyst settling test using the slurry loading tank, an external filter assembly was immediately converted into a catalyst settling vessel by installing a dip-tube from the top. During this test, the temperature of the vessel was maintained at 177-232°C (350-450°F). The reactor-wax withdrawn from the dip-tube after one hour's settling contained less than 0.05 wt % of catalyst. A daily reactor-wax removal rate of about 1,700 g was achieved. During twenty-two to twenty-nine DOS, the H₂+CO conversion varied only slightly (from 41 to 36 mol %) and methane + ethane yield was steady at 4.4 wt %. The slight decrease in H₂+CO conversion may be due to catalyst aging or some damage during the settling operation when the catalyst was removed from the synthesis gas atmosphere. The long-term effect on the F-T catalyst due to the on-line catalyst settling is unknown.

Figure 29 shows the schematic arrangement of the catalyst-settling vessel. The slurry from the reactor is brought into the catalyst settling vessel via valve V-1 which is then closed to isolate the slurry in the vessel from the reactor. The slurry can then be purged with H₂ or N₂ to remove any dissolved gases. It is then allowed to settle in the vessel for the desired length of time. The virtually catalyst-free reactor-wax can be withdrawn from the top by the dip-tube, leaving the concentrated catalyst slurry in the vessel. The concentrated slurry can then be pressurized back into the reactor.

A series of experiments were carried out to evaluate the following important factors for F-T catalyst settling:

- Settling Time
- Temperature
- Dip-Tube Position
- Magnets Beneath the Vessel
- Dilution with Light Hydrocarbons

The results are summarized in Table 22. The results show that a reactor-wax containing less than 0.2 wt % of catalyst can be obtained after settling for one hour at 177-204°C. They also show that magnets were beneficial in accelerating the settling process. Further, they show that a continuous H₂ purge at 1 cm³/s was detrimental to the reactor-wax/catalyst separation (Experiment #5). The dilution of slurry with an equal amount of dodecane significantly improved the settling as shown in Experiment #7. A higher dip-tube position also improved the separation (Experiments #2 and 3). Higher settling temperature somewhat improved the separation efficiency (Experiments #4 and

FIGURE 29

**SCHEMATIC OF A CATALYST SETTLING VESSEL
FOR FISCHER-TROPSCH
REACTOR-WAX REMOVAL**

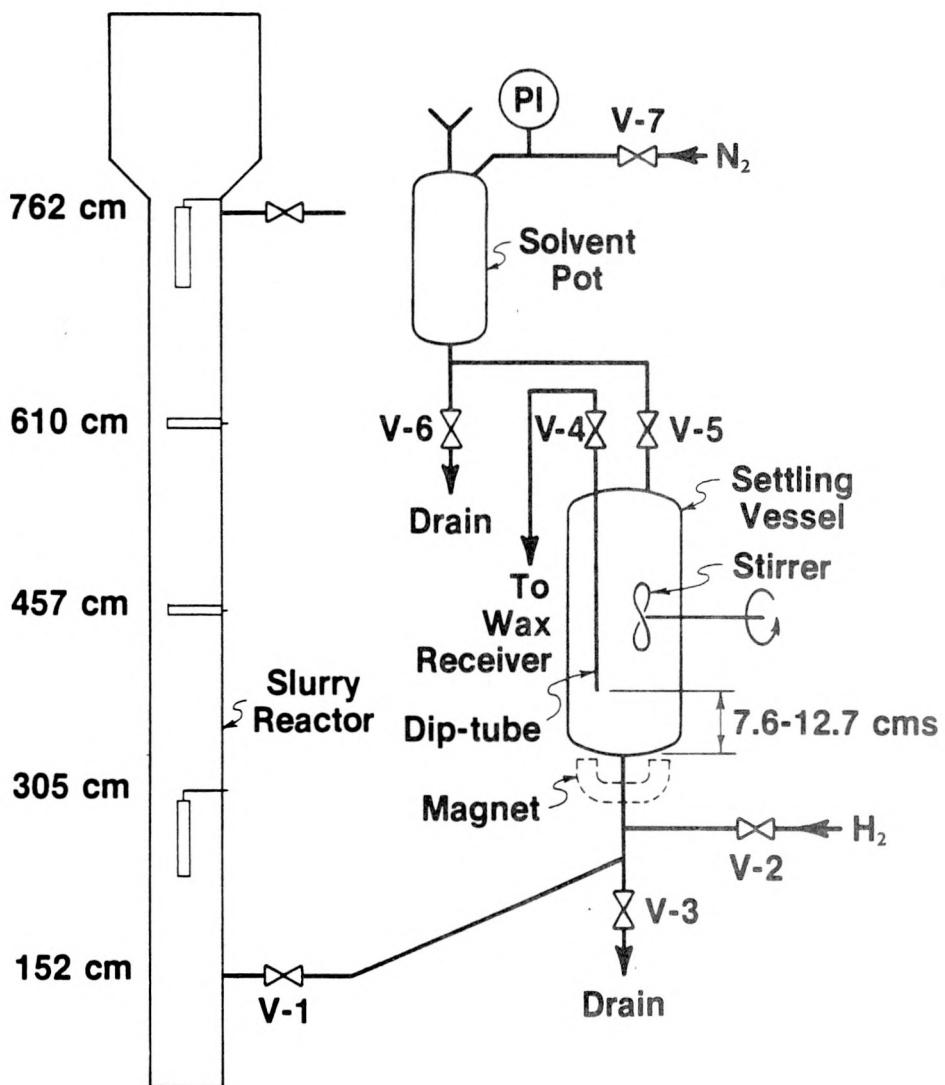


Table 22

Results of Fischer-Tropsch Catalyst Slurry Settling Study

Exp. No.	Temp. °C	Dip-Tube Position from Bottom	Magnet	Settling Time, Mins.							
				0	10	20	30	45	60	120	180
<u>Catalyst Concentration in Reactor-Wax After Settling, Wt %</u>											
1	204	7.6	No	7.4	-	-	-	-	6.85	2.44	1.25
2	204	7.6	Yes	8.69	-	-	-	-	0.08	.005	.005
3	204	10.2	Yes	9.5	-	-	-	-	.05-0.2	-	-
4	204	10.2	Yes	5.5	-	0.03	0	0	-	-	-
5 ⁽¹⁾	204	10.2	Yes	5.6	-	-	2.08	1.4	0.88	-	-
6	177	10.2	No	2.6	-	-	0.44	-	0	-	-
7 ⁽²⁾	177	10.2	No	3.5	0	0	-	-	-	-	-

(1) Continuous 1 cm³/s hydrogen purge.

(2) The slurry was diluted with equal volume of n-dodecane.

6).

At twenty-nine DOS, a test of adding fresh I-B catalyst without pretreatment to the slurry reactor was carried out. Fresh catalyst (493 g) was mixed with 283 g of Mobil F-509 and 2,000 g of used reactor-wax, and added to the slurry reactor. This raised the catalyst loading in the reactor to about 12 wt %. As seen from Figure 27, the H_2+CO conversion increased slightly from 38 to 42%, but dropped slowly back to 40% at thirty-four DOS. The fresh catalyst did not seem to be activated at the synthesis conditions. The variation on methane + ethane yield was also small. This run was voluntarily terminated at thirty-seven DOS.

Table E-1 of Appendix E gives the operating conditions and material balances carried out during the run, while Table E-2 reports the corresponding hydrocarbon product compositions. Since there was substantial and continuous catalyst loss during the first seventeen days of operation, the synthesis operation was not steady. Hence, the material balances carried out during this period were not reported. All reported material balances were adjusted by deducting the estimated dodecane content from the total hydrocarbon liquids. The dodecane was used for washing the slurry settling tank at the end of each settling operation.

It seems that for all balances the weights of hydrocarbons produced per Nm^3 of H_2+CO converted were somewhat higher than $207 \text{ gHC}/Nm^3$ H_2+CO converted, estimated based on a formula of $CH_{2.1}$ for all hydrocarbons. This may be due to the following causes:

- The presence of oxygenates changes the stoichiometric balance of the synthesis reaction. For example, it was roughly estimated that the hydrocarbons produced in this run may contain about 3.5 wt % of oxygen due to the high oxygenates content as described later. Then, the stoichiometric weight of the hydrocarbons (including oxygenates) produced per Nm^3 H_2+CO converted shall have been increased to 217 instead of 207 g.
- Part of the dodecane used for washing the slurry settling tank could have been present in the reactor and some of it could have converted to other hydrocarbons. This unaccounted amount of dodecane could have increased the total hydrocarbon yield per Nm^3 of H_2+CO converted.
- Another speculation is that there may be a slight underestimation of the H_2+CO conversion due to some inaccuracies in analysis. At lower levels of H_2+CO conversion accompanied in this run, these inaccuracies may accentuate the error in H_2+CO conversion calculation.

Table E-3 shows a set of typical F-T hydrocarbon selectivities from this run (26.3 DOS).

Occasionally, the reactor-wax was analyzed for carbon-number distribution and viscosity; the results are summarized in Table E-4. The reactor-wax before seven DOS may still contain some amount of the start-up medium as indicated by a peak carbon number of 35. The compositions of reactor-wax at seventeen and thirty DOS are similar and, hence, these represent the steady-state reactor-wax composition under these conditions. The peak carbon number of the equilibrium reactor-wax is 27, with an average carbon number of about 29.4, which is higher than the average carbon number (28) of the reactor-wax obtained during Run CT-256-3. This is expected because of the higher operating pressure used in the current run. The higher average carbon number is also reflected in the higher viscosities measured (two to three times higher). Based on the literature correlations (Shah, et al., 1982) the bubble-column gas holdup is inversely proportional to a 0 to 0.17 power of the viscosity. The maximum reduction of the gas holdup resulting from the higher viscosity is about 17%, not a large reduction.

The acid numbers of the F-T liquid hydrocarbons were substantially higher (ranging from 10 to 32 mgKOH/g) than those of Run CT-256-3 (1-3 mgKOH/g). The acid numbers of the aqueous phase were also higher (35-109 mgKOH/g) compared to 2-7 mgKOH/g for Run CT-256-3. The effect of these high acid numbers on the second-stage catalyst performance was not studied.

F. Run CT-256-5

1. Highlights

The fifth BSU run, designated Run CT-256-5, was started on February 17, 1983, and shut down voluntarily after thirteen days. The objective of the run was to evaluate a new first-stage F-T catalyst (Fe/Cu/K₂CO₃, designated I-C). The second-stage ZSM-5 reactor was not run. The major events of this run and ranges of process variables and operating results are summarized in Tables 23 and 24, respectively.

Major highlights of the run were:

- The catalyst was activated at the same conditions as those for synthesis (250°C, 1.48 MPa).

Table 23

Major Events in Run CT-256-5

<u>DOS</u>	<u>Event</u>
0-1.2	Started synthesis (1st-stage only); 250°C; 1.48 MPa; 6.0 cm/s
1.2	250--->240°C; 3.5 cm/s
2.0-3.0	Lost appox. 25% of catalyst
3.4	240°C; 3.5--->3.1 cm/s
4.4	240--->245°C
6.2	245--->250°C; 3.2 cm/s
8.3	3.2--->3.0 cm/s
13.0	Cold shutdown

Table 24

Ranges of Process Variables and Operating Results
(Run CT-256-5)

<u>First-Stage Process Variables</u>	<u>Range</u>
Temperature, °C	240-250
Pressure, MPa	1.48
Superficial Feed-Gas Velocity, cm/s	3.0-6.0
SV, NL/gFe-hr	2.1-2.7
Catalyst Loading, Wt %	10-20
<u>Operation Results</u>	
H ₂ +CO Conversion, Mol %	50-70
Methane + Ethane Yield, Wt % HC	1.6-3.5
Reactor-Wax Yield, Wt % HC	57-85

- The ranges of operating conditions for the first-stage reactor were:

Temperature, °C	240-250
Pressure, MPa	1.48
H ₂ /CO Feed Ratio, Molar	0.7
Superficial Feed-Gas Velocity, cm/s	3.0-6.0
SV, NL/gFe-hr	1.7 2.7

The H₂+CO conversion ranged from 50 to 72%, and the methane + ethane yield from 1.6 to 3.5 wt % of the total hydrocarbons produced.

- The reactor-wax yield was extremely high, ranging from 57 to 85 wt % of total hydrocarbons produced.

At the conclusion of the run the slurry was allowed to cool in-situ, without exposing it to air. In this way the catalyst may be used again at a future date. Catalyst loading at the start of this run was 20%, the same as in the previous run.

2. First-Stage Fischer-Tropsch Reactor Operation

To achieve an initial space velocity of 2.7 NL/gFe-hr, the superficial gas velocity was set at 6.0 cm/s, the highest ever attempted in the first-stage slurry reactor. No adverse effects of this were detected, and the activation of the catalyst proceeded smoothly. Figure 30 shows the conversion, as well as the methane and ethane yields, for the entire run. Material balances were performed daily after three DOS, and are tabulated in Table F-1 of Appendix F. From Figure 30 it is seen that the H₂+CO conversion rose steadily over the first twenty-four hours to 62%, while at the same time, the methane and ethane selectivity dropped to about 1.7 wt % of the total hydrocarbons produced. Under these conditions, the reactor-wax yield was over 85 wt % of hydrocarbons, which was more than what could be handled by the catalyst settling system. It was, therefore, decided to lower the synthesis gas throughput (3.5 cm/s) and the temperature (240°C), so that the conversion would remain nearly constant, while the reactor-wax make would be reduced. Initially, the conversion dropped to 54%, but it reached 60% after six hours. Reactor-wax withdrawals were begun at this time, lasting twelve hours each day, which was more than enough to keep up with the reactor-wax production for the rest of the run. Figure 31 is a plot of the cumulative reactor-wax production during the run. Table F-2 and F-3 tabulate the compositions of the non-wax and reactor-wax hydrocarbon products for different times on stream. Table F-4 summarizes two sets of F-T hydrocarbon selectivities. One represents those at 240°C (3.8 DOS) and the other those at 249°C (8.8 DOS).

FIGURE 30
SYNTHESIS GAS CONVERSION
AND METHANE & ETHANE YIELD

**(RUN CT-256-5;
 1ST-STAGE CATALYST I-C: PPTD Fe/Cu/K₂CO₃)**

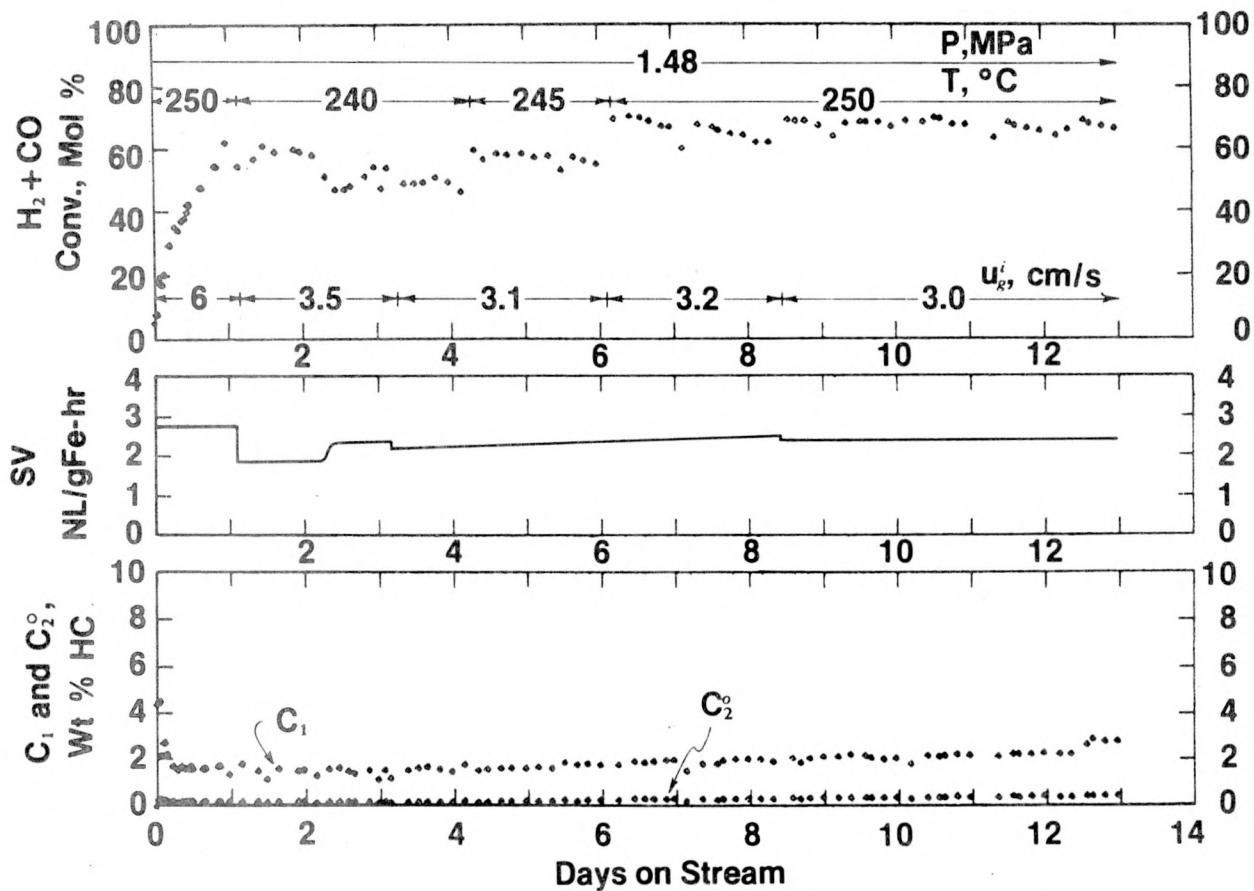
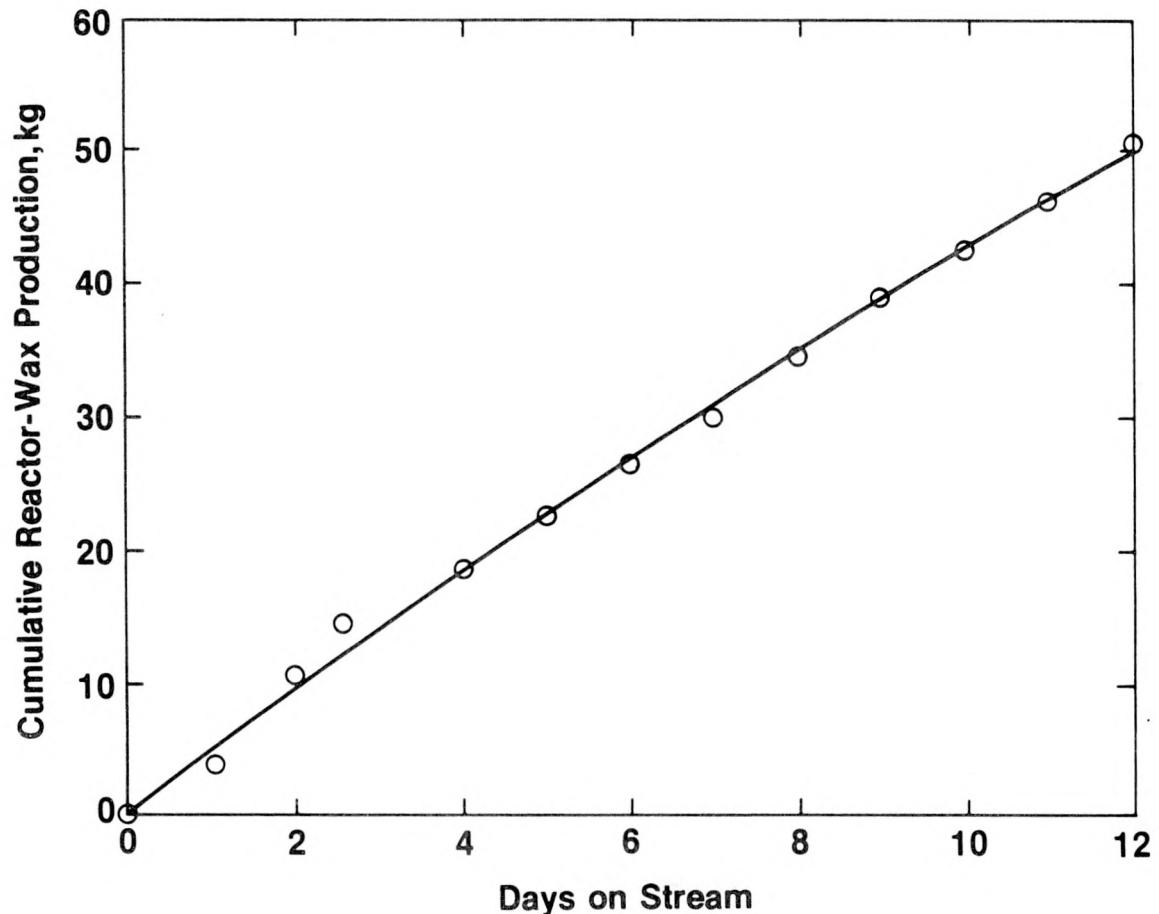


FIGURE 31
CUMULATIVE REACTOR-WAX PRODUCTION
FROM FIRST-STAGE
FISCHER-TROPSCH REACTOR
(RUN CT-256-5)



The reactor-wax withdrawal was carried out smoothly up to three DOS. Unfortunately, however, an operational error had occurred while draining wax at that time, and approximately 25% of the catalyst in the slurry reactor was accidentally removed. This caused the H_2+CO conversion to drop to 50%. The superficial gas velocity was then reduced to 3.1 cm/s to increase the H_2+CO conversion. After this point, catalyst losses were relatively constant, averaging less than 1% of the total inventory per day.

At four DOS, the reactor temperature was raised to 245°C which resulted in higher H_2+CO conversion (60%), but no appreciable change in the methane or ethane yield. Over the next two days, however, gradual catalyst losses dropped the conversion to 56%, at which time the temperature was increased to 250°C where it remained for the balance of the run. Initially, the conversion was as high as 70%, but gradually declined to 63% in two days due to a slight catalyst loss. At this point the superficial gas velocity was lowered by 6% to compensate for the catalyst losses. This brought the conversion back to 69%, and it remained between 66 and 70% for the rest of the run.

The catalyst loss after eight DOS was substantially less than the loss at the earlier time due to an improved shorter dip-tube design of a new on-line slurry settling tank at the 152 cm level. This also resulted in less reactor-wax withdrawal per operation.

The methane + ethane yield increased slowly but constantly during this run. Changing temperature did not show any short-term effects. It appears that at low temperature (240°C) the methane + ethane yield changed more slowly than at higher temperature. This may indicate a long-term aging effect.

Figure 32 shows the reactor-wax yield as a function of the methane yield, covering all the BSU runs. The range of methane yield covered by Run CT-256-5 was 1.5 to 2.8 wt % of total hydrocarbons produced. Similar data from literature are also included in this figure showing good agreement.

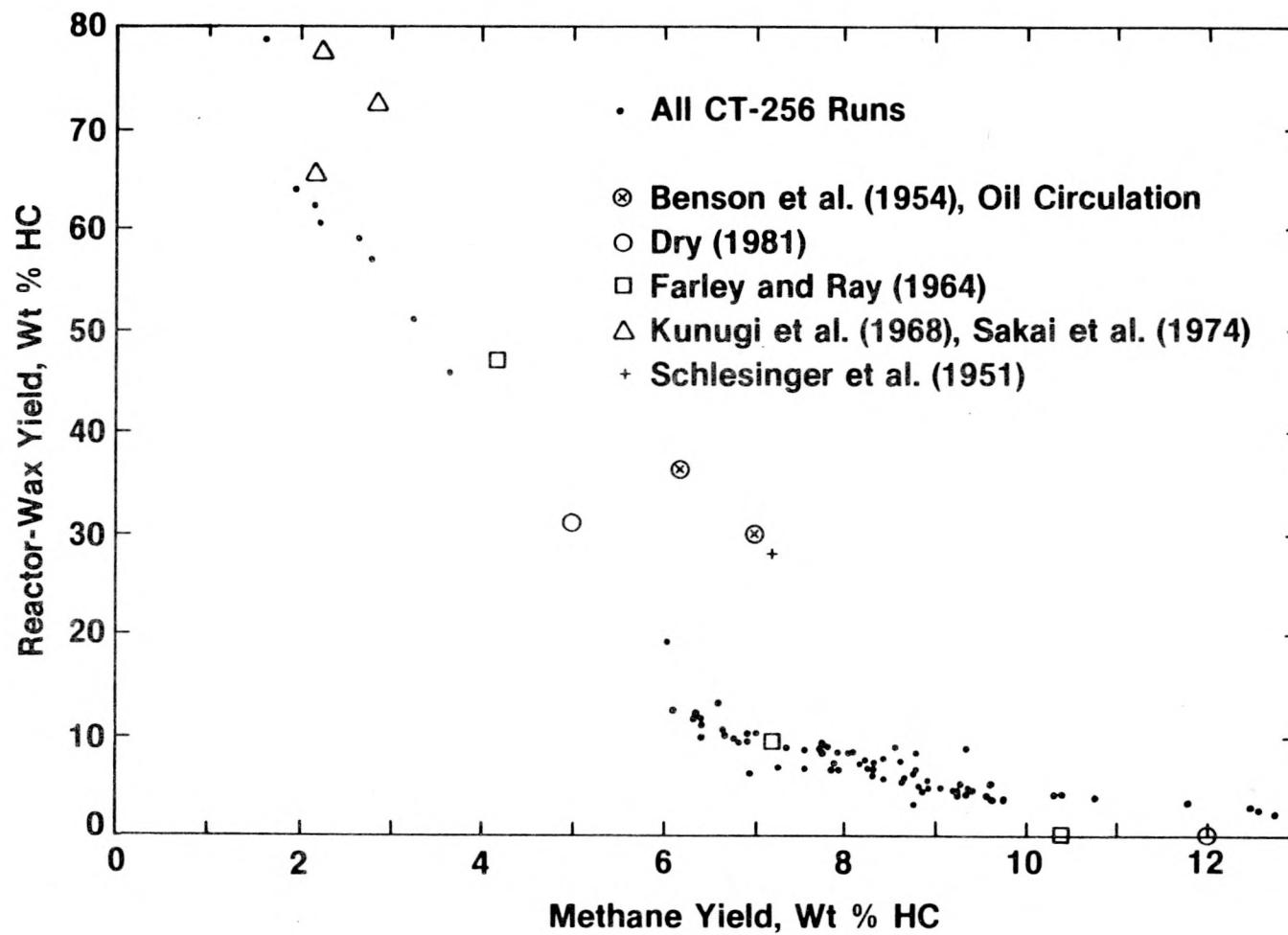
Run CT-256-5 was ended after thirteen days when a seal on the Mobiltherm circulating pump ruptured. This caused the reactor temperature to drop, and it was decided to perform a cold in-situ shutdown. That is, the slurry was allowed to solidify in the reactor under nitrogen flow. In this way the slurry may be reused in the future.

Similar to what was observed in Run CT-256-4, the acid number of a F-T liquid hydrocarbon sample was substantially higher (27 mgKOH/g) than those of Run CT-256-3 (1-3 mgKOH/g). The acid number of an aqueous sample was also higher (92 mgKOH/g), compared to 2-7 mgKOH/g from Run CT-256-3. Since the second-stage reactor was not operating during this run, the

FIGURE 32

REACTOR-WAX YIELD VERSUS METHANE YIELD

-601-



effect of these high acid numbers on the ZSM-5 performance is unknown.

G. Slurry Reactor Hydrodynamic Studies

1. Bubble-Column Gas Holdup

The bubble-column reactor of the BSU was designed to gather gas holdup data using a differential pressure (DP) measuring system, and catalyst concentration data using a slurry sampling system (see Section IV.C for detailed description of these systems). Such data are essential for analyzing the performance of the reactor, for providing essential parameters for a slurry reactor mathematical model, and for characterizing factors in scale-up of the slurry reactor.

During Run CT-256-1, the DP measuring system was inoperative due to plugging of the DP nozzles and lines. However, the average gas holdups were estimated by accounting for the quantity of the reactor-wax between the view-ports along the slurry reactor and the feed-gas distributor. These estimations were done at the beginning and the end of the run. In Run CT-256-3, after modifications, the DP measuring system performed well and gas holdup profiles were estimated. The highlights of these experiments are:

- In Run CT-256-1, the initial gas holdup was very high (about 63 vol % at 2.2 cm/s feed-gas superficial velocity) probably due to the initial reactor-medium used. At the end of the run the gas holdup was 29% at 1.8 cm/s.
- There were no significant changes in gas holdup during the major part of Run CT-256-3.
- The average gas holdup increases with decreasing slurry level. This is consistent with the existence of a three-zone gas holdup profile first postulated by Langemann and Koelbel (1967).
- At low gas velocities, a hysteresis phenomena was observed, i.e., increasing the velocity did not instantly increase the gas holdup. This may have been due to catalyst settling at the low velocity, and difficulty to reentrain the catalyst at the higher velocity.
- The measured gas holdups were consistently higher than those reported by Deckwer, et al, (1980).

At the beginning of Run CT-256-1, a given quantity of the slurry was loaded into the first-stage bubble column reactor. By observing the slurry level at the viewport at 762 cm height, a gas holdup of 63 vol % at 2.2 cm/s superficial gas velocity was estimated. Such a high gas holdup was unexpected and greatly limited the initial loading of the F-T catalyst during the run. At the end of the run, slurry was withdrawn in stages by observing the slurry levels at the three viewports along the reactor. The quantities of the slurry withdrawn between viewports were measured and used to estimate the average gas holdups:

DOS	u_{gm} cm/s	w_c wt %	L cm	<u>Avg. ϵ_g, Vol %</u>	
				<u>This Study</u>	<u>Deckwer, et al. (1982b)</u>
0.0	2.2	6.7	762	63	13
60.8	1.8	2.5	762	29	10
61.1	2.2	2.5	610	32	13
61.1	2.2	2.6	305	42	13

By comparing the average gas holdups of 762 cm column height at both the beginning and the end of the run, a drastic reduction in the gas holdup was observed. This was probably due to changing slurry medium during the run. The startup reactor-wax was very different from the equilibrium reactor-wax later established in the reactor (see Section VI.B for detailed description of startup wax used). The gas holdups at 762, 610 and 305 cm height estimated at the end of the run show that the average gas holdup increases when the column height decreases. This observation is consistent with that of Langemann and Koelbel (1967) in a non-reacting, cold-flow system. Similar results were also observed in a 2.5 cm ID hot-flow, non-reacting column, as reported later in Section VIII.E. A description of the existence of a three-zone gas holdup profile, first postulated by Langemann and Koelbel (1967) to explain this phenomena is also included in that Section. The above table also includes the gas holdups estimated from the correlation $\epsilon_g = 0.053 (u_g)^{1.1}$ developed by Deckwer, et al. (1980). These estimated values are consistently below the corresponding experimental values.

Table 25 summarizes overall gas holdups taken from different times on-stream of Run CT-256-3. It can be seen from this table that the holdup did not change very much over the first seventy-five days on-stream. However, the data from seventy-nine to eighty-one DOS show a hysteresis effect of the gas holdup. That is, after the velocity was dropped to 1.1 cm/s, the gas holdup did not respond instantly with raising the velocity. This may have been due to catalyst settling at the low velocity as described earlier, and difficulty in re-training

Table 25

Summary of Estimated Gas Holdup from DP-Cell Data
 (Run CT-256-3)

DOS	9.2	75.5	78.6	78.8	80.8
u_g^i , cm/s	3.9	2.6	1.1	2.6	2.6
T, °C	260	267	260-267	260-267	267
P, MPa	1.48	2.51	2.51	2.51	2.51
w_c , Wt %	14.3	13.9	11.7	12.0	12.0
ϵ_g , Vol %	26.6	19.7	6.8	9.3	19.8

the catalyst at the higher velocity. Figure 33 illustrates the typical gas holdup profiles along the bubble-column reactor in Run CT-256-3. This profile is similar to that reported by Langemann and Koelbel (1967) in cold-flow bubble-columns.

The gas holdup near the top of the column is high, due to the fact that the bubbles have to disengage from the slurry, i.e., an end effect. At the bottom of the column there is a short zone where the gas holdup changes dynamically with distance. This arises from the bubble dispersion, formation, and coalescence. After that the holdup decreases, probably due to the fact that the gas volume contracts as the reaction proceeds. Two separate profiles show that the gas holdup is similar at the beginning and the end of the run, with absolute differences due to the change in the gas velocity.

2. Bubble-Column Catalyst Settling

Uniform catalyst distribution in bubble-column reactors is important for obtaining effective use of the catalyst and for maintaining a uniform slurry temperature. During operation of the BSU, catalyst concentration profiles were occasionally obtained by taking slurry samples from several fixed locations of the bubble-column reactor and then by burning off the wax from the samples. The solids concentration profiles for different days on-stream of Run CT-256-3 are plotted in semi-log fashion in Figure 34 corresponding to different gas velocities. The straight lines shown by this plot indicates that the trend of the catalyst concentration profile follows very well the established particle settling mathematical model in bubble-columns (Kato, et al., 1972). Highlights of this figure are:

- Increased velocity decreases the catalyst settling, so a flatter profile is achieved.
- The profile is steeper during the hydrodynamics upset at eighty-two DOS, indicating increased catalyst settling. The profile after the upset is slightly flatter.

No meaningful catalyst concentration profile data are available between ten and eighty-two DOS. It also is not clear if the steeper concentration profile at the end of the run could be completely attributed to lower gas velocity.

A "hydrodynamic upset" of the slurry reactor occurred at eighty-two DOS, probably due to catalyst settling, resulting in a low H_2+CO conversion and a 5°C lower temperature at the upper portion of the reactor. The upset disappeared after eight hours of high gas velocity operation, but reappeared after the velocity was lowered (see Section VI.D for description of Run CT-256-3).

FIGURE 33

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN
GAS HOLDUP PROFILES

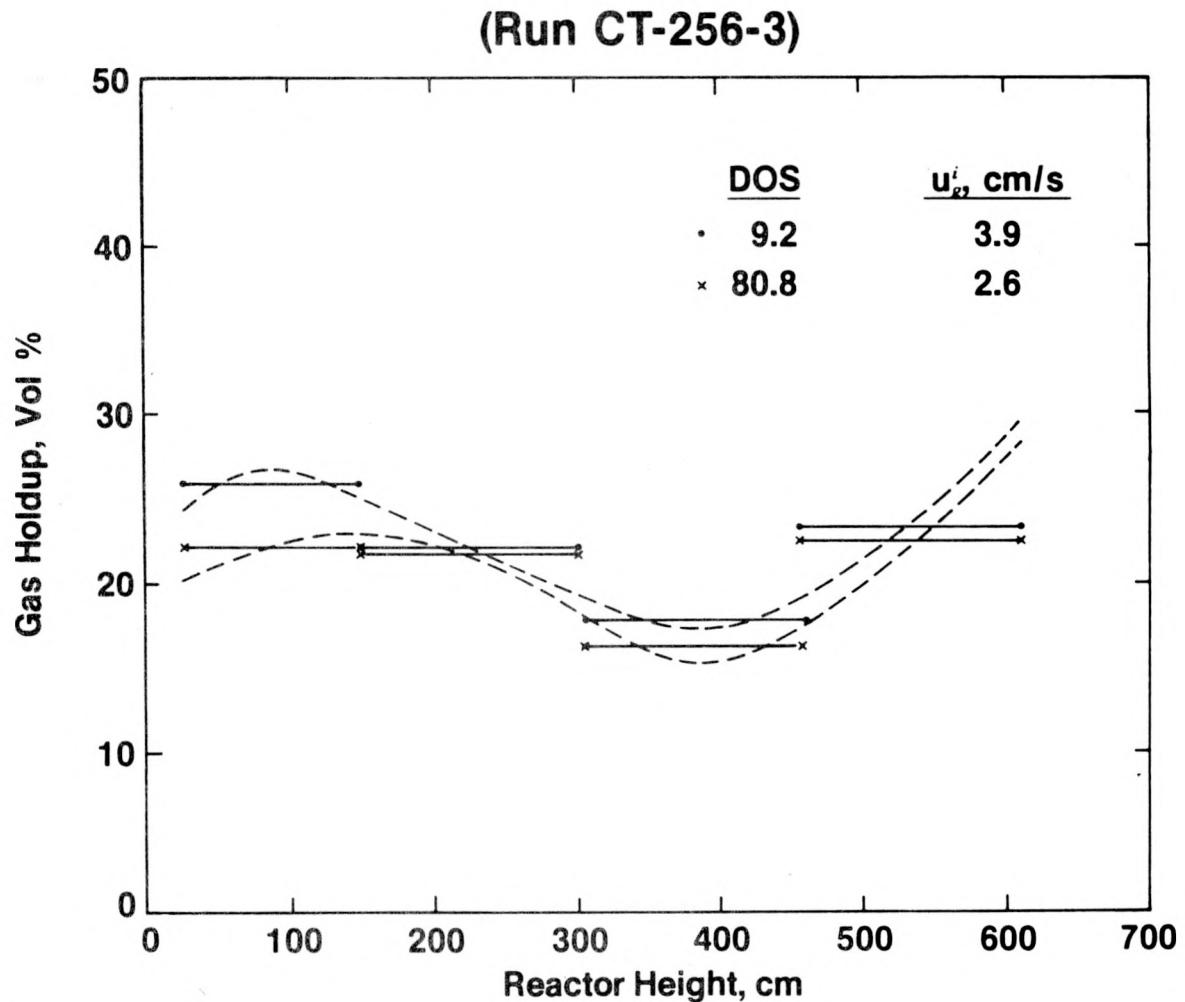
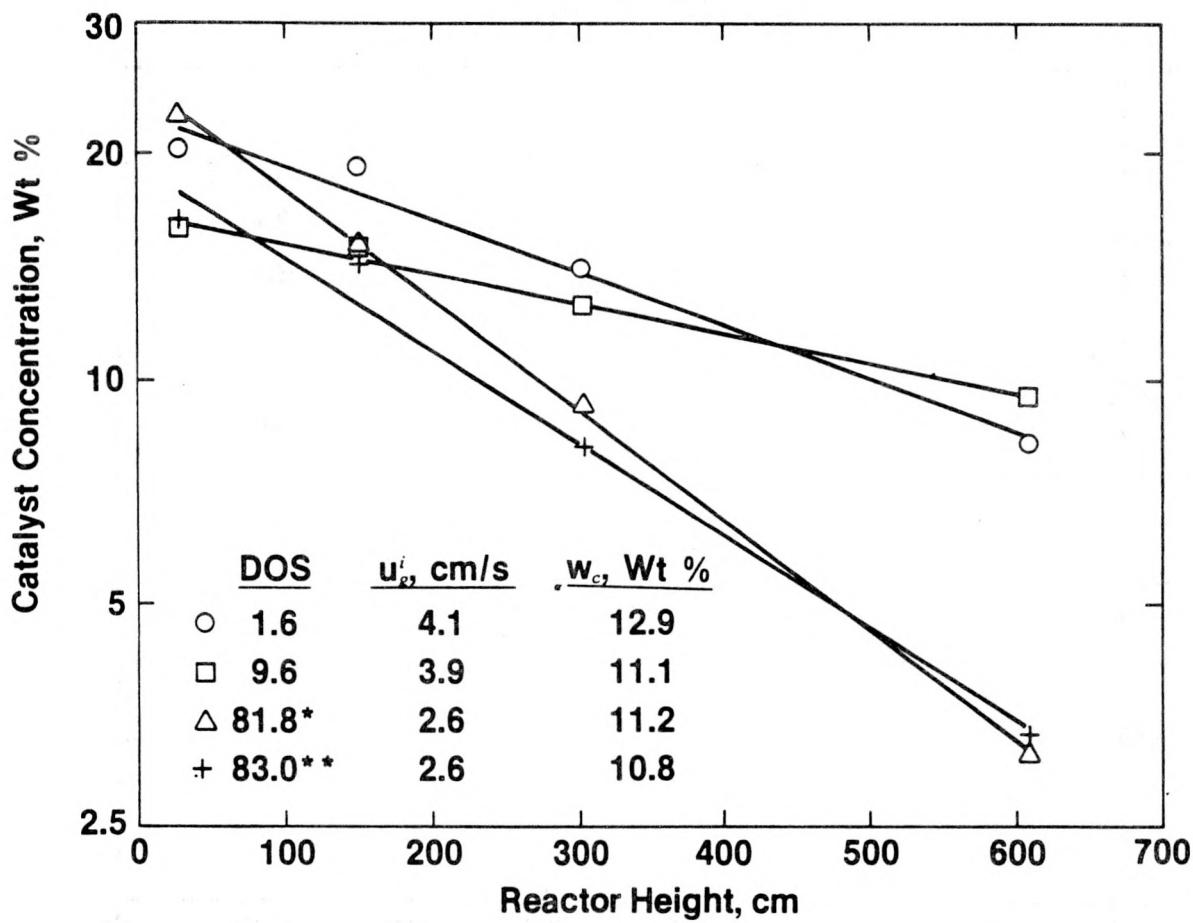


FIGURE 34

SLURRY FISCHER-TROPSCH BUBBLE-COLUMN
CATALYST CONCENTRATION PROFILES

(Run CT-256-3)



*During hydrodynamic upset

**After hydrodynamic upset was corrected

VII. Fischer-Tropsch Bubble-Column Reactor Mathematical Models and Their Applications

A. Introduction

The design and operation of the second-stage ZSM-5 fixed-bed reactor are rather straightforward. On the other hand, the slurry Fischer-Tropsch reactor is unconventional and involves complicated transport phenomena. A realistic mathematical model of such a system would be extremely useful in aiding the pilot plant reactor design and the data interpretation.

There were several published mathematical models of Fischer-Tropsch bubble-column reactors, e.g., Deckwer, et al. (1981a and 1982b), Satterfield and Huff (1980), and Stern, et al. (1983). Each of these models accounted for certain features of the Fischer-Tropsch bubble-column reactor, but none were sufficiently complete to provide good reactor design and data interpretation. For example, Deckwer et al. (1981a and 1982b) used single component (H_2) models and simple first-order kinetics for the F-T reaction; Satterfield and Huff (1980) simplified the model further by assuming no volume contraction by the F-T reaction; Stern, et al. (1983), although using a multi-component (H_2 , CO , CO_2 , H_2O) model, did not consider the interaction between the F-T and the water-gas shift reactions and used an unrealistic expression for the volume contraction due to the F-T reaction.

In this chapter, some simple, single-component (H_2) F-T reactor mathematical models were developed first to evaluate the F-T bubble-column performance and to determine the conditions for optimal utilization of the reactor volume. An improved multi-component mathematical model was then developed. This sophisticated model takes into account the existence of both the F-T and the water-gas shift reactions, the non-linear kinetic expressions for both reactions, and multi-component (H_2 , CO , CO_2 and H_2O) transport phenomena.

B. Transport Phenomena in Slurry Fischer-Tropsch Reactors

In a slurry F-T reactor, the following transport and kinetic steps occur:

1. Transfer of the reactants from the bulk gas phase to the gas-liquid interface.
2. Transfer of the reactants from the gas-liquid interface to the bulk liquid phase.

3. Mixing and diffusion of the reactants in the bulk liquid phase.
4. Transfer of the reactants to the external surface of the catalyst particles.
5. Diffusion of the reactants inside the catalyst pores to the catalyst active sites.
6. Conversion of the reactants to products at the active sites.
7. Diffusion of reaction products from the active sites to the catalyst particle surface.
8. Transfer of the products from the catalyst to the bulk liquid.
9. Transfer of the products from the bulk liquid to the gas-liquid interface.
10. Transfer of the products from the gas-liquid interface to the bulk gas.

The first six transport and kinetic steps contribute the resistances to transfer the reactants from the bulk gas to the catalyst and their conversion to products. Steps 7-10 contribute the resistances to transfer the products from the catalyst to the bulk gas. Of these, steps 5 and 7, the internal diffusion resistance, are negligible due to the very small size of the catalyst particles, usually $\leq 50\mu\text{m}$.

In order to determine the relative resistance contributed by each transport step, it is sufficient to evaluate the transport of H_2 (Steps 1-4). Figure 35 shows a schematic concentration profile, and definitions and typical values of those resistances. The values of the parameters used in calculating the typical values of those resistances are summarized in Table 26.

The largest resistance among all the steps is the kinetic resistance. However, the resistance attributed to the diffusion of H_2 from the gas-liquid interface to the bulk liquid is also important. Other resistances are negligible. Hence, only Steps 2, 6, and 9 are considered in constructing mathematical models.

FIGURE 35

MASS-TRANSFER RESISTANCES IN A GAS-LIQUID-SOLID SYSTEM

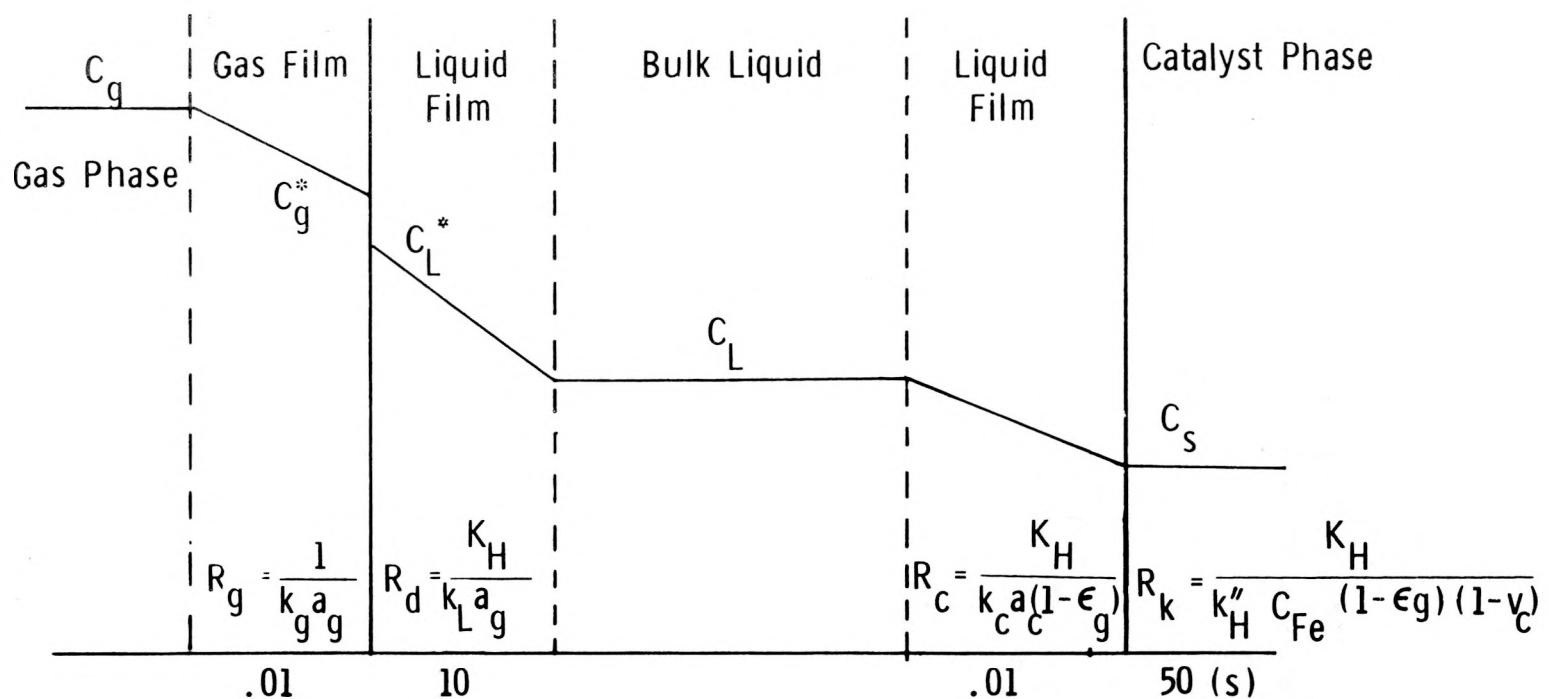


Table 26

Parameters Used in Single-Component
F-T Slurry Reactor Mathematical Model Calculations

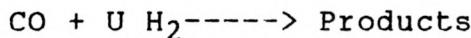
$T = 265^\circ C$ ($509^\circ F$)	$C_C = 0.1 \text{ g/cm}^3$ (6.2 lb/ft^3)
$P = 1.38 \text{ MPa}$ (200 psia)	$f = 0.7$
$u_g^i = 4 \text{ cm/s}$ (0.13 ft/s)	$U = 1/1.55$
$d_C = 2.5 \mu\text{m}$	$d_B = 0.7 \text{ mm}$
$\epsilon_g = .243$	$k''_H = 1.1 \text{ cm}^3 \text{ liquid/s-gFe}$
$K_H = 4.4$	$k_L = .013 \text{ cm/s}$
$k_C = .39 \text{ cm/s}$	$k_g = 3.43 \text{ cm/s}$
$\rho_C = 2.6 \text{ g/cm}^3$	

C. Bubble-Column Mathematical Models

1. Single-Component (H_2) Models

Single-component mathematical models were developed to assist in design and operation of the bench-scale bubble-column reactor. The major assumptions of these simple models are:

- Mass transfer resistance to diffusion at the liquid side of the gas-liquid interface.
- Single Fischer-Tropsch reaction



with first order rate in H_2

$$r_H = k_H'' C_{HL} \text{ (Mol H}_2/\text{gFe-s)}$$

- Constant H_2/CO usage ratio U
- Molar contraction due to synthesis reaction is a linear function of synthesis gas conversion
- Constant bubble-size and gas holdup
- Steady-state isothermal and isobaric operation
- Plug flow gas

The material balance equations are:

Gas Phase

$$\frac{d(u_q - C_{Hq})}{dz} = k_{LH} a_q (C_{HL} - C_{Hq}/K_H) \quad (5)$$

Convection in Gas Phase Diffusion from Gas-Liquid Interface to Liquid

Liquid Phase

Non-Mixed (NM):

$$k_{LH} a_g (C_{HL} - C_{Hg}/K_H) = -k_H'' C_{Fe}(1-v_C)(1-\epsilon_g) C_{HL} C_C / C_{Ca} \quad (6)$$

Diffusion from Gas-Liquid Interface to Liquid

Kinetic Dissipation at Catalyst Surface

Perfectly Mixed (PM):

$$\int_0^L k_{LH} a_g (C_{HL} - C_{Hg}/K_H) dz = -k_H'' C_{Fe}(1-\epsilon_g)(1-\epsilon_c) C_{HL} L \quad (7)$$

Diffusion from Gas- Kinetic Dissipation at
Liquid Interface Catalyst Surface
to Liquid

Axially dispersed (AD):

$$E_L (1-\epsilon_g) (1-\epsilon_c) d^2 C_{HL}/dz^2 = k_{LH} a_g (C_{HL} - C_{Hg}/K_H) \quad (8)$$

Axial Dispersion in Diffusion from Gas-Liquid
Liquid Phase Interface to Liquid

+ $k_H'' C_{Fe} (1-\epsilon_g) (1-\epsilon_c) C_{HL} C_c/C_{ca}$

Kinetic Dissipation
at Catalyst Surface

with following boundary conditions:

$$C_{Hg} = C_{Hg}^i \quad dC_{HL}/dz = 0 \text{ at } z = 0 \quad (9a)$$

$$dC_{HL}/dz = 0 \text{ at } z = L \quad (9b)$$

Catalyst Settling

$$E_c d^2 C_c/dz^2 + u_{cs} dC_c/dz = 0 \quad (10)$$

Catalyst Axial Catalyst
Dispersion Settling

$$E_c dC_c/dz + u_{cs} C_c = 0 \text{ at } z = 0 \text{ or } z = L \quad (11a)$$

$$\int_0^L C_c(z) dz/L = C_{ca} \quad (11b)$$

The non-mixed (NM) and perfectly mixed (PM) liquid models represent extremes of liquid mixing, while the axial dispersion (AD) model represents the liquid mixing predicted by correlations using axial dispersion coefficients from open literature. The NM model is similar to that used by Deckwer et al. (1981a), although Deckwer erroneously stated that the model represents perfect mixing in the liquid. The new model used here also accounts for the catalyst settling, while Deckwer et al. (1981a) neglected that effect. The AD model is similar to that described by Deckwer et al. (1982b), with simplifications of

no axial dispersion in the gas and isothermal operation.

The catalyst concentration along the bubble-column reactor can be obtained directly by solving equations (10)-(11), as:

$$C_C/C_{Ca} = Pe_C(\exp(-Pe_C \bar{z}))/(1-\exp(-Pe_C)) \quad (12)$$

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

$$u_g = u_g^i (1 + \alpha X_{H_2+CO}) \quad (13)$$

where α is the constant molar contraction factor.

Introducing equations (12) and (13) into equations (5)-(9) and then converting them to dimensionless form yields:

Gas Phase

$$((1+\alpha^*)/(1+\alpha^*\bar{y})^2) d\bar{y}/d\bar{z} = St_d (\bar{x}-\bar{y}) \quad (14)$$

Liquid Phase

NM Case:

$$St_d (\bar{y}-\bar{x}) = St_k C_C \bar{x} \quad (15)$$

PM Case:

$$\int_0^1 St_d (\bar{y}-\bar{x}) dz = St_k \bar{x} \quad (16)$$

AD Case:

$$Pe_L^{-1} d^2 \bar{x}/d\bar{z}^2 = K_H St_d (\bar{x}-\bar{y}) + K_H St_k C_C \bar{x} \quad (17)$$

with following boundary conditions:

$$\bar{y}=1 \quad d\bar{x}/d\bar{z} = 0 \quad \text{at } \bar{z} = 0 \quad (18a)$$

$$d\bar{x}/d\bar{z} = 0 \quad \text{at } \bar{z} = 1 \quad (18b)$$

For the NM and PM cases, the equations can be solved analytically, giving the H_2 conversion as an implicit function of the parameters:

NM Case:

$$L = -u_g^i R_d (\alpha^* X_H^e + (1+\alpha^*) \ln(1-X_H^e)) - E_c (\ln B_1) / u_{cs} \quad (19)$$

where:

$$B_1 = (P_e_c + B_2 (1 - \exp(-P_e_c))) / (P_e_c - B_2 (1 - \exp(P_e_c))) \quad (20)$$

$$B_2 = R_k / R_d \quad (21)$$

PM Case:

$$L = -u_g^i R_d (\alpha^* X_H^e + (1+\alpha^*) Y \ln(1-X_H^e/Y)) / (1+\alpha^* Z) \quad (22)$$

where Y is defined as $(1-Z)/(1+\alpha^*Z)$ and X_H (H_2 conversion) as $1-u_g C_{Hg} / u_g^i C_{Hg}^i$. By integration of Equation (5) and substitution of the resulting equation into Equation (7), a relation between Z and X_H^e is established as follows:

$$Z = X_H^e / St_k \quad (23)$$

Substitution of Equation (23) into Y and Equation (22) gives the implicit relation between X_H^e and L .

For the AD case, the model equations are non-linear, due to the variation of the gas superficial velocity with the molar contraction (term $(1+\alpha^*)/(1+\alpha^*\bar{y})^2$ in Equation (14)). A solution can be obtained by using an orthogonal collocation method (Villadsen and Michelsen, 1978).

Basically, the method uses a linear combination of one of the many families of orthogonal polynomials as a trial solution to the dependent variables. In the present application, the Jacobi polynomials with a weighting function $\bar{z}(1-\bar{z})$ are used. This family of polynomials is defined by the following equation:

$$P_j(\bar{z}) = \sum_{i=0}^j (-1)^{j-i} \gamma_{ij} \bar{z}^i \quad (24)$$

where

$$\gamma_{0j} = 1 \text{ for all } j \quad (25a)$$

$$\gamma_{ij} = \gamma_{i-1,j} (j-i+1)(j+i+2)/i(i+1) \quad (25b)$$

The orthogonality relation is given as

$$\int_0^1 \bar{z} (\bar{z}-1) P_i(\bar{z}) P_j(\bar{z}) d\bar{z} = 0 \quad \text{if } i = j \quad (26)$$

The trial solutions for both \bar{x} and \bar{y} , truncated to Nth order polynomials as

$$\bar{x} = \sum_{i=0}^{N+1} a_i P_i(\bar{z}) \quad (27a)$$

$$\bar{y} = \sum_{i=0}^{N+1} a_{N+2+i} P_i(\bar{z}) \quad (27b)$$

are substituted into Equations (14) and (17), and boundary conditions (18a) and (18b). The collocation method dictates that the trial solutions satisfy these equations exactly at the N interior collocation points, which are the zeros of the Nth order polynomial, and at two boundaries. This results in $2(N+2)$ algebraic equations containing $2(N+2)$ unknowns. However, the resulting algebraic equations are nonlinear; therefore, an iterative scheme is used to solve these equations. In the current application, the Newton-Raphson routine is used. The criteria of the iteration scheme is that the successive dependent variables at all collocation points and the reactor exit are within 0.1% of each other. Another independent iterative scheme involves a convergence of the hydrogen concentration in the reactor exit, which is used to evaluate some parameters used in the model calculation. The criteria for this iteration is that its successive values are within 1% of each other. It was found that five collocation points were sufficient to give accurate results in most cases.

The correlations used to estimate the various model parameters are given in Table 27. All the parameters are defined in the Nomenclature.

2. Multi-Component Model

This improved model includes multi-component (H_2 , CO , CO_2 , and H_2O) mass transfer; water-gas shift reaction; and, non-linear kinetics. This model gives a more realistic understanding of the F-T slurry reactor performance which will be discussed in Section D. The major assumptions different from those of the single component model are:

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

Table 27

**Correlations Used In F-T Slurry Reactor
Mathematical Model Calculations**

<u>Correlations⁽¹⁾</u>	<u>References</u>
$\rho_L = .758 - .555 \times 10^{-3}(T-373)$, g/cm ³	Deckwer, et al. (1982b)
$\mu_L = .052 \exp(-6.905+3266/T)$, g/cm-s	Deckwer, et al. (1982b)
$D_{LH} = 7.35 \times 10^{-3} \exp(-2285/T)$, cm ² /s	Satterfield & Huff (1980)
$K_H = (2.291 \times 10^4 \exp(-1.2326+1583/T))/R_G T$	Peter & Weinert (1955)
$\mu_{sl} = \mu_L(1 + 4.5 v_C)$, g/cm-s	Deckwer, et al. (1982b)
$\epsilon_g = .053 u_g^{1.1}$	Deckwer, et al. (1982b)
$k_L = .31(\mu_{sl}g(\rho_{sl}-\rho_g)/\rho_{sl}^2)^{1/3} Sc^{-2/3}$, cm/s	Calderbank & Moo-Young (1961)
$Sh \geq 2$	Saenger & Deckwer (1981)
$E_L = 3.676 u_g^{.32} d_R^{1.34}$, cm ² /s	Shah & Deckwer (1982)
$E_C = u_g d_R (1+8 Fr^{.85})/13 Fr$, cm ² /s	Kato, et al. (1972)
$u_{cs} = 1.2 u_{ct} \left(\frac{u_g}{u_{ct}} \right)^{.25} \left(\frac{1-v_C}{1-v_C^*} \right)^{2.5}$, cm/s	Kato, et al. (1972)
$Re = Ar/18$	Kato, et al. (1972)

⁽¹⁾T in °K.

- Two consecutive reactions:

- Fischer-Tropsch



$$r_1 = k_1 [H_2][CO]/([CO] + k_3[H_2O]) \quad (29)$$

- Water-Gas Shift



$$r_2 = k_2 ([CO][H_2O] - [H_2][CO_2]/k_4)/([CO] + k_3[H_2O]) \quad (31)$$

- Gas holdup varies with the local gas-superficial velocity.
- Non-mixed liquid.

The rate expression for the Fischer-Tropsch reaction, Equation (29), follows the work by Dry (1976). In both the rate expressions (29) and (31), [] signifies volumetric concentrations. Note that the same denominator is used in both rate expressions. This is consistent with the hypothesis of competitive adsorption of active species on the same catalytic active sites (Langmuir-type adsorption isotherm, Satterfield, 1980). Only the [CO] and [H₂O] appearing in the denominator indicate that both are strongly absorbed on the catalyst active sites.

Material balances for the gas- and liquid-phase of the components H₂, CO, CO₂ and H₂O (denoted by subscripts 1, 2, 3, 4, respectively), yield:

$$d(u_g C_{gi})/dz = -k_{Li} a_g (C_{gi}/K_i - C_{Li}), \quad i = 1, \dots, 4 \quad (32)$$

Convection in Gas Phase	Diffusion from Gas-Liquid Interface to Liquid
----------------------------	---

for the gas-phase, and

$$k_{Li} a_g (C_{gi}/K_i - C_{Li}) = -(1 - \epsilon_g)(1 - v_c) C_F e^{\sum S_{ij} r_j}, \quad i = 1, \dots, 4 \quad (33)$$

Diffusion from Gas- Liquid Inter- face to Liquid	Kinetic Dissipation at Catalyst Surface
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for the liquid-phase, with the following inlet conditions:

$$C_{gi} = C_{gi}^i \text{ at } z = 0, \quad i = 1, \dots, 4 \quad (34)$$

where r_1 and r_2 are, respectively, the F-T and the water-gas shift reaction rates given by Equations (29) and (31), and S_{ij} ($i = 1, \dots, 4$; and $j = 1, 2$) are elements of the stoichiometric matrix.

The molar contraction resulting from the F-T reaction is the same as that used in the single component model (Equation (13)).

In dimensionless form, Equations (32) to (34) become:

$$d(\bar{u}_g \bar{C}_{gi})/d\bar{z} + St_{di}(\bar{C}_{gi} - \bar{C}_{Li}) = 0 \quad (35)$$

$$St_{di}(\bar{C}_{gi} - \bar{C}_{Li}) + \sum S_{ij} St_{kj} \bar{r}_j = 0 \quad (36)$$

$$\bar{C}_{gi} = \bar{C}_{gi}^i \text{ at } \bar{z} = 1 \quad (37)$$

for $i = 1, \dots, 4$.

A solution for this set of non-linear equations can be obtained using the orthogonal collocation method (Villadsen and Michelsen, 1978). This method dictates that the trial solutions (linear combinations of orthogonal polynomials described in Subsection VII.C.1), satisfy the gas-phase and the liquid-phase equations exactly at the N interior collocation points, the inlet point, and the exit point. This results in a system of $8N+12$ non-linear algebraic equations, which are solved simultaneously by a Newton-Raphson routine. The convergence criterion of the iterative scheme is that the successive dependent variables at all collocation points be within 0.1% of each other. It was found that five collocation points were sufficient in most calculations as shown in Figure 36. The correlations used to calculate the parameters are summarized in Table 28. Those correlations that are common to both simple-component and multi-component models are given in Table 27.

Note that using variable gas holdup and interfacial area along the reactor length gives virtually identical results as the case of an average gas holdup and interfacial area as discussed later (see Subsection VIII.D.2.b). In the current case, the use of variable gas holdup and interfacial area actually simplifies the numerical iteration scheme, avoiding the necessity of an additional iteration on the parameters St_{kj} and St_{di} (which are dependent on ϵ_g and a_g).

FIGURE 36

EFFECT OF NUMBER OF COLLOCATION POINTS ON THE
PREDICTED F-T BUBBLE-COLUMN PERFORMANCE
(Base Case)

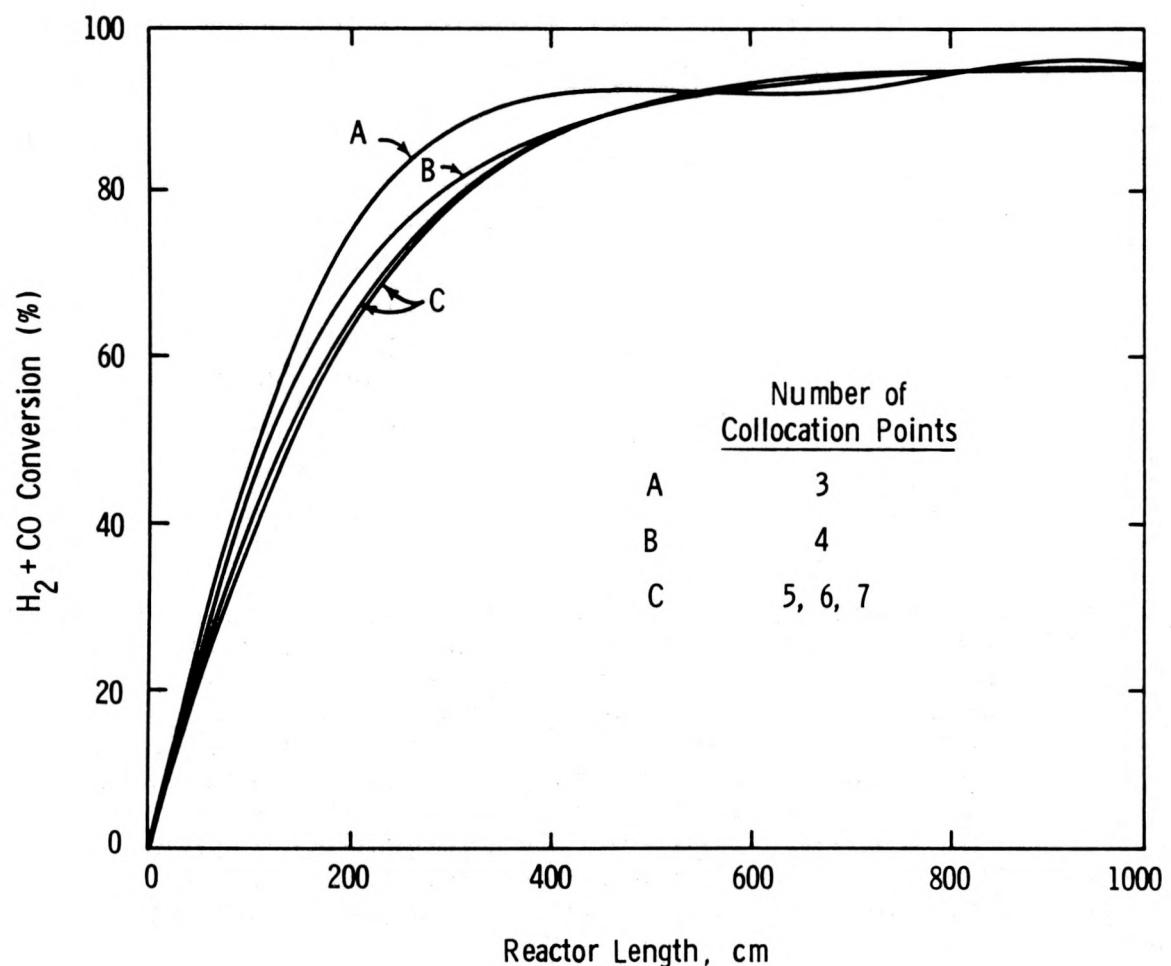


Table 28

Correlations for Solubility and Diffusivity⁽¹⁾Solubility (cm³ liquid/cm³ gas) $H_2 \quad 746 \quad T^{-1} \exp (639.9/T)$

Experimental

Koelbel, et al. (1955)
Peter & Weinert (1955) $CO \quad 878 \quad T^{-1} \exp (440.2/T)$

"

"

 $CO_2 \quad 2970 \quad T^{-1} \exp (-608.4/T)$

"

"

 $H_2O \quad 6740 \quad T^{-1} \exp (-1270/T)$

"

"

Diffusivity (cm²/s) $H_2 \quad 3.90 \times 10^{-2} \exp (-2877/T)$ Experimental + Correlation⁽²⁾

Peter & Weinert (1956)

 $CO \quad 5.99 \times 10^{-4} \exp (-1633/T)$ Experimental + Correlation⁽³⁾

Zaidi, et al. (1979)

 $CO_2 \quad 3.70 \times 10^{-4} \exp (-1437/T)$ Experimental + Correlation⁽²⁾

Hayduk & Cheng (1971)

 $H_2O \quad 9.6 \times 10^{-4} \exp (-1633/T)$

Experimental + Correlation

Hayduk & Cheng (1971)

⁽¹⁾ T in °K.⁽²⁾ Extrapolation using correlation of diffusivity with liquid viscosity.⁽³⁾ Estimates of D_{l2} from correlation produced mass transfer coefficients which fitted experimental data.

D. Applications

1. Single Component Model

The major accomplishments are:

- Identified the important parameters and estimated their effect on reactor performance.
- Estimated the effect of axial mixing and catalyst settling on reactor performance.
- Determined operating conditions which yield maximum utilization of bubble-column reactor volume for bench-scale unit.

a. Estimation of Kinetic Constants for Fischer-Tropsch Reactions

Kinetic constants are essential parameters for the slurry F-T reaction mathematical models. Some effort was spent to estimate the constants based on the published experimental data in slurry F-T operations. Data from five sources were used (Koelbel, et al. (1955), Koelbel and Ralek (1980), Schlesinger, et al. (1954), Mitra and Roy (1963), and Kunugi, et al. (1968)). All data were based on bubble-column operations since no data from other slurry reactor types were found at the time.

Since data from bubble-columns contain both mass transfer and kinetic effects, the estimated kinetic constants depend strongly on the assumptions used to describe the mass transfer phenomenon. All the data, except that from Koelbel, et al. (1955), were obtained from long and slim bubble-columns. Hence, it is expected that the effect due to liquid-phase axial dispersion is very small. Therefore, it was decided to use a model of Non-Mixing liquid phase in treating these data. This approach is similar to that used by Deckwer, et al. (1981). Basically the model assumptions are the same as those described in Section IV.B. In addition, it was assumed that the catalyst is uniformly distributed in the reactor.

The experimental data from the five sources, all on Fe-base catalysts, are summarized in Table 29 and the estimated kinetic constants are given in Table 30. There the kinetic resistances as percentages of the total resistances are also given. These are defined as

$$R_k/(R_k+R_d)$$

where R_k and R_d are, respectively, the kinetic resistance for H_2 conversion and the H_2 diffusional resistance from the gas-liquid interface to the bulk liquid (see Figure 35). In Section VII.B,

Table 29

Selected F-T Conversion Data in Bubble-Column Reactors

<u>Authors</u>	<u>Catalyst</u>	<u>Temp.</u> ($^{\circ}$ C)	<u>Pressure</u> (MPa)	<u>Reactor</u> d_R (cm) x L (cm)	<u>Superficial</u> <u>Inlet Gas</u> <u>Velocity</u> (cm/s)	<u>Inlet</u> <u>H_2/CO</u>	<u>Hydrogen</u> <u>Conversion</u>	<u>H_2/CO</u> <u>Usage</u> <u>Ratio</u>	<u>Catalyst</u> <u>Loading</u> (Wt %)
Koelbel, et al. (1955)	Pptd Fe	268	1.2	129 X 770	9.5	0.67	86	0.63	28.4
Koelbel and Ralek, (1980)	Pptd Fe	266	1.1	4.7 X 350	3.5	0.67	85	0.65	15.4
Schlesinger, et al. (1954)	Fused Fe	258	2.17	7.6 X 305	1.54	1.0	63.9	0.81	21.1
Mitra and Roy (1963)	Fe pptd on Kieselgur	260	1.13	5.1 X 305	1.48	1.33	89.7	1.27	17.0
Kunugi, et al. (1968)	Pptd Fe	266	1.12	5.0 X 550	3.78	0.59	80.8	0.59	4.8

Table 30

Estimated F-T Kinetic Constants on Fe-Catalysts

(Non-Mixing Liquid Phase Single-Component Model)

<u>Authors</u>	<u>Temperature (°C)</u>	<u>k''_H (1)</u>	<u>Kinetic Resistance as % of Total Resistance</u>
Koelbel, et al. (1955)	268	0.931	0.92
Koelbel and Ralek (1980)	266	1.12	0.80
Schlesinger, et al. (1954)	258	0.203	0.84
Mitra and Roy (1963)	260	0.848	0.68
Kunugi, et al. (1968)	266	2.28	.89

(1) Intrinsic kinetic rate constant defined as
 $r_H/(1-\epsilon_g)(1-v_C)C_{HL}C_{Fe}$, (cm³ liquid/s-gFe).

it was shown that these two are the only important resistances among the six steps attributed to the transfer of H_2 from the gas phase to the catalyst and to the H_2 conversion on the catalyst.

The same five sets of data were evaluated by Deckwer, et al. (1981a) for the kinetic constants. They report rate constant values which are very similar to those reported on Table 30 except that the values from the first two and the last sources are about 7% less than the corresponding values from Deckwer, et al. (1981a). This small discrepancy is probably due to their assumptions that the H_2/CO usage ratio is the same as the inlet H_2/CO ratio and that the H_2 conversion is the same as the $H_2 + CO$ conversion.

By comparing the intrinsic kinetic rate constants, k_H'' , given in Table 30, the following conclusions can be drawn:

- The catalysts from Koelbel, et al. (1955), Koelbel and Ralek (1980), and Mitra and Roy (1963) have catalytic activity within the range $0.85-1.1 \text{ cm}^3 \text{ liquid/s-gFe}$.
- The catalyst used by Kunugi, et al. (1968) is about 2.3 times more active than those mentioned above.
- The fused-iron catalyst used by Schlesinger, et al. (1954) has a relatively low activity level.
- The kinetic resistance is much larger than the corresponding diffusional resistance provided the gas bubble size is sufficiently small (in this study, $d_B = 0.7 \text{ mm}$).

Among the five sets of bubble-column data, the first set by Koelbel, et al. (1955) was obtained in a large reactor (1.29 m ID). Since a large reactor may result in a substantial axial dispersion due to the relatively free movement of the liquid, the data must be examined more closely. Table 31 shows the estimated intrinsic rate constants obtained by using the three different liquid-phase mixing models: non-mixed (NM), perfectly mixed (PM) and axially dispersed (AD). The predicted rate constant from the PM model is more than double that from the NM model. However, using liquid phase mixing correlations from the literature and the AD model results in only a 2-10% increase in the rate constant over that predicted by the NM model.

A k_H'' of $1.1 \text{ cm}^3 \text{ liquid/gFe-s}$ at a nominal temperature of 266°C is recommended for a precipitated Fe-type catalyst. This value is based on data obtained by Koelbel and Ralek (1980) in bench-scale bubble-column and will be used at base case for current calculations.

Table 31

Estimated Kinetic Rate Constants Using
Different Liquid-Phase Mixing Single-Component Models⁽¹⁾

<u>Intrinsic Kinetic Rate Constant</u>	<u>Liquid-Phase Axial Mixing Models</u>		
	<u>Non- Mixing</u>	<u>With Axial Mixing</u>	<u>Perfectly- Mixed</u>
k_H''	.93	.95 ⁽²⁾	2.09

(1) Rheinspressen-Koppers Demonstration Plant data from Koelbel and Ralek (1980).

(2) This value is based on using the equivalent hydraulic diameter (25.4 cm) as the effective reactor diameter. Using the free-flow area diameter as the effective reactor diameter gives a value of 1.02.

b. Parametric Study

The results of the parametric study show:

- An active catalyst is essential if high synthesis gas conversion is to be obtained with a reasonable reactor height.
- With a plug-flow gas phase, perfect mixing in the liquid phase will substantially increase the reactor height required to achieve high synthesis gas conversion.
- The effect of molar contraction during the F-T reaction on the synthesis gas concentration is large, and should be included in the mathematical model.
- The size of bubbles in the slurry reactor has to be maintained small to reduce the mass transfer resistance and achieve high synthesis gas conversion.

Other major effects (axial dispersion, catalyst settling, and optimal gas velocity) are discussed in subsequent subsections. The base case parameters used in calculations are those given in Table 26.

Figure 37 shows the effect of kinetic rate and liquid phase mixing on H_2 conversion. It is essential to have a very active catalyst to obtain high conversion within a reasonable reactor height. The liquid phase mixing has a large effect on the required reactor length within the high conversion region. It is expected that the bubble-column reactor in the bench-scale pilot plant will have limited liquid phase mixing and that its performance will fall between the Non-Mixing case and the Perfectly-Mixed case. Nevertheless, unless the catalyst is extremely active, a large reactor height is necessary to achieve high conversion.

F-T synthesis reaction is accompanied by a decrease in total number of moles. This molar contraction during the reaction will have two effects on the model formulation:

- changing the concentration of the reactants when the conversion increases
- changing the hydrodynamic properties, such as the superficial gas velocity, the bubble size, the gas holdup, and the gas-liquid interfacial area, along the reactor

FIGURE 37

EFFECT OF KINETIC RATE AND LIQUID PHASE MIXING ON H_2 CONVERSION

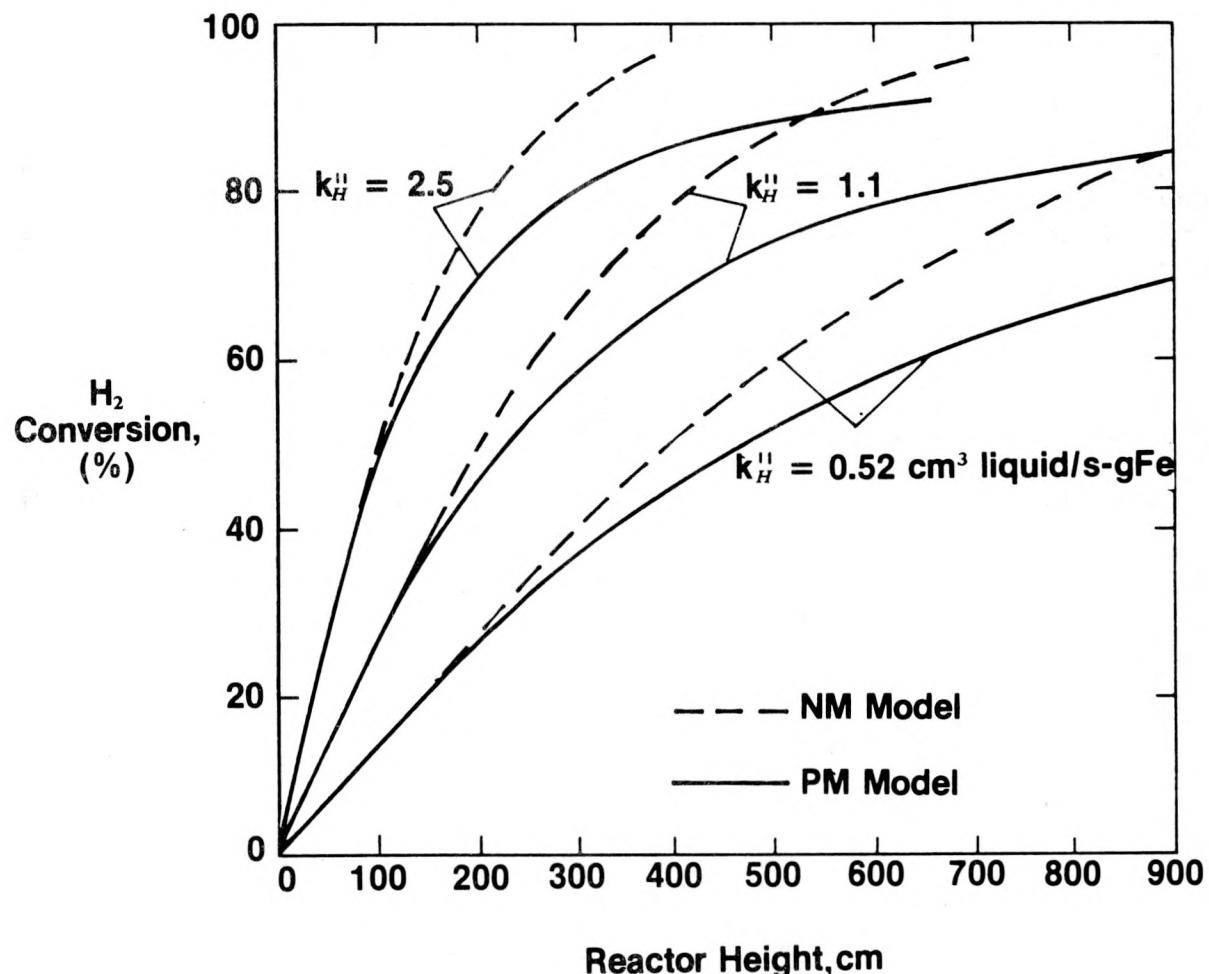


Figure 38 shows the effect of molar contraction during the F-T reaction on the H_2 conversion. Only the effect of the molar contraction on the changing reactant concentration is taken into account here. The comparison is with the case assuming no molar change during reaction. The result shows that the reactor height required is about 30% less at high syngas conversion in the case with 50% molar contraction than that with no molar change. It is important to include this effect of molar contraction in the mathematical model.

Figure 39 shows the effect of bubble size on H_2 conversion. Bubble size has a very large effect on column performance. It is extremely important to have small gas bubbles. The same figure also shows the result of infinite catalytic activity. At infinite catalytic activity, the only resistance to H_2 conversion is the diffusion from the gas-liquid interface to the bulk liquid phase. In other words, this is the best one can do by raising the catalyst conversion activity level.

The effect of the changing hydrodynamic properties along the reactor on the reactor performance is rather complicated. The changing gas-liquid interfacial area (a_g) and gas holdup (ϵ_g) affect both the gas-liquid interface to bulk-liquid transfer resistance (R_d) and the kinetic resistance (R_k). To thoroughly examine this effect, calculations on the following four cases were done:

Cases	u_g in $\epsilon_g = 0.053(u_g)^{1.1}$	Bubble Size	Remarks
1	u_g	Constant	Present base case (constant ϵ_g and a_g)
2	u_{gm}	Constant	Constant ϵ_g and a_g
3	$u_g(z)$	Constant	Variable ϵ_g and a_g
4	$u_g(z)$	Variable	Variable ϵ_g and a_g , but constant number of bubbles

where u_{gm} is the arithmetic average of the inlet and outlet gas superficial velocities.

The equations and the solution for Cases 1 and 2 are given in Section VI.C. In Cases 3 and 4, both the gas holdup and the gas-liquid interfacial area vary with the H_2 conversion. An analytical solution is not available. A method of numerical integration, i.e., trapezoidal quadrature, was used to integrate the resulting differential equation.

Calculations illustrating the effect of variations of hydrodynamic parameters on bubble-column performance are shown in Figure 40 for the case of Non-Mixing liquid phase. For $k_H''=1.1$ cm^3 liquid/s-gFe, the differences in model predictions are small

FIGURE 38
**EFFECT OF MOLAR CONTRACTION
DURING REACTION ON H_2 CONVERSION**

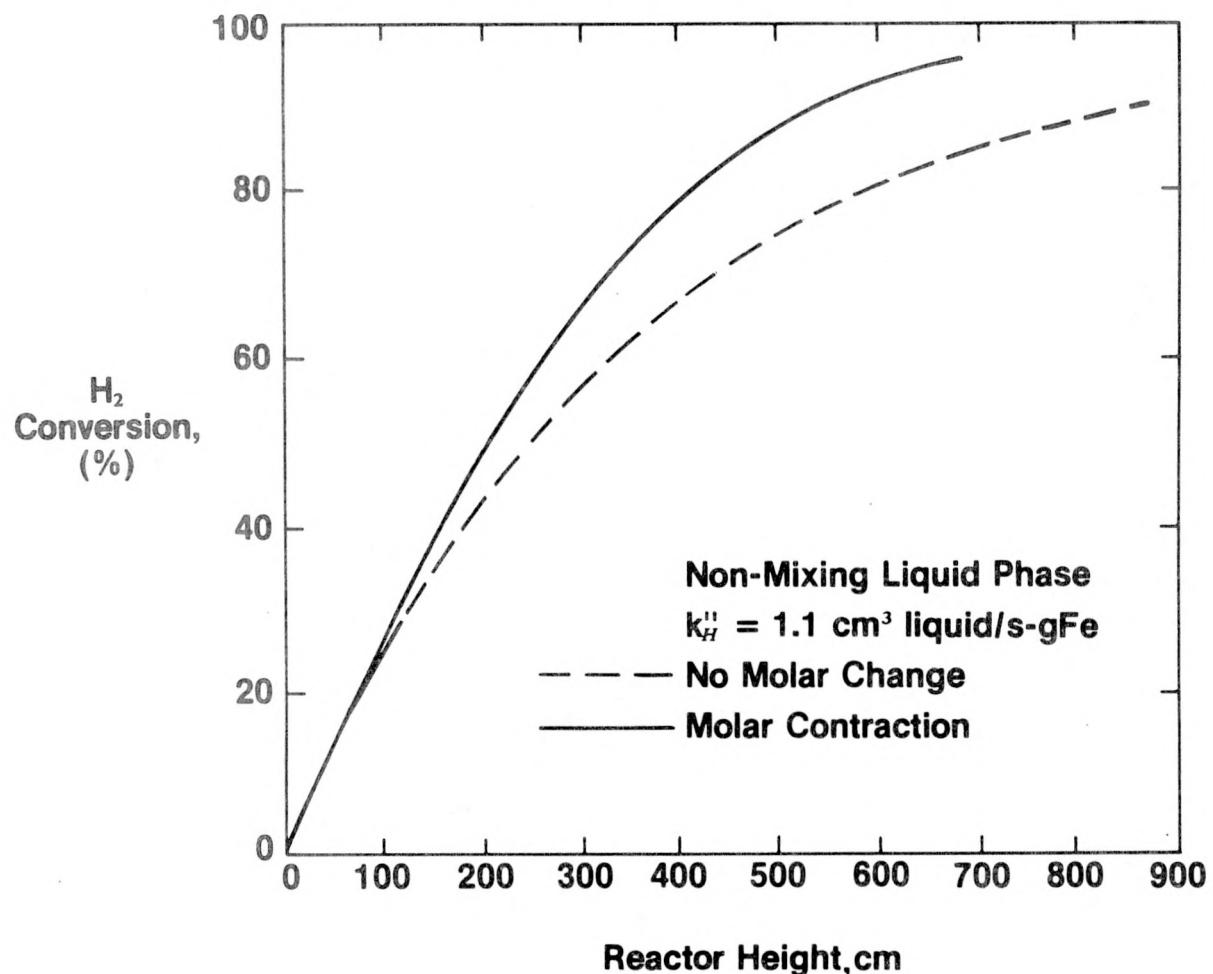


FIGURE 39

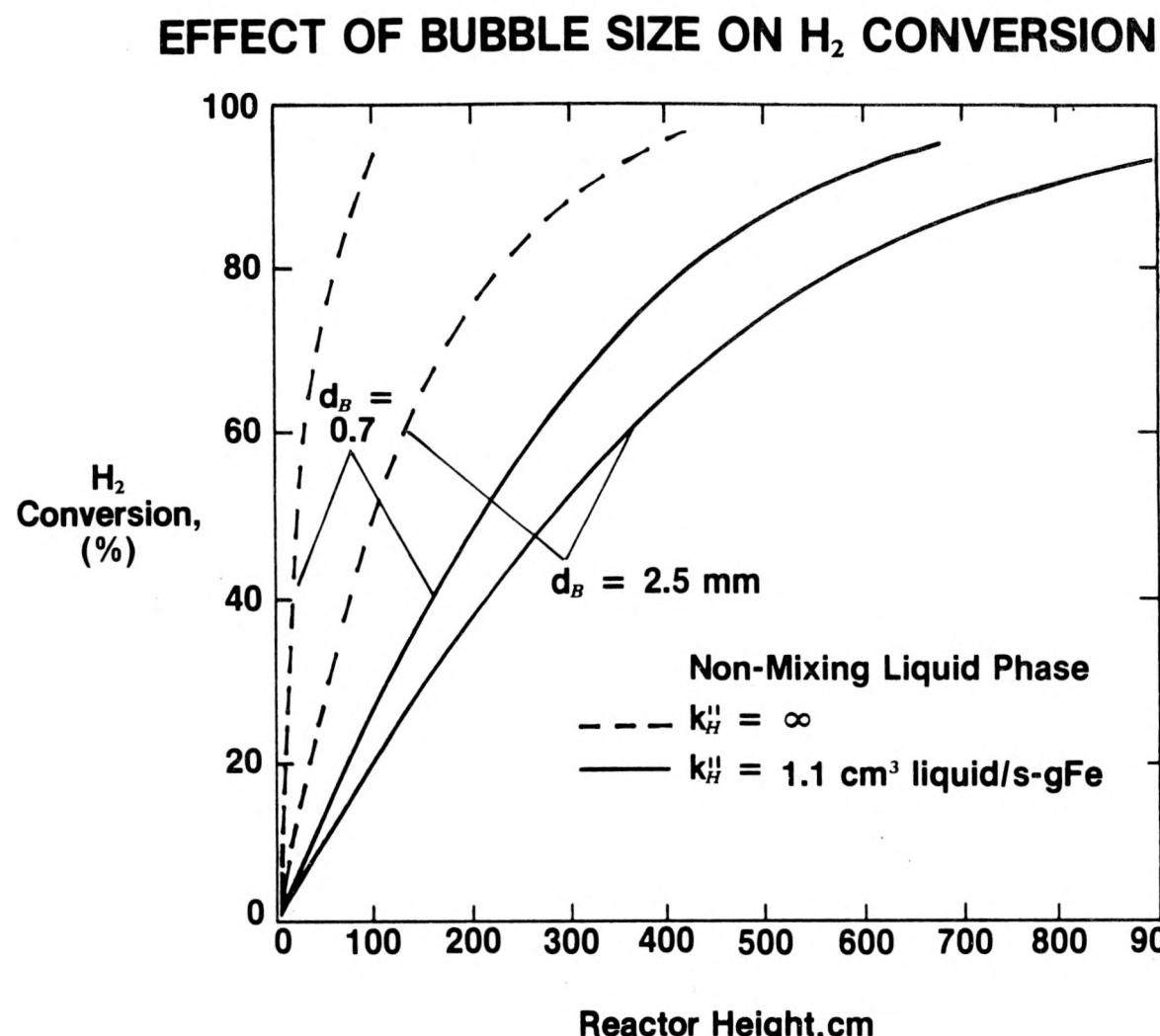
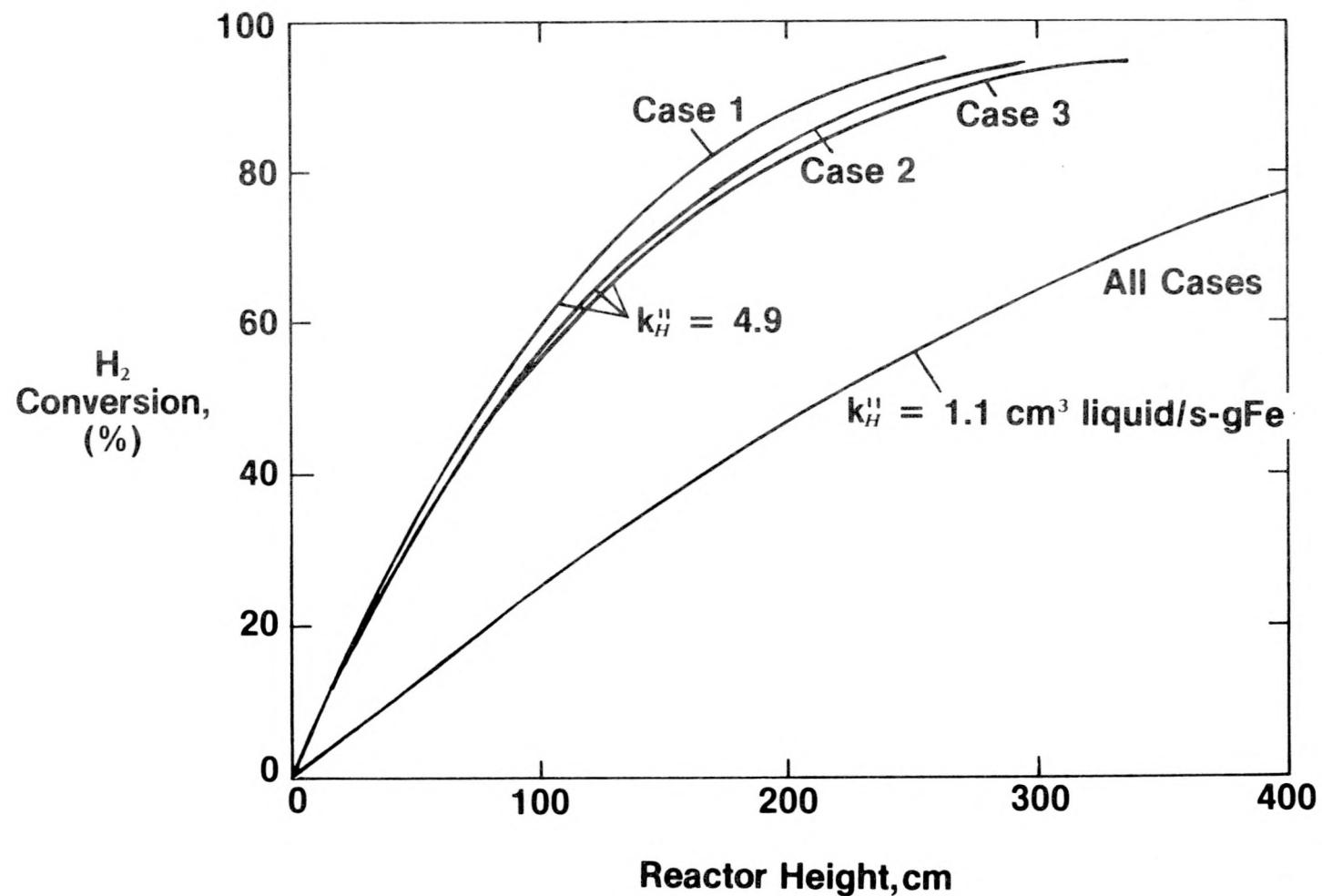


FIGURE 40

EFFECT OF HYDRODYNAMIC PARAMAETERS ON
 H_2 CONVERSION



and the results for all four cases can be represented by a single curve. For $k_H''=4.9 \text{ cm}^3 \text{ liquid/s-gFe}$, three curves, corresponding to Cases 1, 2 and 3, are shown in Figure 40. The results obtained for Case 4 fall very close to that of Case 2 and are not shown. Although the deviation between Cases 1 and 3 are quite significant, there is very small deviation between Cases 2 and 3. Consequently, the use of the average gas holdup and gas liquid interfacial area is sufficient to describe the changing hydrodynamic properties along the reactor resulting from the molar contraction of the F-T reaction.

The effect of the changing hydrodynamic properties on the H_2 conversion in the case of the Perfectly-Mixed liquid phase was evaluated similarly. The differences in results between all four cases are smaller than those between the corresponding cases of the NM model.

The mathematical model, as illustrated by Case 2, using a constant bubble size and the mean value of the gas holdup, gives adequate results for catalysts of activity level less than $k_H''=4.9 \text{ cm}^3 \text{ liquid/s-gFe}$.

c. Effect of Catalyst Settling on Reactor Performance

In the F-T slurry process, fine catalyst particles are suspended in the liquid phase by the bubbling of the syngas. This uplifting force is balanced by the gravitational force on the particles. Therefore, the axial catalyst distribution is generally non-uniform. This non-uniform catalyst distribution will lower reactor performance. The objective here is to evaluate this effect on BSU F-T reactor performance using a catalyst dispersion model coupled with the slurry F-T reactor mathematical model described in Section VII.C. Specifically, the most important variable that affects catalyst distribution is the catalyst size. If the size is small enough, the axial catalyst distribution will be relatively uniform and good reactor performance can be ensured. The primary objective of this study is to determine the maximum catalyst size such that the deviation of reactor performance due to non-uniform axial catalyst distribution will not be significant. Furthermore, Farley and Ray (1964), Schlesinger, et al. (1954), and Koelbel and Ralek (1980) reported that F-T Fe-based catalysts disintegrate during normal operation. The former two reported that catalysts disintegrate to $1-3\mu\text{m}$ size. A secondary objective of this study is to establish that such stabilized catalyst size is small enough for proper operation. It is expected that satisfying the primary objective will automatically accomplish this. For the present study, the NM liquid phase mathematical model is used (Equation (19)). Table 32 gives the values of the parameters used in the calculations.

Table 32

Parameters and Their Ranges Adopted in Single-Component
F-T Reactor Mathematical Model Calculations

Parameters	Base Case	Ranges
Hydrodynamic Parameters	-----	-----
d_B , (cm)	.07	.07-.25
k_L , (cm/s)	.02	.02-.09
ϵ_g	.053(u_{gm}) ^{1.1}	(.053-.106)(u_{gm}) ^{1.1}
Reaction Parameters	-----	-----
k_H'' , (cm ³ Liquid/s-gFe)	1.1	.5-2.0
U	.645	.6-.69
$-\alpha$.5	.5-.6
Physical Parameters	-----	-----
D_{HL} , (cm ² /s)	10^{-4}	10^{-4} - 10^{-3}
f_{Fe}	.67	-
K_H , (cm ³ Liquid/cm ³ Gas)	4.4	2.2-6.6
ρ_L , (g/cm ³)	.667	-
ρ_s , (g/cm ³)	5.2	-
μ_L , (g/s-cm)	.022	-
Operation Parameters	-----	-----
d_R , (cm)	5.08	5.08-1.29
f	.7	.6-.7
P , (MPa)	1.48	-
T , (°C)	265	-
$u_{g,i}$, (cm/s)	4	2-9.5
w_{Fe}	.10	.05-.20

A parametric study of this axial catalyst dispersion effect shows that the deviation of the F-T bubble-column reactor performance from that with a uniform catalyst distribution is the largest when:

1. The catalyst loading is low.
2. The feed gas superficial velocity is high.

Consequently, to study the same effect on the BSU F-T reactor performance, the maximum deviation is expected at the lowest catalyst loading of about 5 wt % Fe and the highest feed-gas superficial velocity of about 7 cm/s. The effect of a non-uniform catalyst distribution can be represented as the percentage increase in reactor length required to achieve the same hydrogen conversion as that estimated using a uniform catalyst distribution. These results are given in Figure 41 with catalyst sizes from 10 to 50 μm . If one considers that a 15% longer reactor length is an acceptable deviation, then the acceptable catalyst size is below 40 μm for 90% hydrogen conversion.

In open literature, many sizes of the fresh Fe-based catalysts have been mentioned. However, the slurry reactor diameters and the feed-gas superficial velocities are not exactly those used in the current study. Koelbel and Ralek (1980) mentioned a 30 μm catalyst for a 5.1 cm diameter bench-scale unit at a 3.5 cm/s feed-gas superficial velocity, and the same size catalyst for the Rheinsprussen demonstration plant (1.29m reactor and 9.5 cm/s feed-gas superficial velocity). Schlesinger, et al. (1951) used catalyst smaller than 60 μm for a 7.6 cm diameter reactor and a feed-gas superficial velocity of about 2.5 cm/s. Sakai and Kunugi (1974) used a 1 μm catalyst for a 5.1 cm diameter reactor and a 3.8 cm/s feed-gas superficial velocity.

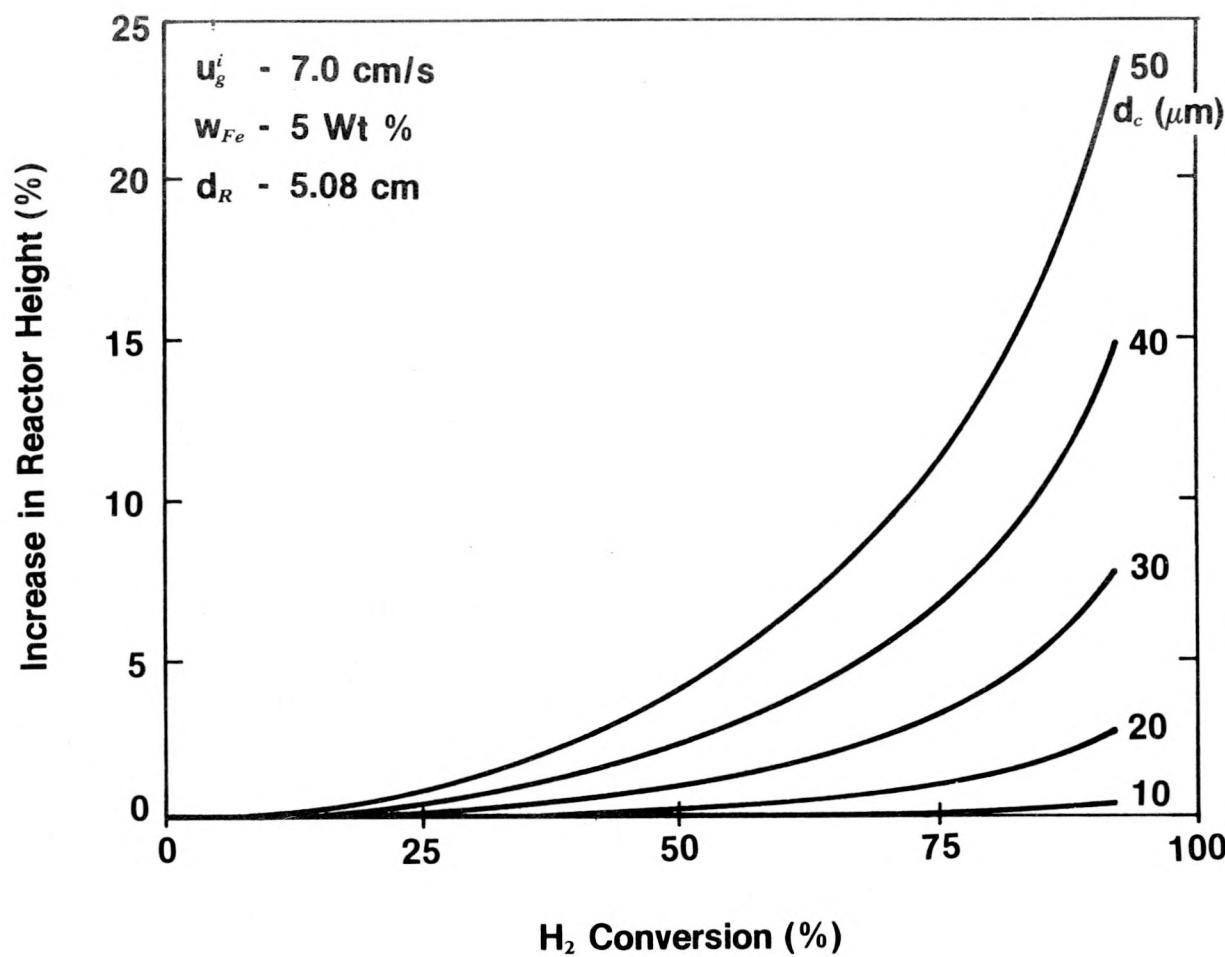
As mentioned in the first paragraph of this subsection, catalyst disintegration to sizes below 5 μm may be expected during normal operation. Since this size is much smaller than the 40 μm limit recommended for the fresh catalyst, no operational difficulties due to catalyst non-uniform distribution are expected.

d. Optimum Reactor Space-Time Yield

One of the questions often raised in the discussion of the F-T reactor performance is the possible disadvantage due to the inherently low catalyst density in slurry reactors. In other words, it requires a larger reactor volume to hold the same amount of catalyst than the conventional vapor-phase F-T reactors. This larger reactor volume may pose a penalty as a higher cost for the final product. Consequently, it is important to examine the Space-Time-Yield behavior of a F-T slurry reactor

FIGURE 41

EFFECT OF AXIAL CATALYST DISTRIBUTION ON
BSU F-T REACTOR PERFORMANCE



in order to search for an optimal STY operation. The Space-Time-Yield used here is defined as:

$$\text{STY} = (\text{gMol H}_2\text{+CO Converted}/\text{hr}\cdot\text{cm}^3 \text{ Expanded Slurry}) \quad (38)$$

Based on the current mathematical model, the yield is strongly dependent on the catalyst loading and the gas velocity. Using the NM mathematical model, Figure 42 shows results of calculations for the BSU F-T reactor operation. Only the results for the 90% hydrogen conversion are given. As expected, the STY depends strongly on the catalyst loading. Note that, in the current mathematical model, the hydrodynamic properties of the column are assumed to be independent of the catalyst loading. Deckwer, et al. (1982b) mentioned that this independence exists up to 16 wt % of catalyst in the slurry. However, Koelbel and Ralek (1980) indicated that the optimum catalyst loading is about 10 wt % in terms of the iron in the slurry. Higher catalyst loading increases the viscosity of the slurry and thus decreases the gas-liquid interfacial surface area. Based on these two references, the question of the optimal catalyst loading will need further investigation. The calculated results for the high catalyst loadings shown in Figure 42 can only be used as a guide for future studies.

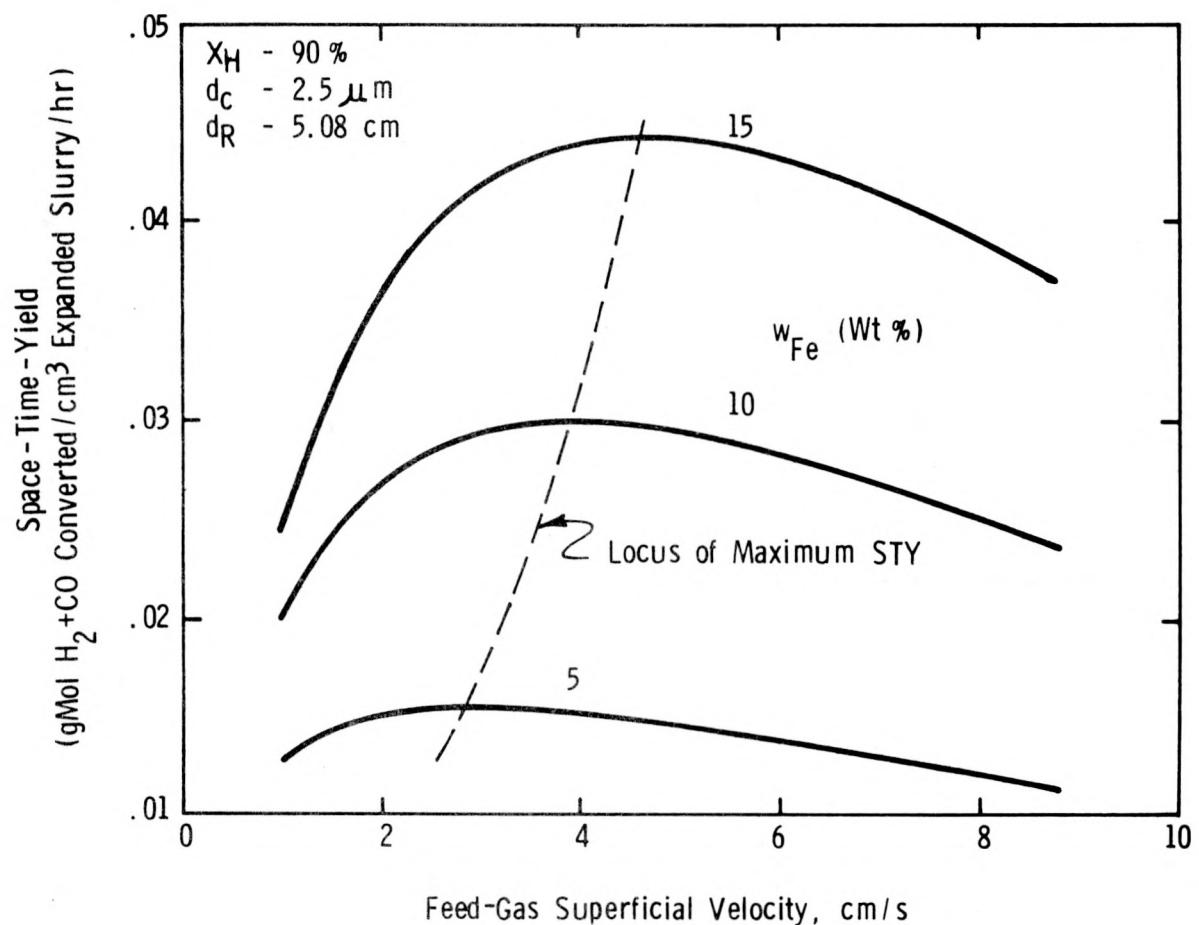
The dependence of the STY on the gas velocity is very interesting because maximum STY's exist for each curve. The physical interpretation of this phenomenon is that, at low gas velocity, the STY is low because the gas-liquid interfacial surface area is low; while, at high gas velocity, the STY also is lower because the slurry-bed expansion becomes an overriding factor. In Figure 42, a dotted line indicates the locus of the maximum STY. For catalyst loadings between 5-15 wt % Fe, the feed gas superficial velocities at which the maximum STY occurs vary from 2.8 to 4.6 cm/s. Caution should be given in interpreting the results at the high end of the gas velocity, since, according to Deckwer, et al. (1982a), the flow in the BSU F-T column may approach "slug flow" regime at about 8 cm/s gas velocity.

e. Effect of Liquid-Phase Axial Mixing

Calculations in Subsection VII.D.1.b have shown that the state of the liquid phase axial mixing has a large effect on slurry F-T reactor performance. That conclusion was drawn by using two extreme states of the liquid phase mixing, i.e., non-mixing (NM model) and perfect-mixing (PM model). The actual state of the axial liquid mixing lies somewhere between these two extremes. The purpose of this work is to investigate the effect of this liquid phase axial dispersion on BSU F-T reactor performance using a physical model similar to the one adopted by Deckwer, et al. (1982b) in which an axial dispersion coefficient is used (Equations (14), (17), and (18)).

FIGURE 42

EFFECT OF CATALYST LOADING AND GAS VELOCITY
ON BSU F-T REACTOR PERFORMANCE



The major results of the calculations are:

- The effect of the liquid-phase axial mixing on the BSU F-T reactor performance is estimated to be small to moderate.
- The effect of the liquid-phase axial mixing on large-scale F-T bubble reactor performance can be significant. However, this effect is greatly complicated by the existence of cooling tubes in large-scale reactors. Further experimentation to evaluate the hydrodynamic behavior of large-scale reactors is recommended.

Table 32 lists the parameters adopted in the current mathematical model calculations. To evaluate the effect on the reactor performance due to the axial liquid-phase mixing, a parametric study was done to find out the effect of major parameters on the directional change in the reactor performance. This exercise is essential in establishing a combination of parameters that will give the largest effect on the reactor performance due to the axial liquid-phase mixing. If this case shows a small effect, then it can be concluded that the effect is small in all cases enveloped by the ranges of the parameters under consideration. There are two types of perturbation of these parameters. One type results from the variation within the operational range of parameters, such as the reactor temperature, reactor pressure, catalyst loading, inlet H_2/CO ratio, superficial feed-gas velocity, and reactor diameter. The other type is the variation of the parameters due to the uncertainty of these parameters, such as the gas bubble size, gas holdup, hydrogen solubility, hydrogen diffusivity, intrinsic kinetic rate constant, H_2/CO usage ratio, and contraction factor. All parameters listed in Table 32 are subjected to parametric study except for the Fe-content in the catalyst, catalyst solid density, liquid density and viscosity, reactor pressure, and reactor temperature. The variations of the liquid density and viscosity are reflected in the variation of the liquid-side mass transfer coefficient. Finally, the variation of the reactor temperature is mainly reflected in the variation of the intrinsic kinetic rate constant; while the variation of the reactor pressure is reflected in the variation of the gas velocity.

The base case values of the parameters are given in Table 32 together with the ranges of the variations of each parameter. The lower and upper bounds of the gas bubble diameter are those reported by Deckwer, et al. (1982b) and Satterfield and Huff (1980). Those for the liquid-phase hydrogen diffusivity are obtained from the Wilke-Chang correlation (Deckwer, et al. (1982b) and Calderbank, et al. (1963)). Those for the hydrogen solubility coefficient and the intrinsic kinetic

constant are obtained by varying the base case value by $\pm 50\%$. Those for the contraction factor are those measured by Deckwer, et al. (1982b). Those for the H_2/CO usage ratio are given arbitrarily but within a reasonable limit. Lastly, the upper bound of the gas holdup is obtained by doubling the base case value.

The liquid-phase axial mixing is described using a constant dispersion coefficient. A correlation for this coefficient recommended by Deckwer, et al. (1982b) is adopted here (Table 27). The correlation includes data obtained with the superficial gas velocity up to 90 cm/s and with the reactor diameter up to 60 cm. Some of these data may very well be in the turbulent flow region. However, most of the data were obtained in systems of air-water, and some were in systems of air-aqueous glycerine. It is not clear if data obtained from these systems can be applied to our present system. In the current study, the calculated effect of the liquid-phase axial mixing on the F-T bubble-column performance is compared against those of the Non-Mixing ($E_L=0$) and the Perfectly-Mixed ($E_L=\infty$) cases.

Table 33 summarizes results of this parametric study. It shows the variations of the parameters that result in an increase in calculated effect on the F-T bubble-column performance due to the existence of the liquid-phase axial mixing. An increase in this effect is measured by an increase of the following parameter

$$(1-X_H^e)_{AD}/(1-X_H^e)_{NM}$$

where the subscript AD denotes the case with the existence of the liquid-phase axial dispersion and the subscript NM denotes the case of non-mixing liquid-phase. In conclusion, to obtain a case that gives the largest effect due to the existence of the liquid-phase axial dispersion, one shall use the upper-ranged values of the liquid side mass transfer coefficient, intrinsic kinetic rate constant, H_2/CO usage ratio, contraction factor, liquid-phase hydrogen diffusivity, catalyst loading in the reactor slurry, reactor diameter, and lower-ranged values of the gas bubble size, gas holdup, hydrogen solubility coefficient, superficial feed-gas superficial velocity, and inlet H_2/CO ratio. If the predicted effect of this case of largest liquid-phase axial dispersion is small, then one can conclude that the effect is small for all cases within the ranges of the parameters.

The effect of the liquid-phase axial mixing on the BSU F-T reactor performance can now be estimated using the largest effect case at 5.1 cm reactor diameter. The result of this calculation is plotted in Figure 43, given as the hydrogen conversion versus the reactor length. For comparison, the results for both the non-mixing and the perfectly-mixed liquid cases are plotted in the same diagram. The curve representing

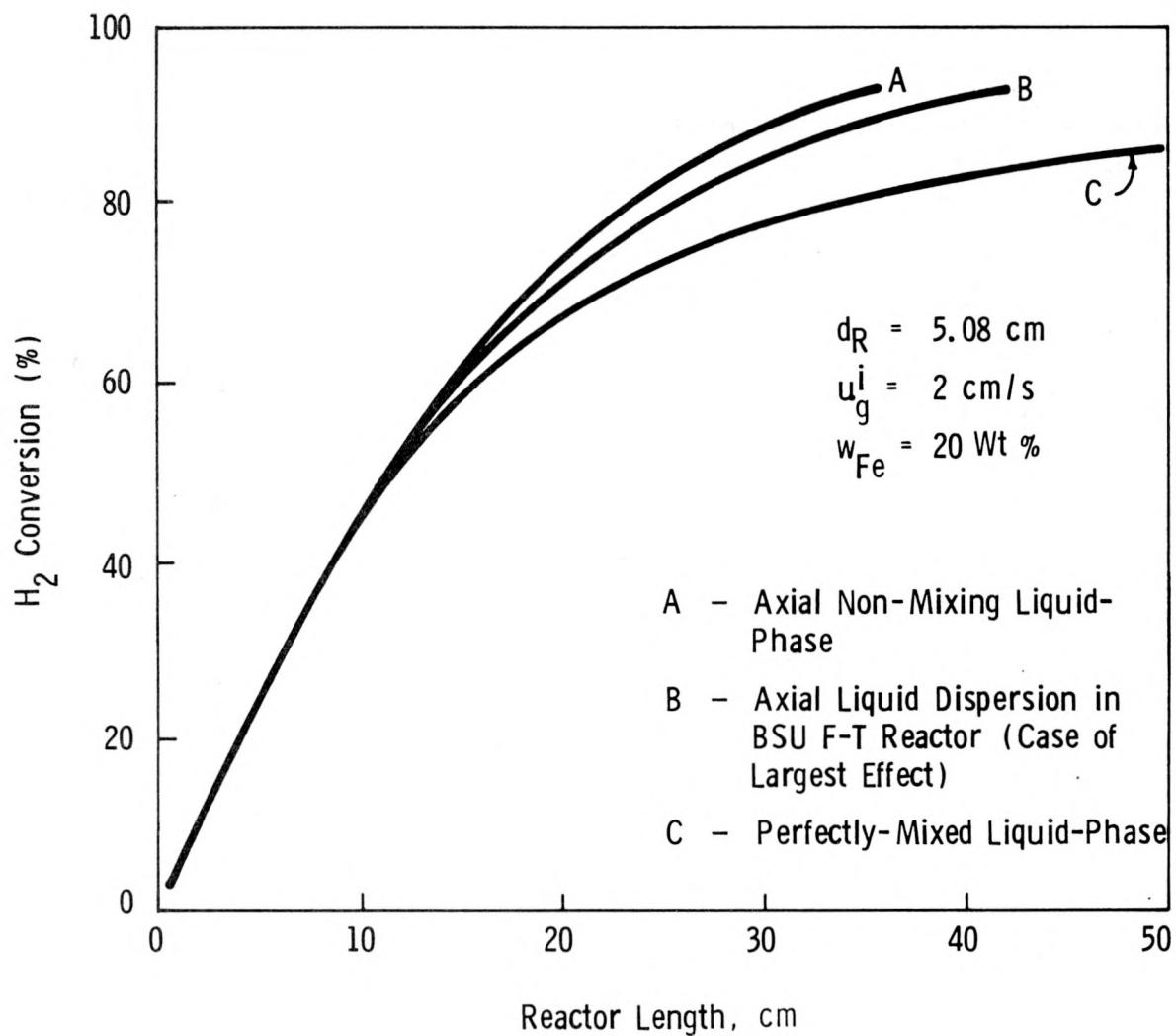
Table 33

Variation of Parameters That Results in an Increase of the
 Calculated Effect of the Liquid-Phase
Axial Mixing on the F-T Bubble-Column Performance

<u>Parameters</u>	<u>Variation</u> ⁽¹⁾	<u>Parameters</u>	<u>Variation</u> ⁽¹⁾
<u>Hydrodynamic Parameters</u>		<u>Physical Parameters</u>	
d_B	D	D_{HL}	I
E_L	I	K_H	D
k_L	I		
ϵ_g	D		
<u>Reaction Parameters</u>		<u>Operation Parameters</u>	
k_H''	I	d_R	I
U	I	f	D
$-\alpha$	D	u_g^i	D
		w_f^{Fe}	I
		$L(1-\epsilon_g)$	I
<u>Dimensionless Parameters</u>			
Pe_L	D		
St_d	I		
St_k	I		

(1) "D" denotes a decreasing value and "I" denotes an increasing value of a parameter $(1-X_H^e)_{AD}/(1-X_H^e)_{NM}$.

FIGURE 43
EFFECT OF AXIAL LIQUID MIXING ON BSU F-T
REACTOR PERFORMANCE



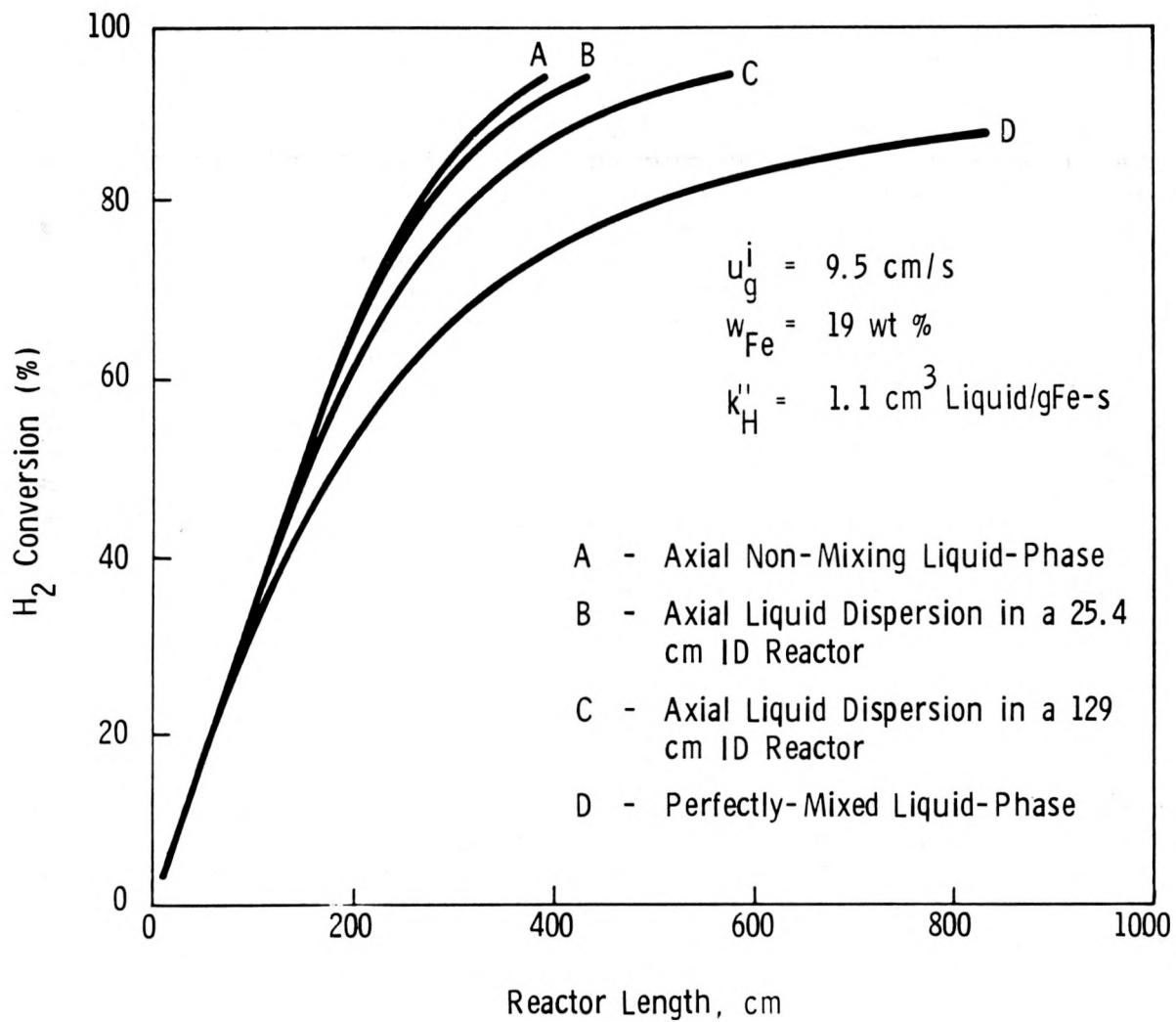
the largest effect case is, as expected, enveloped on both sides by those of the non-mixing and the perfectly-mixed liquid cases. The perfectly-mixed liquid case deviates substantially from the largest effect case; while the deviation between the non-mixing liquid phase and the largest effect case is small to moderate. In the latter comparison, the reactor length required to achieve a 90% conversion is about 15% longer than that estimated using the non-mixing liquid phase approximation. In conclusion, the liquid-phase axial mixing effect is small and shall be included in model calculations only if very accurate results are desired.

In a large-scale F-T reactor, the effect of the liquid-phase axial mixing is expected to become larger because of less hindrance from the reactor wall on the liquid movement. However, there are three factors that greatly complicate this issue. The first factor is that, in a large-scale reactor, the operational gas velocity, whose upper bound is determined by the existence of the gas-liquid slug flow in smaller reactors, become substantially higher. With a higher gas velocity, the effect of the liquid-phase axial dispersion becomes less. The second factor is that a large-scale reactor will contain a large number of cooling tubes in the reactor to remove reaction heat. The existence of the cooling tubes will provide the surfaces that hinder the liquid movement and reduce the liquid-phase axial mixing. The last factor is the possible existence of the churn-turbulent flow-region in a large-scale high gas velocity reactor (Deckwer, et al., 1982a). More studies, particularly non-reacting flow model experiments, are essential in understanding the hydrodynamic behavior of such systems. In the following, a preliminary study was done using the actual operational data of the 155 cm inside diameter and 8.6 m height Rheinpreussen-Koppers demonstration reactor.

To maximize the effect of the calculated liquid-phase axial mixing, the upper bound of the liquid-phase hydrogen diffusivity and the lower bound of the hydrogen solubility coefficient were adopted in the calculation. Assuming that the hydrodynamic description used in the current mathematical model can be applied to this case study, an effective reactor diameter must be estimated to account for the existence of the vertical cooling tubes. One may define this effective reactor diameter as the hydraulic diameter of the free flow area, i.e., the equivalent circular diameter that gives the same perimeter to flow area ratio. The hydraulic diameter of this reactor is 25.4 cm. However, another effective reactor diameter defined as the equivalent circular diameter that gives the same free flow area has also been proposed. This equivalent diameter is 129 cm, which is substantially different from the hydraulic diameter. It is not clear which definition gives a better representation of the actual phenomenon. The effective reactor diameter may lie between these two diameters. In Figure 44, calculated results based on these two diameters are shown together with the two

FIGURE 44

EFFECT OF AXIAL LIQUID MIXING ON LARGE-SCALE F-T
REACTOR PERFORMANCE



extreme cases of the non-mixing and the perfectly-mixed liquid. Using the hydraulic diameter as the effective reactor diameter results in about 10% longer reactor than that required in the non-mixing liquid case, while using the free-flow-area diameter results in about 50% longer reactor. This reactor performance is far from the perfectly-mixed liquid-phase case. Note that if the hydraulic diameter is the proper effective reactor diameter for accounting for the effect of vertical cooling tubes, the reactor scale-up problem will become very simple.

2. Multi-Component Model

In the previous subsection, the F-T bubble-column mathematical model was constructed based on a single reactant component (H_2), and a single first-order F-T kinetic expression. This simple approach allows a quick way of solving the associated mathematical equations. However, these simple-minded assumptions give approximate descriptions of the transport phenomena and the kinetics of the system. For example, since the H_2 diffusivity is substantially higher than the diffusivities of CO and other components, the mass transfer resistance in a single-component model is less than that in a multi-component system. Furthermore, first-order kinetics give an overly optimistic prediction of the H_2+CO conversion at high conversions, where the kinetics approach second-order according to Dry (1976). The multi-component mathematical model also includes a separate water-gas shift reaction which describes a kinetic conversion of CO to H_2 using the H_2O formed in the F-T reactions.

a. Estimate of Kinetic Parameters From A Set of Published F-T Column Data

A set of literature data from a bench-scale F-T bubble-column was used to estimate the kinetic parameters of a precipitated Fe-catalyst (Koelbel and Ralek, 1980). The operation conditions from this data set are summarized in Table 34. In addition to these conditions, the solubilities and diffusivities of all four components were required and estimated either from experimental data or correlation equations as summarized in Table 28. The correlations used to calculate the liquid-side mass transfer coefficient, gas holdup, and liquid density and viscosity were the same as those used in Subsection VII.D.1 (see Table 27). Values of bubble size, catalyst solid density, iron fraction in the catalyst, and molar contraction factor were also the same as those used in the previous section. The parameters are summarized in Table 35 as the base case.

The numerical scheme used to estimate the kinetic parameters was the method of parametric regression, minimizing the following target function:

$$(1 - (X_{H_2+CO})_{\text{calc}}/(X_{H_2+CO})_{\text{exp}})^2 + (1-U_{\text{cal}}/U_{\text{exp}})^2 \quad (39)$$

Table 34

Bench-Scale Bubble-Column Data for Estimating
Kinetics of a Precipitated Fe-Catalyst⁽¹⁾

$T = 266^{\circ}\text{C}$

$f = 0.67$

$P = 1.1 \text{ MPa}$

$f_{\text{Fe}} = 0.67$

$u_g^i = 3.5 \text{ cm/s}$

$U^e = 0.65$

$L = 350 \text{ cm}$

$x_{\text{H}_2+\text{CO}} = 88\%$

$w_{\text{Fe}} = 10\%$

$m = 2.24$ ⁽²⁾

(1) Koelbel and Ralek (1980).

(2) Probstein and Hicks (1982).

Table 35

Parameters and Their Ranges Adopted In
F-T Multi-Component Model Calculations

<u>Operation Parameters</u>	<u>Base Case</u>	<u>Range</u>
T (°C)	265	
u_g^i (cm/s)	4	2-6
w_{Fe}	.10	.05-.15
f	.7	.6-.8
<u>Reaction Parameters</u>		
K_1 (cm ³ liquid/s-gFe)	2.09	
k_2 (cm ³ liquid/s-gFe)	1.52	
k_3	.756	
k_4	34.7	
α	-.5	
m	2.24 ⁽¹⁾	
<u>Physical Parameters</u>		
K (cm ³ liquid/cm ³ gas)	4.55-3.70-1.78-1.18 ⁽²⁾	
D_L (cm ² /s) $\times 10^{-4}$	1.86-.288-.256-.441 ⁽²⁾	
ρ_L (g/cm ³ liquid)	.666	
μ_L (g/cm-s)	.0225	
ρ_s (g/cm ³ solid)	5.2	
f_{Fe}	.67	
<u>Hydrodynamic Parameters</u>		
d_B (cm)	.07	
ϵ_g	$.053(u_g)^{1.1}$	
k_L (cm/s) $\times 10^{-2}$	3.15-.909-.840-1.21 ⁽²⁾	

(1) Probstein and Hicks (1982).

(2) For H₂-CO-CO₂-H₂O, respectively.

The convergence criterion was that this target function was less than 10^{-5} . The resulting kinetic parameters are included in Table 35. This set of kinetic parameters was adopted in the following calculations.

b. Comparison of Single Component and Multi-Component Models

Due to interaction of the water-gas shift and Fischer-Tropsch reaction, the nonlinear kinetics (see above) and the different diffusivities of H_2 and CO , certain features predicted by the multi-component model could not be exhibited by the single component models.

The major differences between the predictions of these two mathematical models are:

- The reactor length required for given H_2+CO conversion is significantly longer at high conversions than that predicted by the single component model.
- The mass transfer limitations are significantly larger (due to CO) than predicted by the single component model.
- The H_2/CO ratio in the liquid phase is larger than that in the gas phase and can be significantly larger than the feed H_2/CO ratio.

Because of the complex kinetic expression used in the current improved model, it was not straightforward to compare the current kinetic constants with the single constant obtained in the previous single-component (H_2) kinetic expression. From Equation (29), the rate expression for the F-T reaction will be reduced to the simple first order kinetic expression previously used when $[CO] \gg k_3[H_2O]$. This occurs at the entrance portion of a F-T bubble-column when a dry synthesis gas is used. However, the rate becomes minute when $[CO]$ and $[H_2]$ become small. This description indicates that the H_2+CO conversion rate at the entrance of a bubble-column is higher than that which is predicted using the first-order model. Nevertheless, when the synthesis gas conversion proceeds, the conversion rate approaches second-order kinetics, and the rate becomes significantly lower. This observation is clearly illustrated in Figure 45. The constants k_2 and k_4 describe the rate of the water-gas shift reaction (Equation (31)), which significantly affects the H_2 , CO , H_2O , and CO_2 concentrations along the reaction path. The estimated equilibrium constant k_4 (34.7) matches exactly the experimental equilibrium constant given by Newsome (1980).

FIGURE 45

COMPARISON OF MULTI-COMPONENT F-T BUBBLE-COLUMN
MATHEMATICAL MODEL WITH SINGLE-COMPONENT MODEL

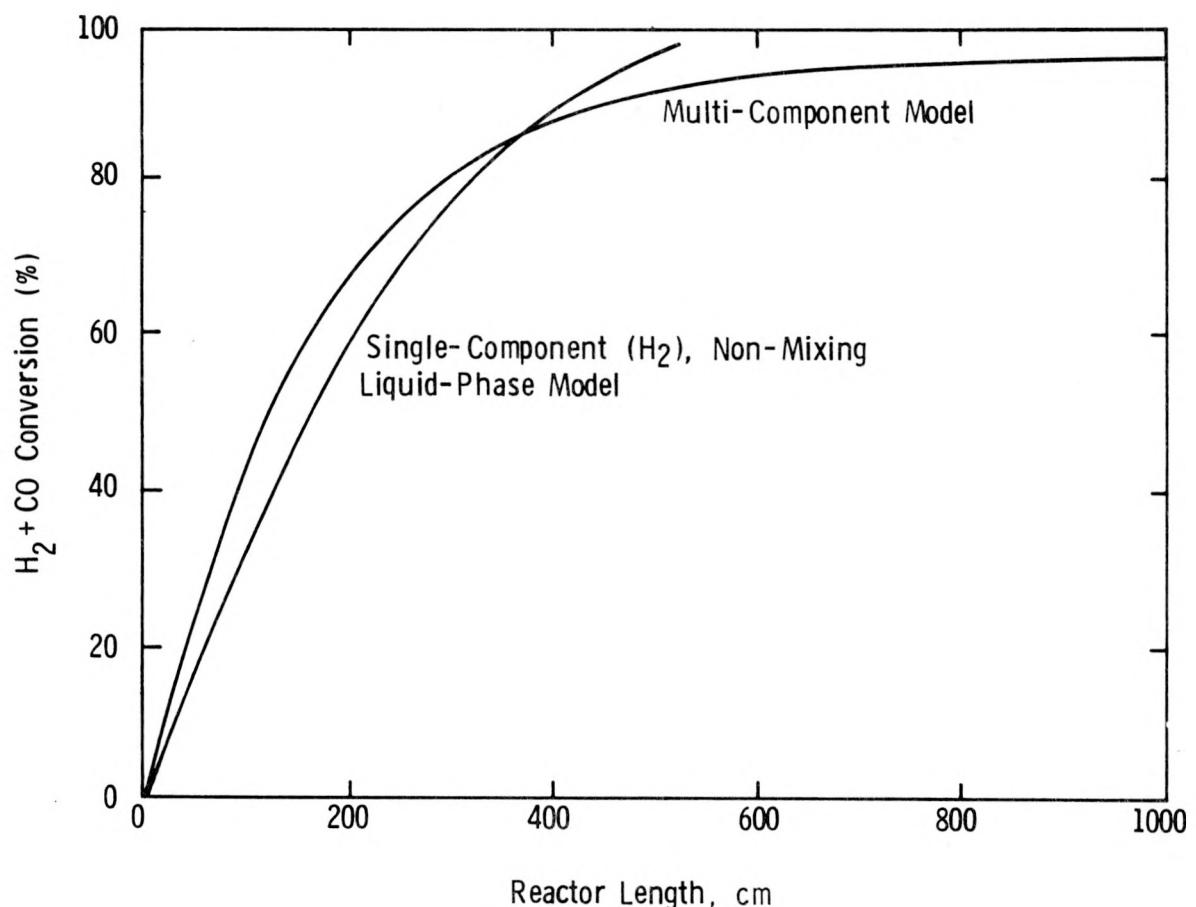


Figure 46 shows the variation of H_2 , CO , CO_2 , and H_2O concentrations in both the gas- and the liquid phase along the bubble-column. Note that CO_2 concentration increases quickly along the column because the water-gas shift reaction favors the CO_2 formation under the given conditions. Also, the H_2O concentration varies only a little after the entrance portion of the column since the rate of its dissipation by the water-gas shift reaction is approximately balanced by its rate of formation due to the F-T reaction. Figure 47 shows the variation of the F-T and water-gas shift reaction rates along the column. The F-T rate decreases quickly along the reaction path. Figure 48 shows the H_2/CO ratios in both the gas- and liquid-phase along the column height. Along most of the column, the H_2/CO ratio in the liquid-phase is higher than that of the gas-phase because the H_2 mass transfer coefficient is substantially larger than that of the CO . It is interesting to see that the H_2/CO ratio has a minimum, and that the water-gas shift reaction rate and the H_2O concentrations have a maximum along the column height. All these phenomena can be properly explained by the existence of the water-gas shift reaction.

The question of how important the mass transfer resistance is across the gas-liquid interface becomes more complex for the multi-component system. Nevertheless, a single component (H_2) model may under-predict a gas-liquid mass transfer resistance, since H_2 has the highest diffusivity (about 6.5 times that of the CO) among the four components used in the current model.

c. Parametric Study

Parametric studies were performed using the multi-component mathematical model and the parameters listed in Table 35. The major results are:

- Varying superficial gas velocities (2, 4, 6 cm/s) and Fe-catalyst loadings in the reactor slurry (5, 10, 15 wt %) has a large effect on the F-T bubble-column performance. However, the effect of increasing the catalyst loading from 10 to 15 wt % is considerably less than that of increasing it from 5 to 10 wt %.
- The effect of varying the feed H_2/CO ratio (.6, .7, and .8) on the F-T bubble-column performance is not significant except in the high H_2+CO conversion region. The reactor exit gas H_2/CO ratio also increases significantly with increasing feed H_2/CO ratios when the conversion is high. This may somewhat affect the catalyst aging and the methane formation rate, both of which depend on the H_2/CO ratio in the gas phase.

FIGURE 46

PREDICTED AXIAL CONCENTRATION PROFILES IN
F-T BUBBLE-COLUMN
(Conditions of Table 34)

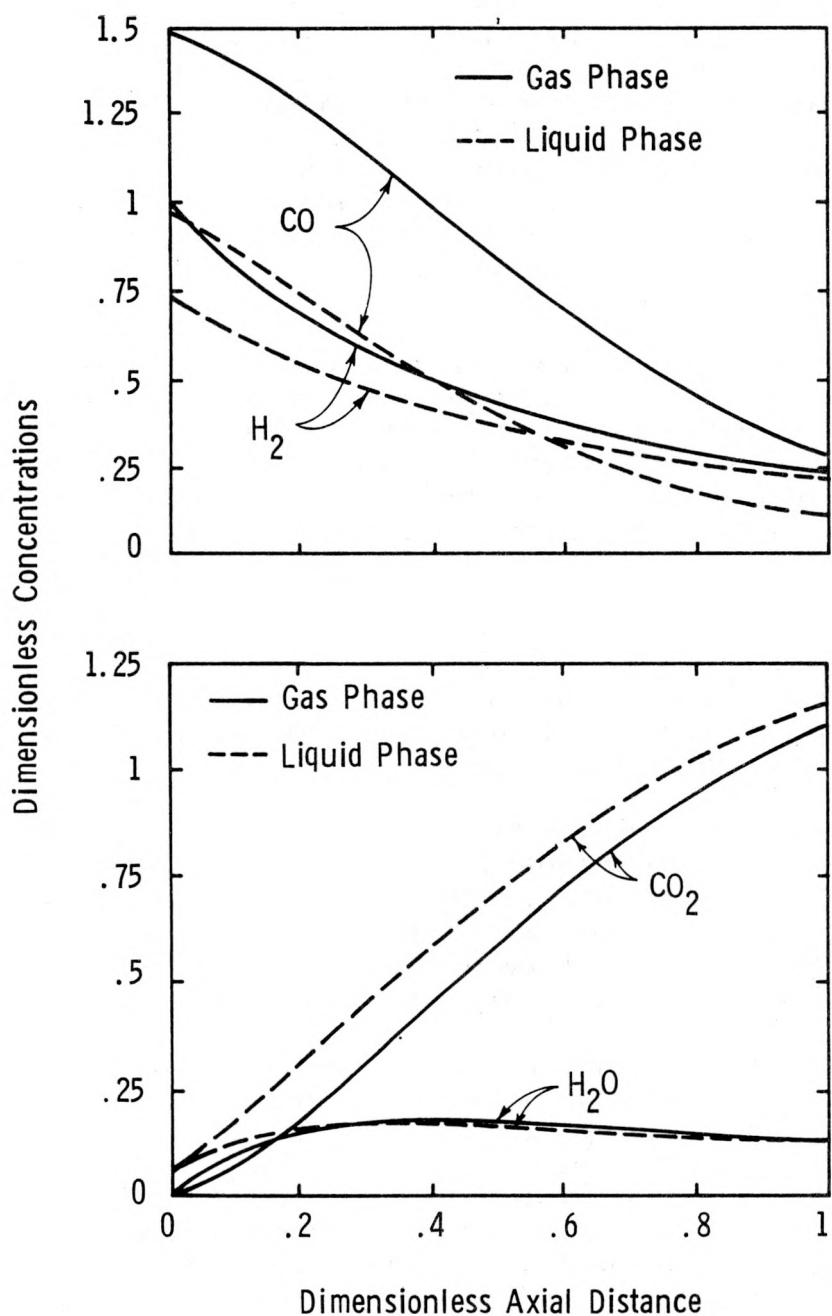


FIGURE 47

PREDICTED REACTION RATES
(Conditions of Table 34)

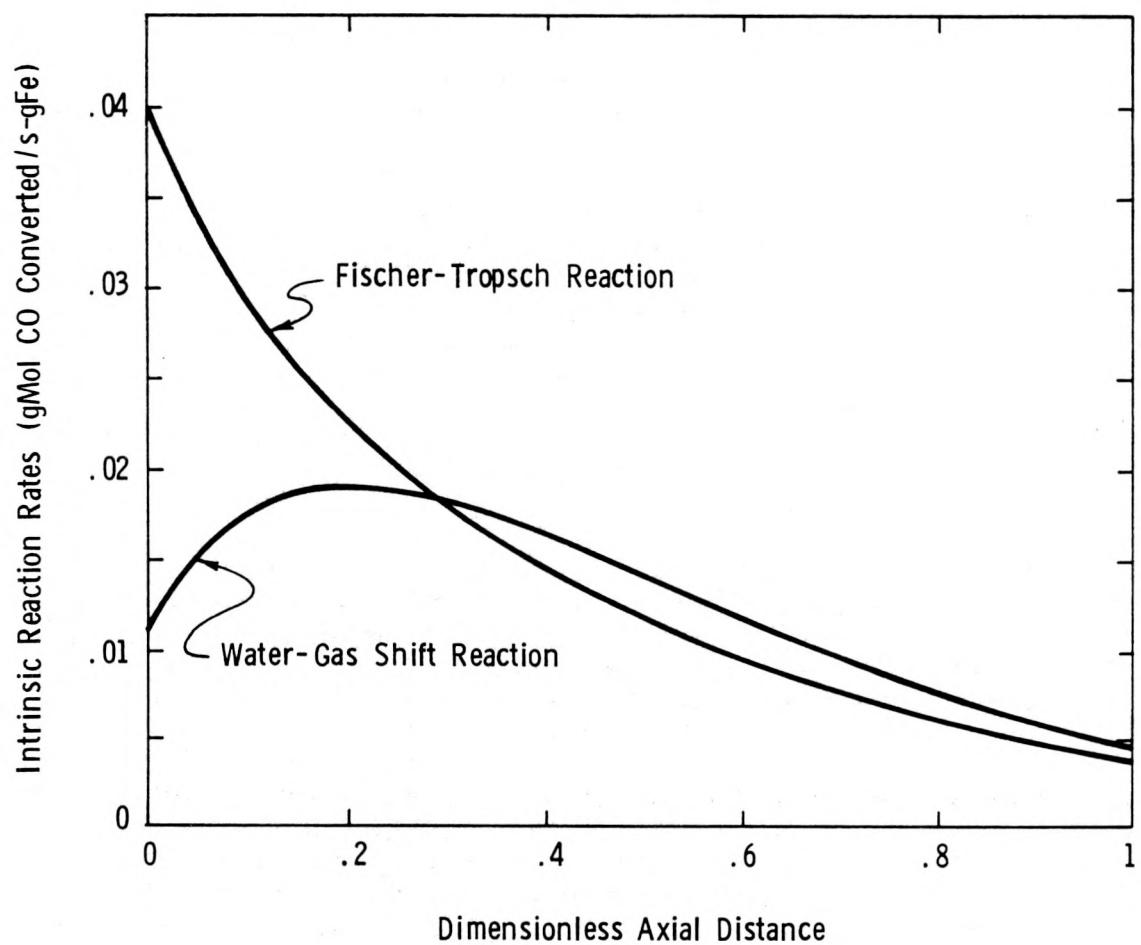
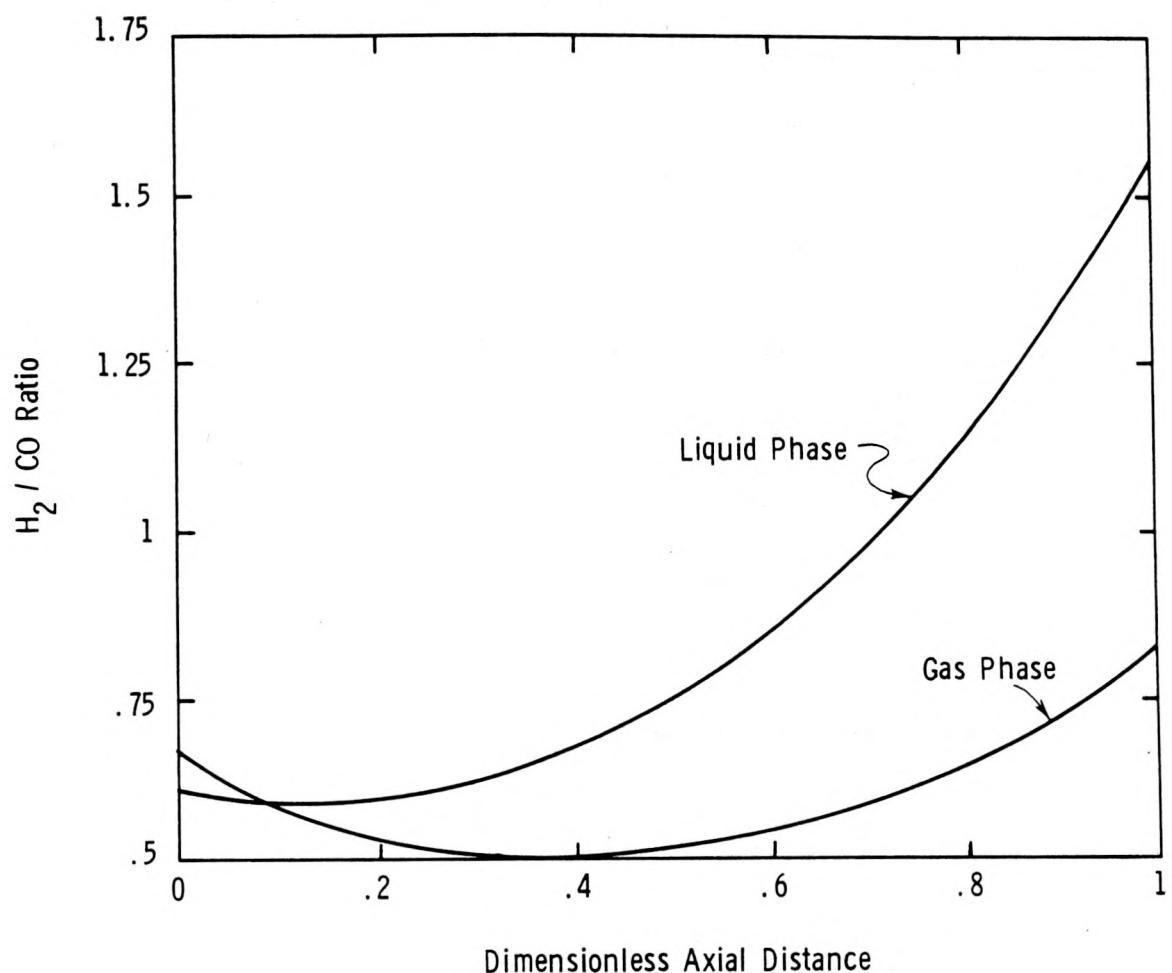


FIGURE 48

PREDICTED H_2/CO RATIO
(Conditions of Table 34)



The parameters studied were the superficial gas velocity, Fe-catalyst loading, and feed H_2/CO ratio. Figure 49 shows that the superficial gas velocity has a large effect on the F-T bubble-column performance. The predicted reactor length becomes substantially longer with higher gas velocity. Figure 50 shows that the Fe-catalyst loading also exerts a significant effect on the F-T bubble-column performance. An increase of Fe-loading from 5 to 10 wt % strongly affects the F-T column performance; however, the effect resulting from an increase of the loading from 10 to 15 wt % is considerably less. Figure 51 shows that the effect of varying feed H_2/CO ratios on the F-T bubble-column performance is not significant except in the high H_2/CO conversion region. The varying feed H_2/CO ratio affects the reactor exit H_2/CO ratio in the high H_2+CO conversion region as indicated in Figure 52. This may somewhat affect the catalyst aging and the methane formation rate, both of which vary with the H_2/CO ratio in the gas phase.

E. Comparison of Fischer-Tropsch Bubble-Column Model Predictions and Experimental Data

The predicted effect of the feed H_2/CO ratio on the exit H_2/CO ratio compares well qualitatively with experimental results from the two-stage bench-scale unit. The trends in Figure 52 (model predictions) and Figure 22 (from Run CT-256-3) are very similar.

In another set of calculations, predicted and measured H_2 and CO conversions and H_2/CO usage ratios are compared (Table 36). The multi-component mathematical model was used in those calculations. The data cover Runs CT-256-2, -3, and -4, in which the same F-T catalyst I-B was used. The intrinsic kinetic parameters were estimated using data from the beginning of Run CT-256-3 (9.2 DOS). These data were chosen because the catalyst was at its start-of-cycle activity. In addition, hydrodynamic data, i.e. gas holdup and catalyst concentration profiles were also available at that time. The intrinsic kinetic parameters were estimated to be

$$\begin{aligned} k_1 &= 0.50 \quad \text{cm}^3 \text{ liquid/gFe-s} \\ k_2 &= 1.35 \quad \text{cm}^3 \text{ liquid/gFe-s} \\ k_3 &= 0.20 \quad \text{and} \\ k_4 &= 37.5 \end{aligned}$$

(See Equations (29) and (31) for the definition of these parameters). Since catalyst aging is not taken into account in the mathematical model, the calculated results are restricted to the start-of-cycle activity of catalyst I-B.

FIGURE 49

PREDICTED EFFECT OF GAS SUPERFICIAL VELOCITY ON
 $H_2 + CO$ CONVERSION

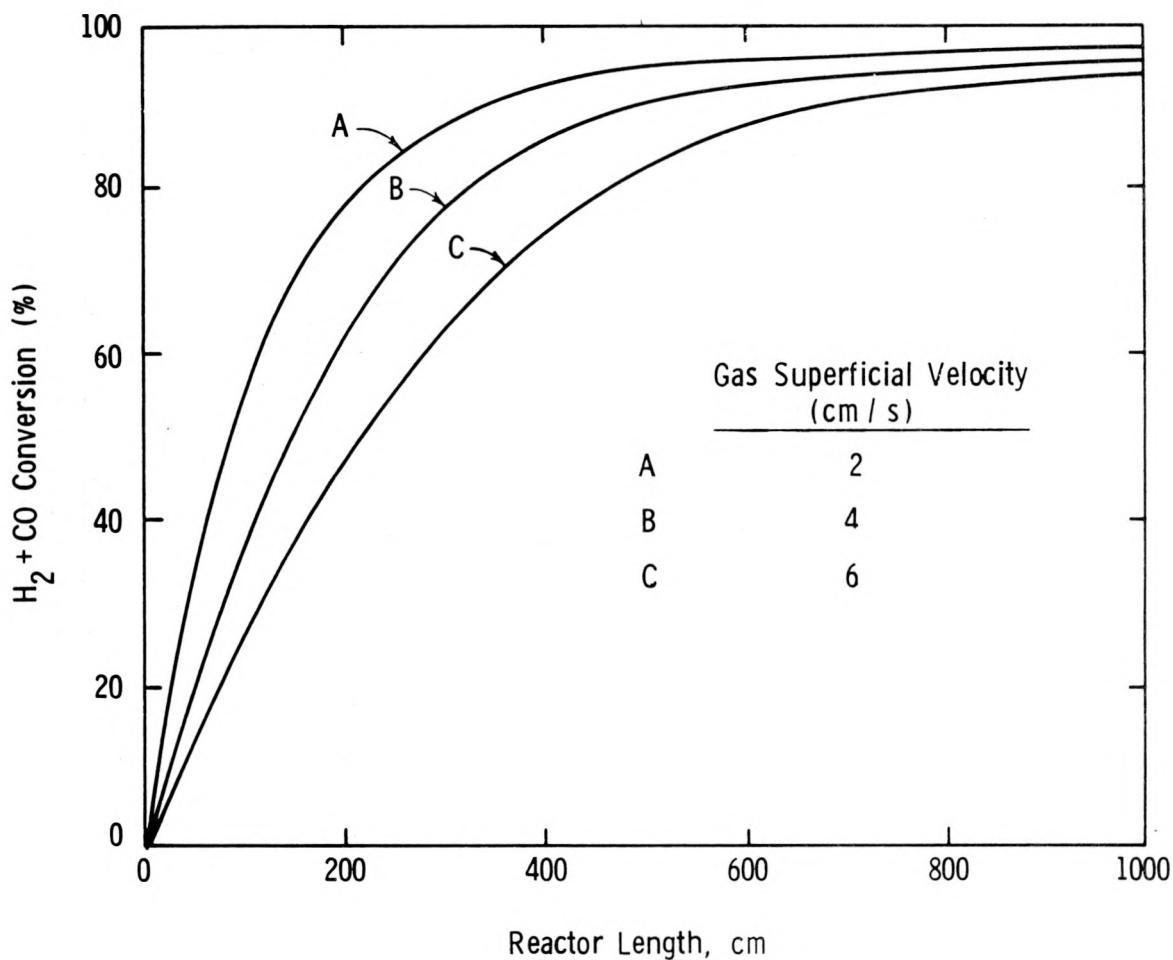


FIGURE 50

PREDICTED EFFECT OF Fe-CATALYST LOADING ON
 $H_2 + CO$ CONVERSION

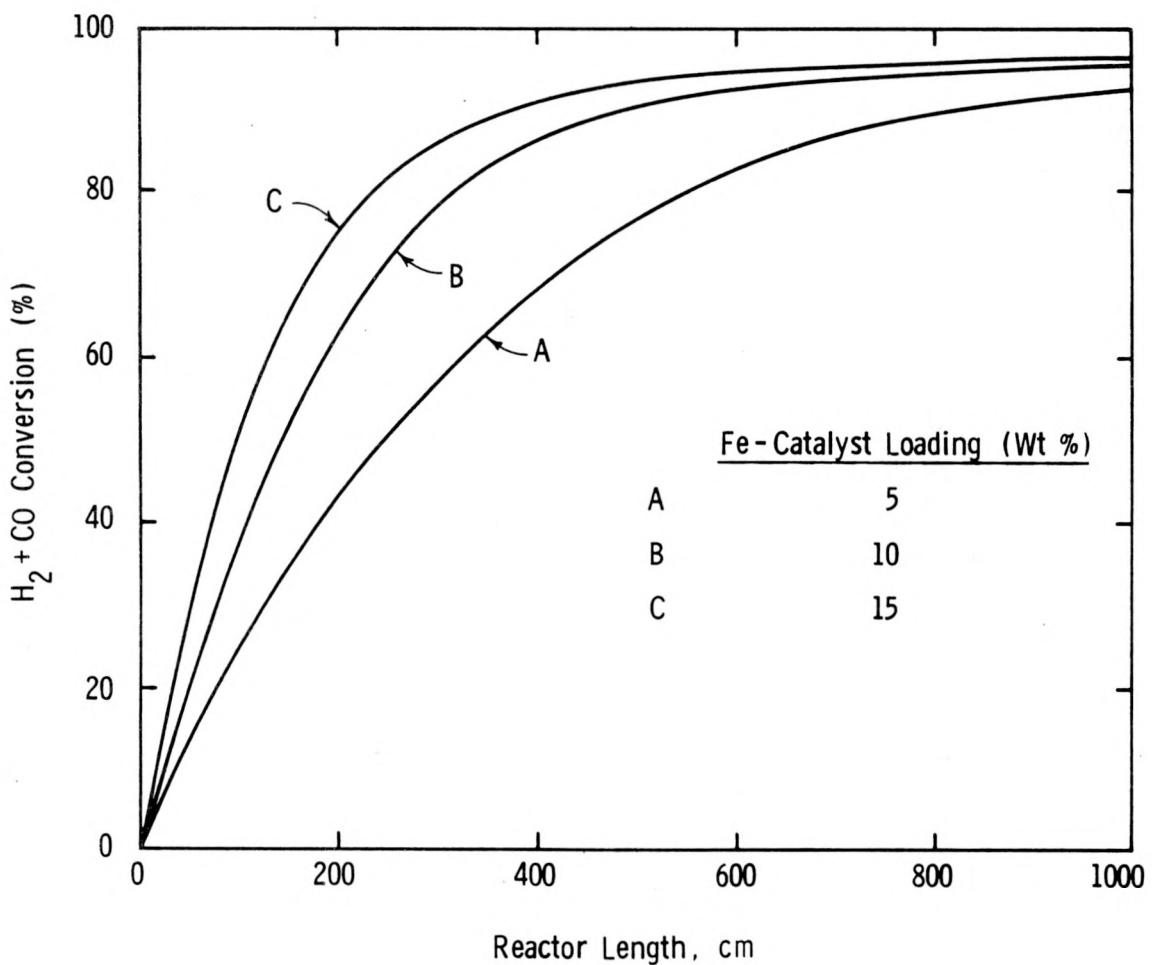


FIGURE 51

PREDICTED EFFECT OF FEED H₂/CO RATIO ON
H₂ + CO CONVERSION

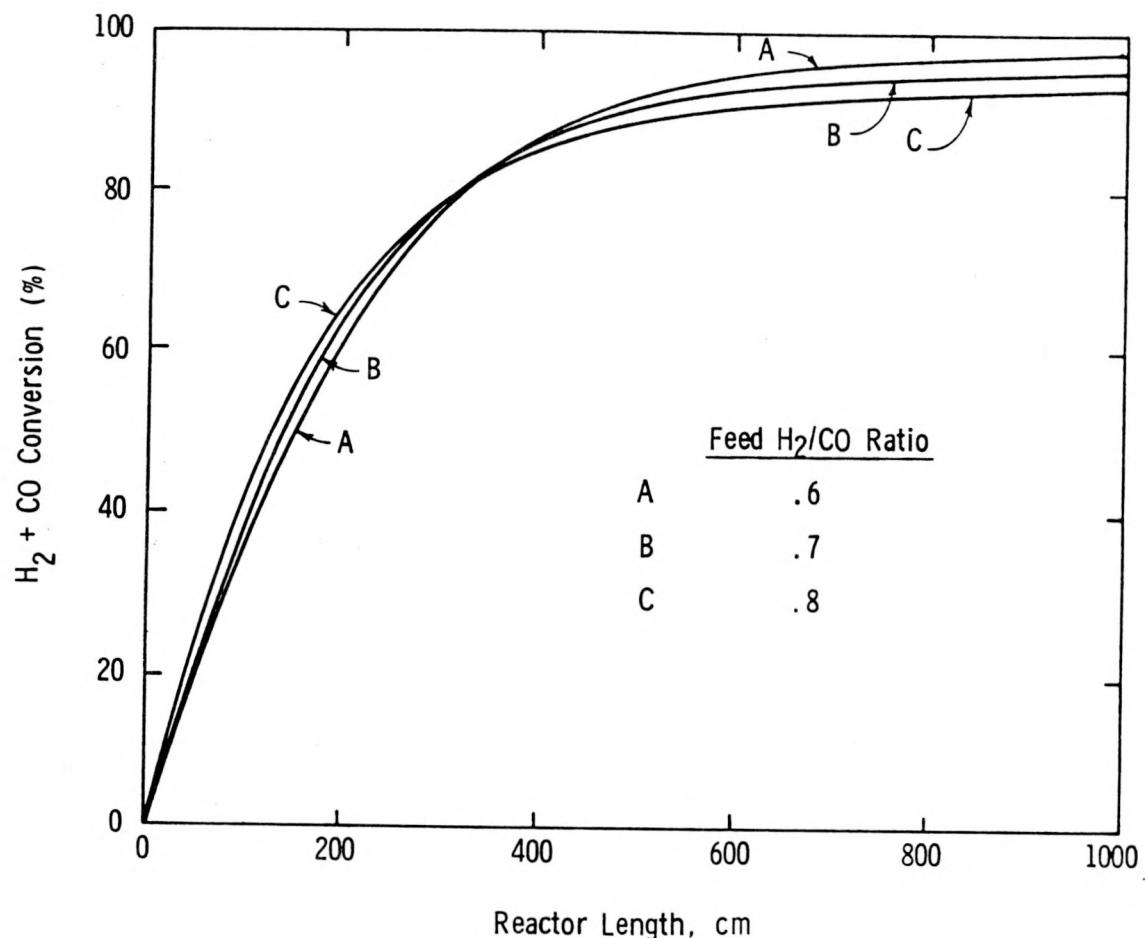


FIGURE 52
PREDICTED EFFECT OF FEED H_2/CO RATIO ON
 H_2/CO RATIO IN GAS PHASE

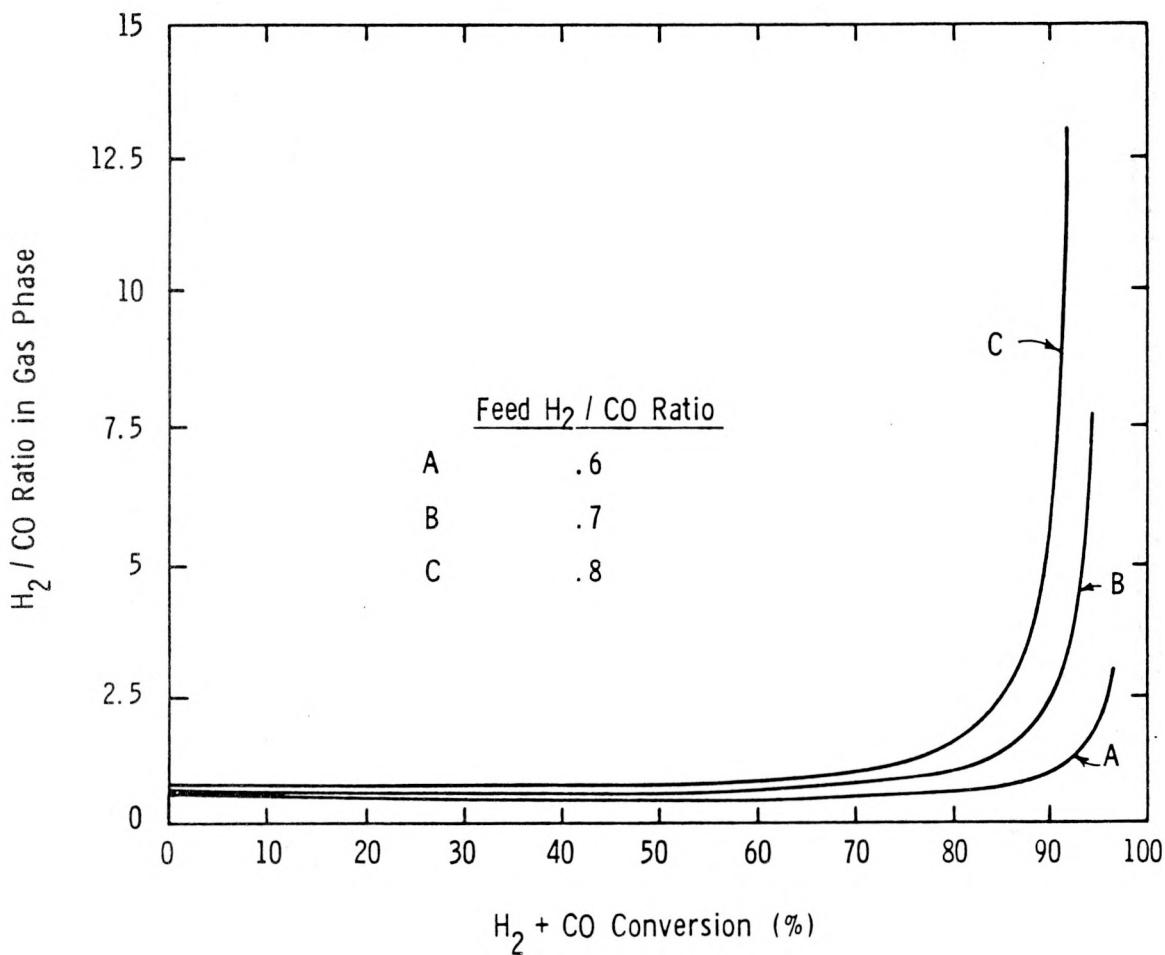


Table 36

Comparison of Multi-Component Slurry F-T Model
Predictions and BSU Bubble-Column Data

Run CT-256-	2	2	3 ⁽²⁾	3	3	3	3	4
DOS	2.9	6.9	9.2	15.8	25.0	35.5	50.5	1.6
Feed H ₂ /CO, Molar	.68	.68	.67	.67	.69	.70	.68	.70
T, °C	259	258	260	260	260	259	261	256
P, MPa	1.14	1.47	1.48	1.48	1.48	1.48	1.50	1.14
u _g ⁱ , cm/s	4.06	3.61	3.90	4.30	3.73	3.41	3.15	4.00
L, cm	762	762	728	762	713	730	671	782
w _C , Wt %	13.7	12.8	14.3	13.7	13.8	12.9	14.4	17.6
N ₂ in Feed, Mol %	4.5	3.9	4.5	12.7	4.5	5.0	6.4	8.3
ε _g , Vol %	26.6 ⁽¹⁾	23.3 ⁽¹⁾	26.6	26.6	21.7	24.7	20.6 ⁽¹⁾	20.0
H ₂ conv., % ⁽³⁾	75.8 (76.8)	77.3 (78.4)	78.3 (79.6)	72.6 (74.1)	78.4 (81.4)	79.1 (80.3)	80.0 (88.0)	64.2 (85.3)
CO conv., % ⁽³⁾	87.3 (87.1)	89.2 (89.3)	91.2 (89.7)	84.4 (82.8)	90.3 (92.7)	92.0 (92.7)	90.4 (97.6)	82.4 (97.1)
H ₂ /CO Usage Ratio ⁽³⁾	.59 (.60)	.59 (.60)	.61 (.60)	.61 (.60)	.59 (.60)	.60 (.60)	.60 (.61)	.55 (.61)

(1) Estimated gas holdup.

(2) Data used to estimate the intrinsic kinetic parameters.

(3) Numbers in parenthesis are predicted values.

Since not all the input data for the model were measured, the following assumptions were used:

- The activation energies were 100 kJ/gmol for the F-T reaction rate constant, k_1 , and 24 kJ/gmol for the water-gas shift reactor rate constant, k_2 . The parameter k_3 was assumed temperature independent, and the temperature dependence of the water-gas shift equilibrium constant, k_4 , follows that of Newsome (1980).
- Gas holdups, where noted, were extrapolated from the data at 9.2 DOS of Run CT-256-3 assuming $\epsilon_g \propto u_g$.
- Other parameters, such as d_B , K_i , D_{Li} , k_{Li} , and reactor-wax and slurry physical properties were the same as those used in the multi-component model calculations (Tables 28 and 35).
- No backmixing of either the liquid or the gas phase is assumed since this effect on the BSU slurry reactor is expected to be negligible.

The activation energy for k_1 is in line with literature data (Deckwer, et al., 1982a). The activation energy for the water-gas shift reaction is unknown and is estimated from that of the k_1 , by assuming that the activation energy is approximately proportional to the heat of reaction.

Table 36 indicates good agreement between predicted and measured results for the two balances of Run CT-256-2 (2.9 and 6.9 DOS), indicating that the kinetics and hydrodynamics at the beginning of this run are similar to those at the beginning of Run CT-256-3. The model is adequate in predicting the effect of varying superficial feed-gas velocity and pressure.

The predicted results from 15.8, 25, and 35.5 DOS of Run CT-256-3 agree well with the experimental results. The model also adequately predicts the effect of superficial feed-gas velocity (all three balances) and N_2 dilution (9.2 and 15.8 DOS). No significant catalyst aging up to 35.5 DOS is detected by comparison of the actual conversion data with the predicted data. The data from 50.5 DOS shows, however, that moderate catalyst aging might have occurred.

The data from the beginning of Run CT-256-4 show that the model significantly overpredicts the H_2 and CO conversions. There are two possible explanations. The first is that catalyst I-B was not activated properly in this run. The other is that the catalyst loading might be much larger than optimum loading. Unfortunately, the concept of optimum catalyst loading is not well understood and is not included in the current model.

VIII. Hydrodynamic Studies Using Non-Reacting Bubble-Columns (1)

A. Introduction and Conclusions

Hydrodynamic data of bubble-column reactors are essential for analyzing the performance of the reactor, for providing essential parameters for a slurry reactor mathematical model and for characterizing factors of the slurry reactor scale-up. Limited work in this area was carried out using existing nonreacting bubble-columns. The conclusions obtained from these studies shall be interpreted cautiously because of the small size equipment used. The physical limitations include the diameter of the 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 larger equipment are strongly recommended.

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 takes 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. (1982b) 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 (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

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

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 strong 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 on 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.

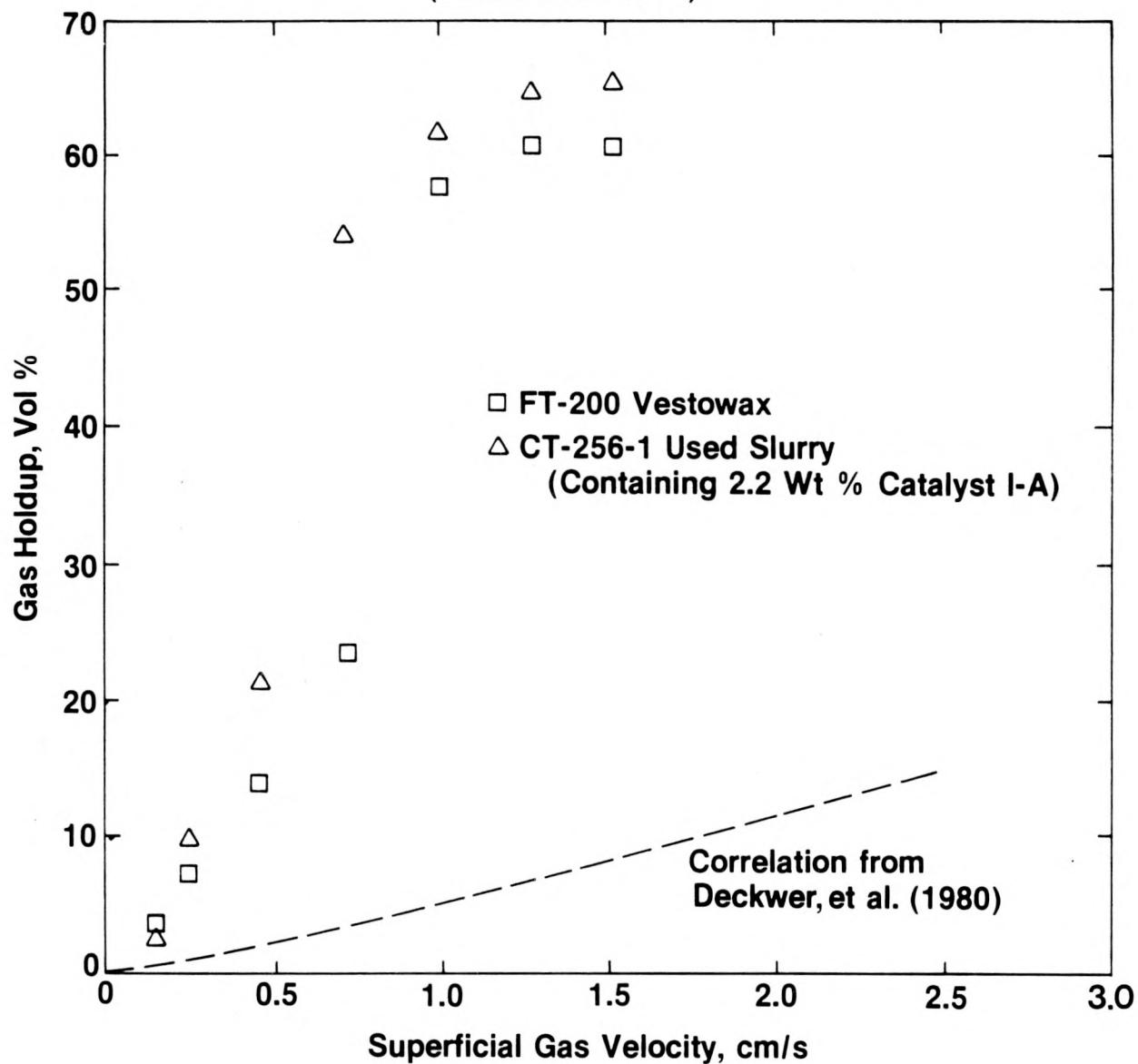
The major conclusions obtained from the current studies are summarized in the following:

- The bubble-column gas holdup decreased 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 superficial 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 superficial 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.

B. 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 53. The expanded slurry consisted of many

FIGURE 53
HOT, NON-REACTING
BUBBLE-COLUMN GAS HOLDUP
(3.2 cm ID Column)



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:

$$\epsilon_g = 0.30 u_g \quad (40)$$

As the velocity was further increased to about 1 cm/s, the wax began to foam excessively. The foaming region expanded both up and down, 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 is 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-256-1 was used. The results are also presented in Figure 53. 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 53 is the gas holdup correlation developed by Deckwer, et al. (1982b), as represented by following equation:

$$\epsilon_g = 0.053 u_g^{1.1} \quad (41)$$

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 are somewhat different from the conditions under which the correlation was established. These conditions include the static height, the column diameter, and the temperature.

C. 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 54 and Table 37. 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.

D. 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. In this study, due to equipment limitation, temperature was maintained below 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 55. 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.

FIGURE 54

**EFFECT OF SOLID CONCENTRATION
ON GAS HOLDUP**

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

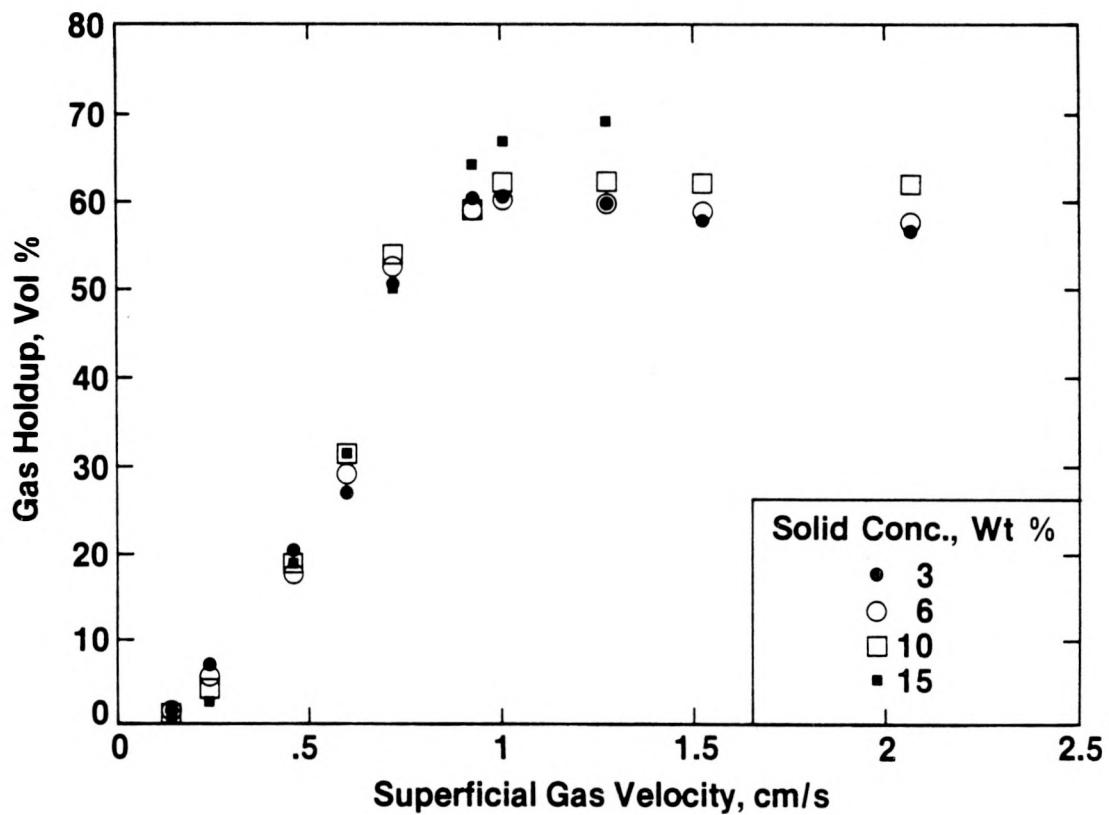


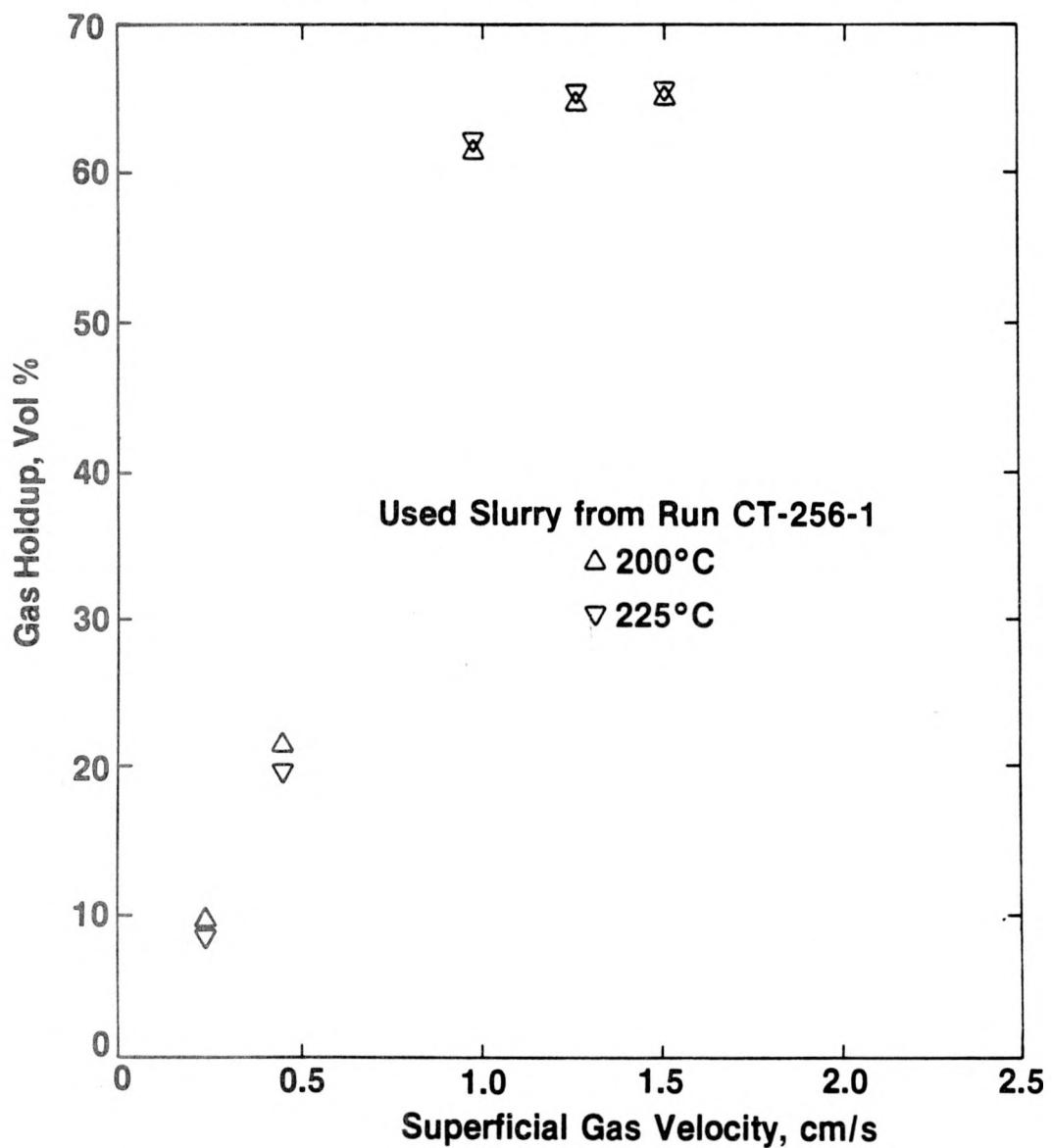
Table 37
Effect of Solid Concentration on Gas Holdup
(3.2 cm ID column. Gas Holdup in Vol %)

u_g cm/s	<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.

FIGURE 55
EFFECT OF TEMPERATURE ON GAS HOLDUP
(3.2 cm ID, Hot, Non-Reacting Column)



E. 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 56 for static heights of 46 and 69 cm. The gas holdup was found to decrease as the liquid height increased. Similar effects were also observed by Langemann and Koelbel (1967). 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 38 and 39. 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/ N_2 system for liquid heights of 60-100 cm. Likewise Yoshida and Akita (1965) observed no effect for larger 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/ CO_2 system. Shulman and Molstad (1950) also observed an effect of column diameter for an air/ H_2O 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

FIGURE 56

**EFFECT OF STATIC LIQUID HEIGHT
ON GAS HOLDUP**
(3.2 cm ID, Hot, Non-Reacting Column)

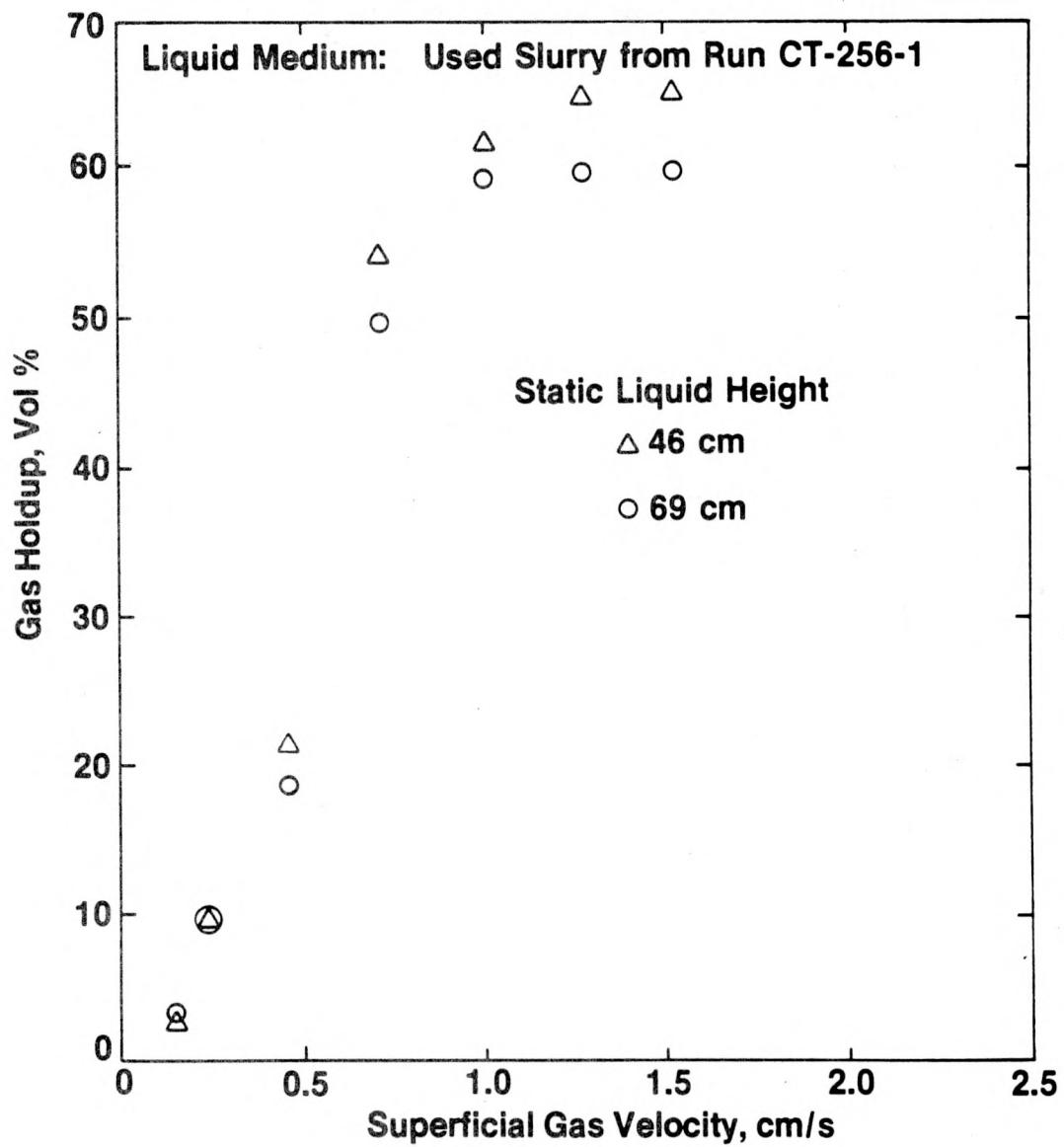


Table 38

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 39

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>15</u>	<u>36</u>	<u>63</u>	<u>169</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	-

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 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. Thus it is advisable to study bubble-column hydrodynamics in a tall column.

IX. Analytical Procedures and Supporting Tests

A. Introduction

The streams that require analysis include carbon monoxide, hydrogen, the combined feed gas, the first-stage F T products (gaseous, aqueous, liquid hydrocarbon, and reactor wax phases), and the second-stage products (gaseous, aqueous, and liquid hydrocarbon phases). The analytical procedures and supporting tests for these streams are summarized in this section.

B. Carbon Monoxide, Hydrogen, and Combined Feed-Gas

These streams are analyzed on-line using a Mobil-developed automated gas chromatographic (GC) system. The same system is used for on-line analysis of the gaseous product streams from both the first-stage and the second-stage reactors.

C. First-Stage Fischer-Tropsch Products

The analysis of the F-T products are very complicated because of the wide boiling range and the diversity of the product components. Figure 57 summarizes the analytical scheme.

The combined gas stream from the cold and chilled condenser is analyzed on-line using the on-line GC system. The stream contains N₂, H₂, CO, CO₂, H₂O, and hydrocarbons. The amount of hydrocarbons heavier than C₈ is insignificant in this stream. A typical GC plot for such a sample is given in (A) of Figure 58.

Non-acidic oxygenates in the aqueous phase are determined by fused silica capillary column GC (FS-GC) as indicated in Figure 59. Acids are determined by ion chromatography. The major oxygenates in the aqueous phase identified by gas chromatography-mass spectrometry (GC-MS) are summarized in Table 40. Normally, the C₁-C₈ linear alcohols are the major components with smaller amounts of ketones, acids, and mixed esters.

The C₅⁺ oxygenates present in the liquid-hydrocarbon phase are determined as previously reported by Di Sanzo (1981). Recently the gas chromatographic analysis has been improved by employing fused silica capillary columns and cool on column splitless injections. Figures 60 and 61 represent typical gas chromatograms of C₆⁺ alcohols and acids, and C₅⁺ ketones and esters, respectively, isolated from the hydrocarbon phase by liquid chromatography (LC). Normally, linear alcohols are the major oxygenates, followed by methylketones. Mixed esters as a result of secondary reactions between the various acids (acetic, propanoic, butyric, etc.) and alcohols are also present. The C₅⁺ acid content has been determined to be generally low (~0.1% wt of

FIGURE 57
ANALYTICAL SCHEME
OF FISCHER-TROPSCH PRODUCTS

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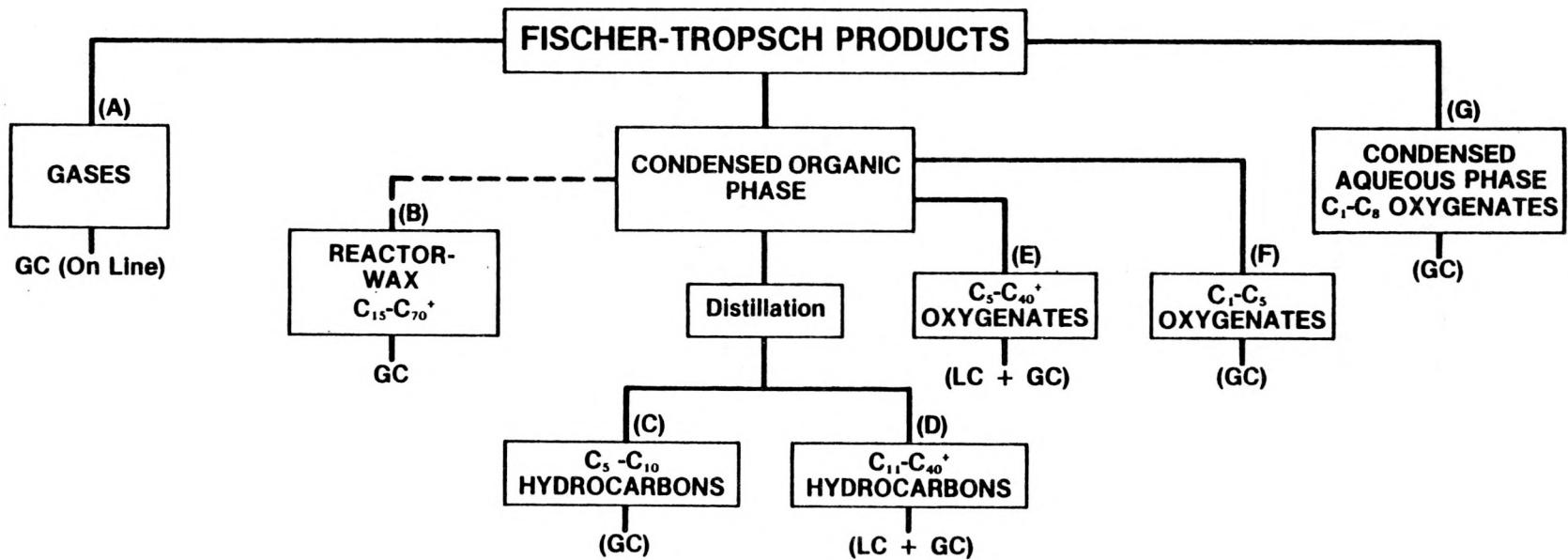
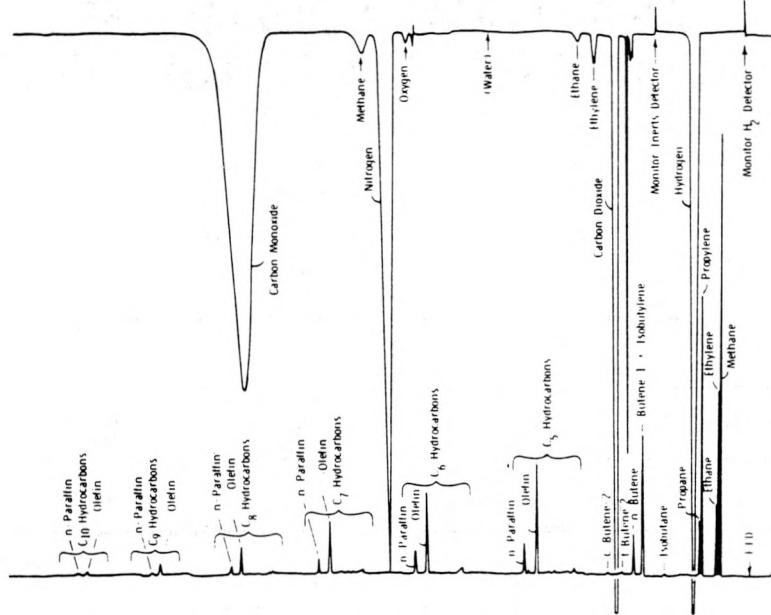


FIGURE 58

(A) FIRST-STAGE REACTOR GAS SAMPLE



(B) SECOND-STAGE REACTOR GAS SAMPLE

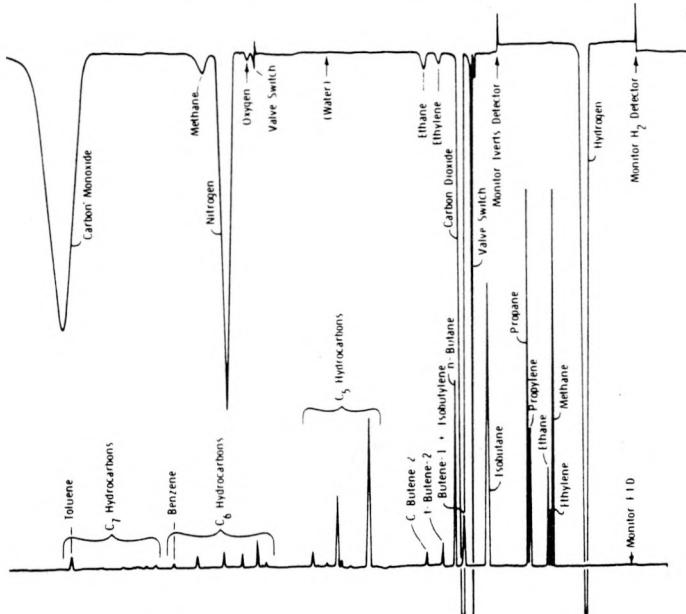
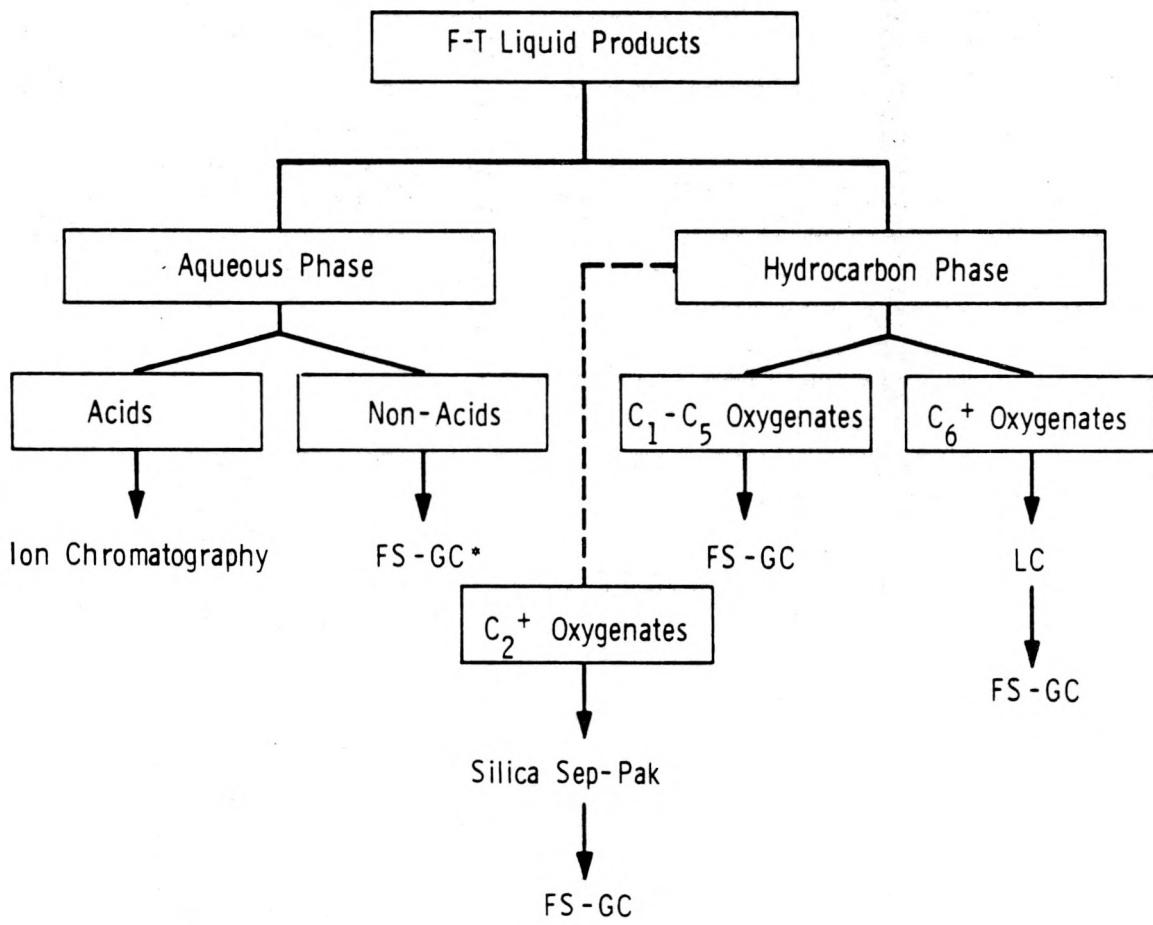


FIGURE 59

**ANALYTICAL SCHEME OF
FISCHER-TROPSCH OXYGENATES**



* FS-GC = Fused Silica Capillary Gas Chromatography.

Table 40
Identities of Major Aqueous Phase Oxygenates

<u>Peak No.</u>	<u>(1)</u>	<u>Oxygenates</u>
1		methanol
2		ethanol
3		acetone
4		isopropanol
5		t-butyl alcohol
6		1-propanol
7		butanal
8		methylethyl ketone
9		2-butanol
10		ethyl acetate
11		isobutanol
12		2-methyl-2-butanone
13		acetic acid
14		1-butanol
15		2-pentanone
16		pentanal+3-pentanone
17		2-pentanol
18		ethyl propanoate
19		propyl acetate
20		methyl butanoate
21		propanoic acid
22		3-methyl-1-butanol
24		1-pentanol
25		2-hexanone
26		butyric acid
27		other C ₆ oxygenates
28		1-hexanol
29		other C ₇ oxygenates
30		1-heptanol
31		other C ₈ oxygenates
32		1-octanol

(1) Identified by gas chromatography-mass spectrometry.

FIGURE 60

GAS CHROMATOGRAM OF C_6^+ ORGANIC PHASE
ALCOHOLS AND ACIDS

C_x = N-Alcohols

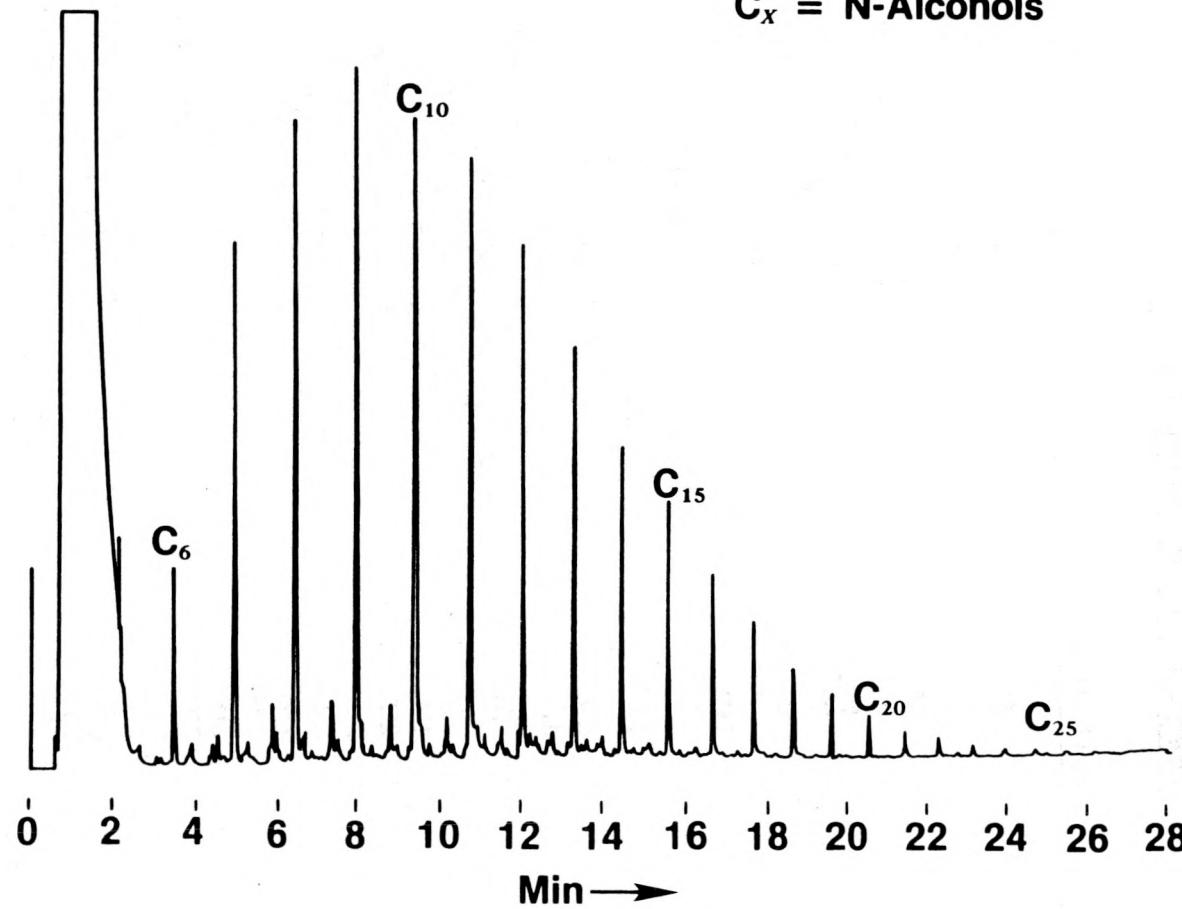
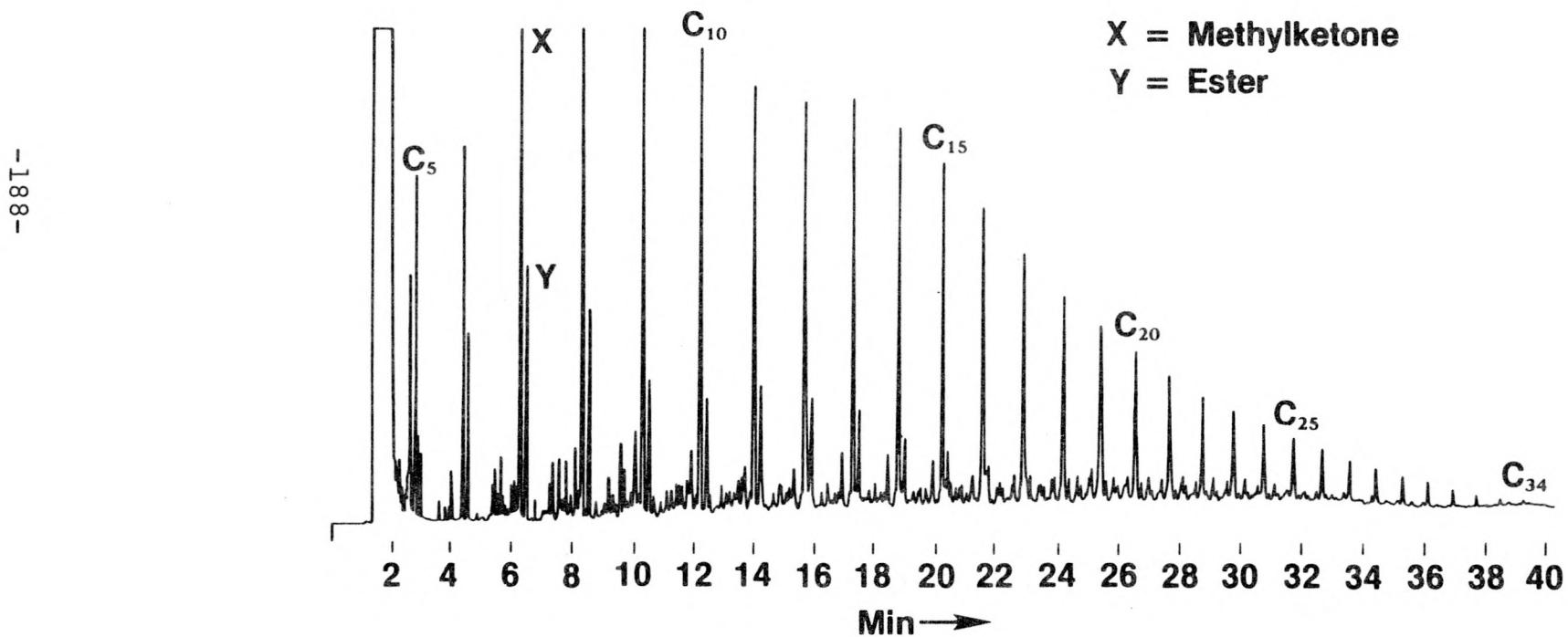


FIGURE 61

**GAS CHROMATOGRAM OF C_5^+ ORGANIC
PHASE KETONES AND ESTERS**



hydrocarbon phase). With these methods, oxygenates up to C₄₀ can readily be determined.

The C₁ to C₅ oxygenates present in hydrocarbon phase are determined by aqueous extraction of the hydrocarbon phase followed by gas chromatographic analysis of the aqueous extract.

An optional analysis for the aqueous F-T product is Acid Number.

The liquid hydrocarbon phase contains mainly olefins and paraffins. The olefinic and paraffinic compositional analysis is carried out by various GC and LC techniques. Carbon number distribution is readily obtained (<1 hour) by a single injection onto an FS-GC capillary column. A typical chromatogram is given in Figure 62. This simple technique will indicate how the major olefins, i.e., linear α -olefins and cis, trans-2 linear olefins, vary with respect to the normal paraffins. Significant changes in the reactor hydrocarbon composition is thus readily detected.

A more detailed analysis is also performed on selected material balances. A liquid hydrocarbon sample is separated into two fractions distilled at 196°C B.P. (about C₁₁) by distillation. The C₁₁⁺ fraction after removing the oxygenates by passage through a silica gel SepPak (Waters Associates, Milford, Mass.) is injected into a gas chromatograph equipped with an olefin scrubber and two flame ionization detectors. By comparing detector signals total olefins/paraffins can be determined. In addition, major components are identified. Figure 63 shows typical chromatograms of these analyses. The C₁₂⁺ olefins/paraffins are determined as described by Di Sanzo (1981).

Other analyses for the first-stage liquid hydrocarbon product include Acid Number, Bromine Number, Hydroxyl Number, and Simulated Distillation.

The reactor-wax withdrawn from the slurry reactor consists of components with a carbon number distribution from about C₈ to C₇₀⁺. A gas chromatographic technique has been developed employing a short (8 m) fused silica capillary column. The reactor-wax (catalyst-free) after being dissolved in hot toluene is injected into the capillary column by the cool on-column injection technique. The latter injection technique minimizes discrimination for the high boiling components. A sample chromatogram is given in Figure 64 for a F-T wax sample employed as a start-up medium in the operation of the two-stage bench-scale pilot plant.

A LC method has also been developed for the determination of oxygenates in the reactor-wax. Total oxygenates is obtained by weighing the isolated oxygenate fraction after solvent evaporation. Carbon number distribution of the oxygenates is

FIGURE 62

TYPICAL GAS CHROMATOGRAM OF
TOTAL LIQUID HYDROCARBON PHASE

-190-

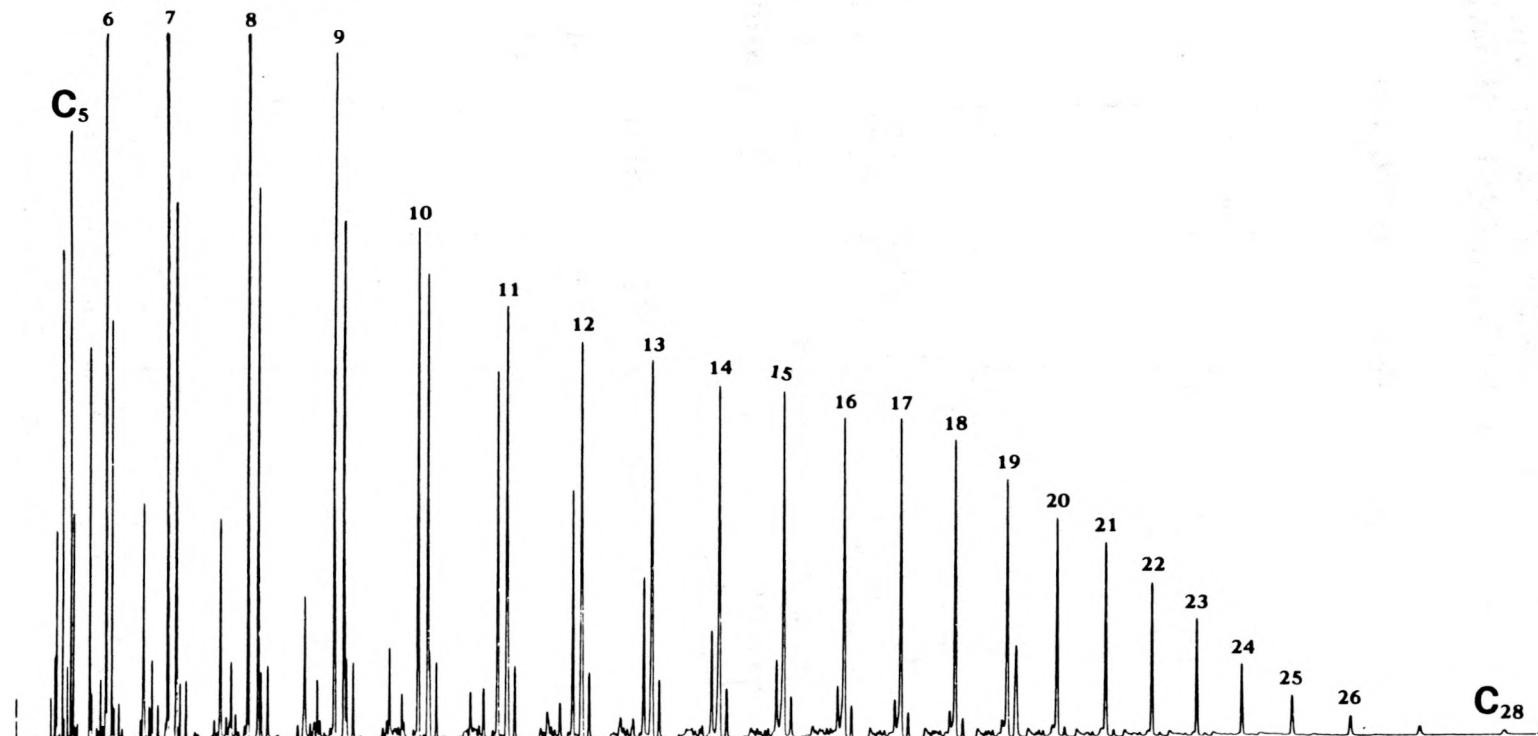
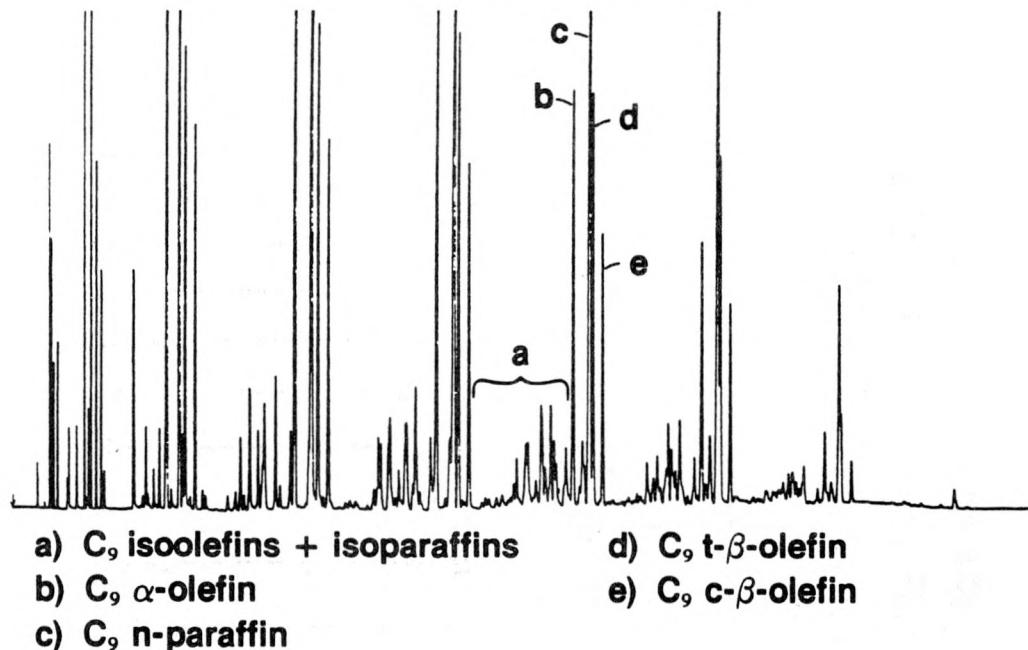


FIGURE 63

TYPICAL CHROMAGRAMS OF C_{11}^- FROM LIQUID HYDROCARBON PHASE

(A) OLEFINS + PARAFFINS



(B) PARAFFINS ONLY

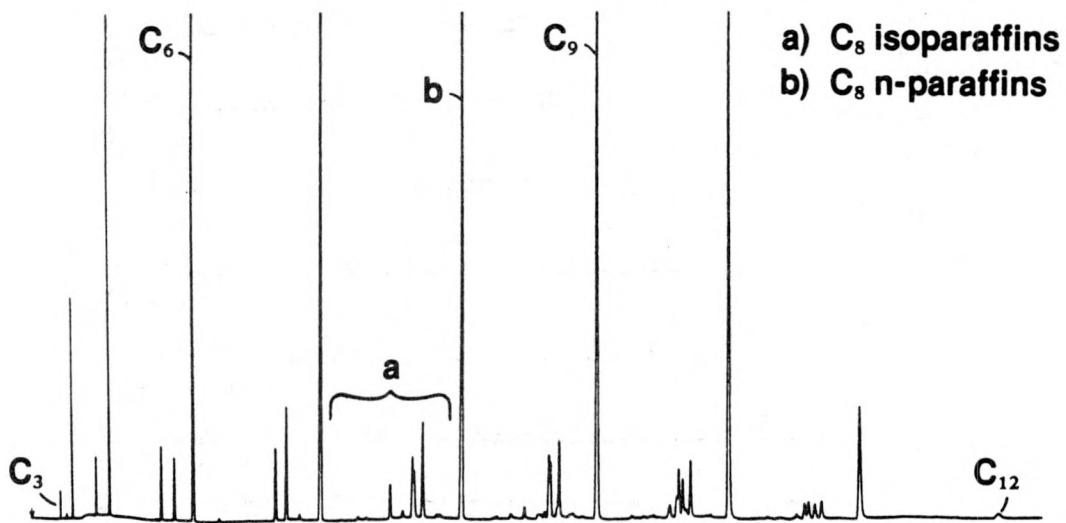
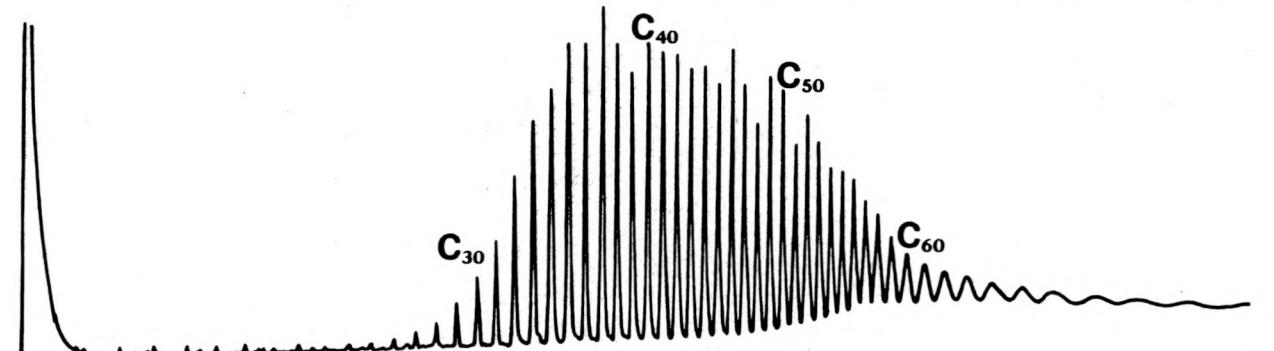


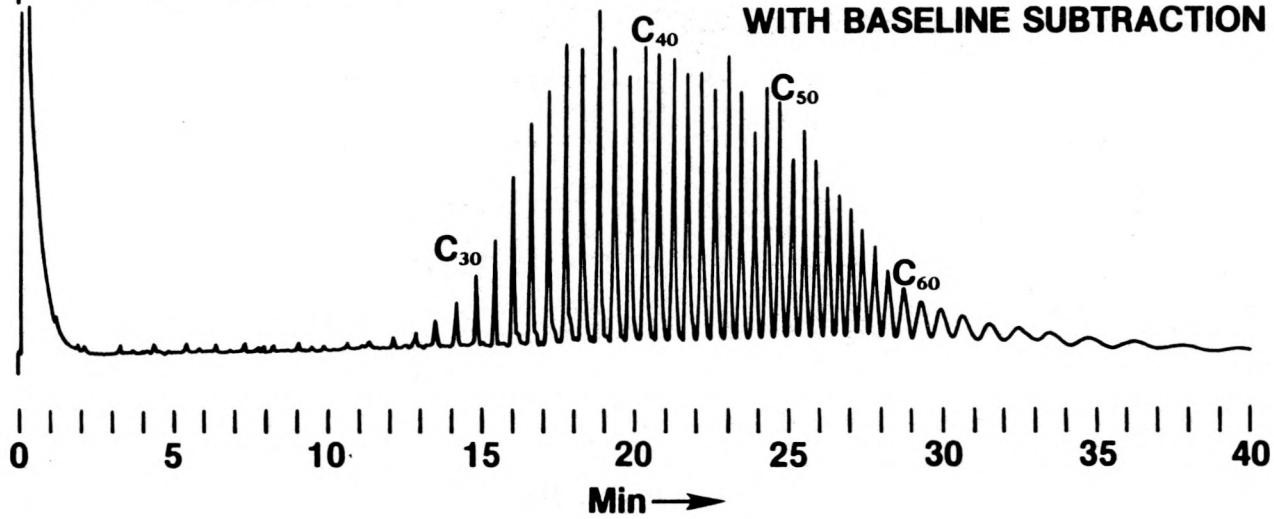
FIGURE 64

GAS CHROMATOGRAM OF
A HEAVY REACTOR-WAX

WITHOUT BASELINE SUBTRACTION



WITH BASELINE SUBTRACTION



then obtained by FS-GC with cool on-column injection. Alcohols and ketones (major oxygenates) can be distinguished chromatographically.

Other analyses for the F-T reactor-wax are Kinematic Viscosity, Surface Tension, Vacuum and Analytical Distillation, and Specific Gravity.

D. Second-Stage ZSM-5 Products

The products from the second-stage ZSM-5 reactor are separated into three streams, i.e., gaseous, aqueous, and liquid hydrocarbons. Analysis of the gaseous product is similar to that of the first-stage gaseous product using an on-line GC system. A typical chromatogram is included as (B) of Figure 58. The aqueous stream from the ZSM-5 reactor contains insignificant amounts of oxygenates and only its pH values are occasionally measured.

Analyses of the liquid hydrocarbon product from the ZSM-5 reactor is more complex. A three-column GC system and an olefin scrubber are used. This setup is similar to a system employed for the Methanol-to-Gasoline process (Bloch, et al., 1977). The system is highly automated and can identify individual components up to approximately C₁₀.

The small amount of components boiling above 204°C are determined by capillary column GC and identified by GC-MS. Finally, a LC method has been developed for the determination of trace oxygenates which may be present.

Other analyses employed for the second-stage liquid hydrocarbon product include Research and Motor Octane Numbers, and Acid Number.

X. Characterization of Gasoline Product

A. Raw Gasoline Characterization Tests

In addition to gasoline yield, the performance of the second-stage ZSM-5 reactor must also be judged by the quality of the gasoline product. In the two-stage BSU, the total gasoline is obtained by combining many streams. The major stream is the C₅+ in the raw gasoline (60-65 wt %) collected in ambient and chilled condensers. Other streams include the C₅+ hydrocarbons in the vapor product, the alkylate produced by alkylating butenes and propylene with i-butane, and the butanes added to achieve proper gasoline vapor pressure. The yields and properties of the finished gasoline can be estimated from material balance data.

A detailed blending calculation was carried out to establish the design base data for the conceptual commercial plant design. It was shown that 63 wt % of the finished 10 RVP (Reid Vapor Pressure) gasoline consisted of C₅+ hydrocarbons from the ambient and chilled condensers. Fifteen percent of the remaining constituents was C₅+ hydrocarbons from the gaseous product stream, 18% was from alkylate, and 4% was n-butane. The properties of the finished gasoline are summarized as follows:

Research Octane, Clear	89
Motor Octane, Clear	83
RVP, psia	10
PONA, vol %	67/13/4/16

Distillation, °C	ASTM	TBP
10 vol %	43	29
30 vol %	59	61
50 vol %	93	72
70 vol %	116	92
90 vol %	141	159

The estimated octane number (R+0) of the total gasoline was very close to that of the raw gasoline, and the final gasoline exhibited similar characteristics of conventional petroleum-derived gasoline. Consequently, it was sufficient to judge the performance of the second-stage ZSM-5 reactor by characterizing the qualities of the raw gasoline samples collected from the two-stage pilot plant.

The properties of raw gasoline collected during Runs CT-256-1, -2, and -3 are summarized in Tables B-8, C-5 and D-8, respectively.

The high aromatic content and high octane number of the raw gasoline collected during Run CT-256-1 reflects strongly the consequence of high severity operation in the second-stage reactor. The unleaded research octane numbers ranged from 95 to 97, while the leaded research octane numbers (R+3) ranged from 100 to 105. The severity indexes of the second stage reactor operation, measured as molar i-butane/(propylene + butenes) ratio, ranged from 1 to 8. An index higher than 1.0 generally reflects a high severity operation which results in low propylene and butene yield and thus low alkylate yield. A low alkylate yield usually coincides with a low total gasoline yield. In Run CT-256-1, the C₅+ hydrocarbon including alkylate was about 73 wt % of the total hydrocarbons produced. The gasoline yield increases with lowering the operating severity, as demonstrated in Runs CT-256-2 and -3.

From the ASTM distillation data, it can be seen that during Runs CT-256-1, -2 and -3, the end point of all samples was higher than the ASTM gasoline end-point specification of 225°C. The analyses of these samples showed that they contained about 3-5 wt % of hydrocarbons with boiling points greater than 225°C. These heavier hydrocarbons were, however, 2-3 wt % of the final total finished gasoline and can be removed easily by simple distillation.

As described in Subsection VI.D.3, the first three samples of Run CT-256-1 exhibited foaming at the end of ASTM D-86 distillation and distillations were stopped prematurely. This unusual phenomenon may be related to the fact that these three samples were obtained under the most severe condition in the second-stage operation, and that their aromatic content was very high. The foaming was not experienced with gasoline samples of Runs CT-256-2 and -3.

Another important property of the raw gasoline was its acid content. Except for a few samples, the acid numbers of the majority of the raw gasoline samples were less than 0.19 mgKOH/g. As described before in Subsection VI.B.3, these acids can be removed by simple water washing. In one instance, a raw gasoline sample (20 g) with an acid number of 0.19 mgKOH/g was washed twice with fifty grams of distilled water. The acid number was reduced to zero after the washing.

Figure 25 (Subsection VI.D.3) shows the research octane numbers, aromatic content, and olefin content of the raw gasoline collected during Run CT-256-3 as a function of second-stage operating severity index. The octane numbers during Runs CT-256-2 and -3 range about 90-94 with severity index of 0.5-2.

B. Raw Gasoline Product Stability Tests

Raw gasoline product samples, taken from Runs CT-256-2 and -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 41, existent (heptane-washed) gum contents of 1 to 4 mg/100 cm³ were found in all samples, thus meeting the 5 mg/100 cm³ maximum specification of ASTM D439 for automotive gasolines. However, total residues on evaporation were very high (ranging up to 170 mg/100 cm³) in several of the tests, indicating the presence of high-boiling, heptane soluble materials. The 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 249°C were measured. The drastic differences in the total gums for some of the samples 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.

Long-term storage stability tests were conducted on a water-washed composite sample (ASTM D974 total acid number of 0.05 mgKOH/g) of Run CT-256-3 to determine the stability of the gasoline product under accelerated oxidation conditions. Metal deactivator at 1 lb per 1,000 bbl and two different antioxidants at 10 lb per 1,000 bbl were added to two separate portions of the unit product prior to the test.

This long-term test involves storage of the test fuel at 43°C with measurement of gum formation during a sixteen week period. Samples are taken at the start and at incremental periods for total and existent gum contents (ASTM D381). Based on our experience, the amount of gum formed during the storage test provides a good correlation with the gum formation during ambient field storage conditions for approximately one year.

Existen (heptane-washed) gum (ASTM D381) contents of 1 to 3 mg/100 cm³ were found in all samples at the start of the storage tests, thus meeting the 5 mg/100 cm³ maximum specification of ASTM D439 for automotive gasolines. The existent gums increased less than 1 mg/100 cm³ after sixteen-weeks of elevated temperature storage, well within the guideline limits (increase of \leq 2 mg/100 cm³) for commercial motor gasolines. Thus,

Table 41

Raw Gasoline Short-Term Stability Tests

<u>Mat.</u> <u>Balances</u>	<u>DOS</u>	<u>Additive</u> <u>Pkg. No.*</u>	<u>ASTM D381 GUMS,</u> <u>mg/100 cm³</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
CT-256-3-57	66.5	1	4	119	620
CT-256-3-57	66.5	2	4	81	710
CT-256-3-63	78.5	1	1	37	660
CT-256-3-63	78.5	2	2	12	825

*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.

satisfactory stability performance would be expected for the products during conventional field storage at ambient temperatures. However, samples taken at the start and at incremental periods contained high-boiling, heptane-soluble materials which resulted in very high and unsatisfactory total residues on evaporation (approximately 150 mg/100 cm³ throughout the test period) in the ASTM D381 test. Federal Specification VV-G-1690B for automotive gasolines, for example, limits the total residue on evaporation to 10 mg/100 cm³ maximum. These high boiling materials would be removed by simple distillation in commercial plants.

In addition to the long-term storage tests, short-term accelerated oxidation stability (ASTM D525) tests were also conducted on these samples. Induction times of 510 to 560 minutes was obtained, verifying that the product has satisfactory resistance to oxidation.

Standard N.A.C.E. (National Association of Corrosion Engineers) corrosion tests were conducted on a water washed composite raw gasoline sample (ASTM D974 total acid number of 0.05 mgKOH/g) of Run CT-256-3 to determine the corrosion tendencies. The N.A.C.E. test method involves contacting a cylindrical steel specimen with a constantly stirred mixture of 91% distilled water (maintained at 38°C) for a period of 3 1/2 hours. Performance is expressed by a scale dependent on a visual observation of the rust on the steel specimen surface.

Metal deactivator at 1 lb. per 1000 bbl. and two different antioxidants at 10 lb. per 1000 bbl. were added to two separate portions of the sample. The N.A.C.E. corrosion tests were conducted on duplicate samples from these two portions and on an additized petroleum-sourced unleaded gasoline. Tests were also run on these fuels with a commercial corrosion inhibitor at a conventional level of 2.1 lb. per 1000 bbl. The steel specimen surfaces were severely rusted in tests of fuel samples without corrosion inhibitor. Testing of the fuels containing the corrosion inhibitor, on the other hand, indicated satisfactory protection, showing zero to less than 0.1% (2 or 3 spots of no more than 1 mm diameter) of the surface rusted. Based on these results, it is concluded that the use of a commercial corrosion inhibitor will satisfactorily control the fuel's corrosion tendencies.

In addition to these tests, two raw gasoline samples from Run CT-256-1 were examined which had ASTM D-974 acid numbers of 0.15 (forty-eight DOS) and 0.28 (twenty-eight to thirty DOS) mgKOH/g. Because of limited sample size available at the time, standard corrosion tests could not be run; however, modified in-house tests were conducted to obtain relative comparisons of corrosion tendencies for the two acid number levels and a conventional petroleum sourced unleaded gasoline. The modified

test used a tall bottle with a galvanized iron strip standing in a bottom water layer, with the gasoline sample above, and with air exposure at the top. Results, judged after four weeks storage at 43°C, indicated trace-to-light corrosion for the 0.15 and 0.28 acid number samples and reference unleaded gasoline. Similar gasoline samples of 150 cm³ were then washed first with 15 cm³ of 15 wt % caustic soda solution and then with 15 cm³ of distilled water, and finally subjected to the same test. However, no significant improvements in the test results were observed.

XI. Conceptual Process Design and Scoping Cost Estimate

A. Introduction

A conceptual process design and scoping cost estimate for a commercial plant producing 27,000 BPSD of 10 RVP gasoline plant has been developed for the two-stage slurry F-T/ZSM-5 process. The objectives of the study are two-fold. One is to study the layout of all the processing units and equipment; the other is to provide guidances for future research and development. The design of the plant is as a battery limit part of a complete coal conversion complex. The feed to this plant is a clean synthesis gas derived from a BGC (British Gas Corporation)/Lurgi slagging gasifier which is not included in this design and cost estimate. The composition and quantity of the feed-gas are those used in a study in a report by Gray, et al. (1980).

The data base used for the conceptual design was obtained from Run CT-256-3 and represents a gasoline mode operation. The data for the first-stage slurry F-T reactor were taken from material balance no. 22, which is typical of 1.48 MPa (200 psig) operation at 260°C. The data for the second-stage ZSM-5 reactor were taken from material balance no. 34, which is typical of operation at a target operational severity-index ($i\text{-C}_4/(C_3^= + C_4^=)$ molar ratio) of about 0.9. The data base was established by adjusting the raw data for atomic balances.

The plant consists of a reactor section and a product recovery section. The reactor section, the integrated two-stage slurry F-T and fixed-bed ZSM-5 reactors, consists of forty slurry F-T reactors and five ZSM-5 reactors. The product recovery section consists essentially of conventional distillation facilities. A CO_2 removal unit and an alkylation unit are also included. The cost of battery limit facilities is estimated at \$700 million using mid-1983 instantaneous cost basis at a Wyoming location. This is strictly a scoping cost estimate and shall not be used for absolute comparisons of investments from other studies or for purposes other than the objectives mentioned above.

For convenience, the conventional engineering units are used throughout this chapter.

B. Scope of Study

The study covers development of a conceptional design and cost estimate of the battery limits facilities for the Mobil two-stage process. The synthesis gas feed is assumed available at the required conditions from advanced gasifiers of the BGC/Lurgi type. Basis of the study and the scope of the

facilities are summarized below:

- The capacity and feed-gas composition have been selected to be compatible with the coal gasification complex in the MITRE Corporation study (Gray, et al., 1980) for DOE.
- The synthesis gas feed from the gasification complex is assumed to be clean and desulfurized.
- The processing scheme, operating conditions, and yields used in this design are data derived from the two-stage bench scale pilot plant experiments. Other aspects of the design, such as the configuration of SFT reactor internals, were obtained from information available in the published literature.
- Product recovery and separation is by conventional distillation. The carbon dioxide produced in the F-T reaction is removed using a hot potassium carbonate absorption system. The recovered propylene, butene, n-butane, and i-butane fractions together with small quantity of imported i-butanes are processed in an alkylation unit to maximize gasoline production. Light hydrocarbon gases are available as an offgas stream for further upgrading to SNG.
- The waxy hydrocarbon stream from the SFT reactors is recovered and filtered for removal of traces of catalyst. The filtered wax is stored for use in preparation of fresh slurry and the balance is assumed exported for further upgrading.
- Facilities are included for the periodic removal of the deactivated F-T catalyst and for preparation and activation of fresh catalyst in a separate system. Also included are ZSM-5 catalyst regeneration and nitrogen circulation facilities. Catalyst manufacturing facilities are not included in the scope of the work.
- The cost estimate of the battery limits facilities is based on instantaneous 1983 costs and a Wyoming location.

C. Conceptual Process Design

1. Feed-Gas Basis

The synthesis gas composition is based on gasification of a Wyoming subbituminous coal from advanced gasifiers of BGC/Lurgi type. The gas is treated for sulfur-compound and

carbon dioxide removal and delivered at the required temperature and pressure for this plant. Composition of the clean synthesis gas to the plant used for design purposes is as follows:

	Rates Lb-Mol/Hr	Composition Mol %
Hydrogen	31,841	29.83
Methane	7,490	7.02
Carbon Monoxide	64,319	60.26
Carbon Dioxide	2,360	2.21
Nitrogen	365	0.34
Ethene	26	0.02
Ethane	341	0.32
Total	106,742	100
Total Lb/Hr	2,111,070	

To raise the H_2/CO ratio in the feed gas used in the design study from 0.5 to the 0.67 basis practiced in the laboratory experiments for the SFT/ZSM-5 process, sufficient steam is added with the gas to promote the water-gas shift reaction within the SFT reactor. The assumption that this reaction takes place adequately at the SFT reactor conditions without affecting the F-T catalyst activity is supported by Koelbel and Ralek (1980) and in-house Mobil research work.

2. Reactor Yields

The first-stage SFT and the second-stage ZSM-5 reactor yields used in the design are shown in Tables 42 and 43, respectively. The yield data and reactor conditions used are derived from process studies in the two-stage bench-scale pilot unit. The overall yield distribution and composition of the hydrocarbon products are as follows:

	Overall Yields Wt % of (H_2+CO) (1)	Hydrocarbon Composition Wt %
H_2O	0.81	---
CO_2	65.81	---
$C_1 = C_2$	2.37	11.6
C_2	0.37	1.2
$C_3 = C_3$	0.43	4.3
$C_4 = C_4$	1.92	5.5
$C_5 + C_6$	0.47	13.2
	1.51	4.8
	2.01	18.4
	13.85	41.0
Total	89.55	100.0

(1) Based on 90% CO conversion.

Table 42
First-Stage Slurry F-T

Components	Reactor Yields	Mol.-Wt.	Lb-Mol
Water		18.02	0.7885
Hydrogen		2.02	8.0730
CO		28.01	5.9880
CO ₂		44.01	26.2889
Methane		16.04	1.8839
Ethene		28.05	0.2298
Ethane		30.07	0.4020
Propene		42.08	0.7660
Propane		44.10	0.1782
N-Butane		58.12	0.1435
C ₄ Olefins		56.11	0.4739
N-Pentane		72.15	0.1213
C ₅ Olefins		70.14	0.3777
N-Hexane		86.18	0.0979
C ₆ Olefins		84.16	0.2533
N-Heptane		100.11	0.0562
C ₇ -Olefins		98.19	0.1244
N-Octane		114.23	0.0574
C ₈ -Olefins		112.21	0.1204
N-Nonane		128.26	0.0530
C ₉ -Olefins		126.24	0.0944
C ₁₀ -C ₁₅ (P+O)		167.82	0.3805
C ₁₆ -C ₂₀ (P+O)		245.95	0.0901
C ₂₁ -C ₂₅ (P+O)		311.75	0.0157
C ₂₆₊ (P+O, Excl. Wax)		384.55	0.0012
Methanol		32.04	0.0801
Formic Acid		46.03	0.0037
Ethanol		46.07	0.1429
Acetic Acid		60.05	0.0092
Acetone		58.08	0.0241
N-Propanol		60.10	0.0710
I-Propanol		60.10	0.0163
Propanoic Acids		74.08	0.0034
C ₄ -C ₉ (Oxygenates)		94.24	0.1206
C ₁₀ -C ₁₅ (Oxygenates)		181.43	0.0274
C ₁₆ -C ₂₀ (Oxygenates)		261.93	0.0028
C ₂₁ -C ₂₅ (Oxygenates)		330.75	0.0002
Slurry Reactor Wax		389.05	0.0829
Lb-Mol per 100 Lb-Mol Feed			47.6438

Table 43
 Second Stage ZSM-5
Reactor Yields

<u>Components</u>	<u>Mol.-Wt.</u>	<u>Lb-Mol</u>
Water	18.02	1.3138
Hydrogen	2.02	8.0794
CO	28.01	5.9928
CO ₂	44.01	26.3099
Methane	16.04	1.8928
Ethane	30.07	0.4046
Ethene	28.05	0.1516
Propane	44.10	0.4561
Propene	42.08	0.3724
N-Butane	58.12	0.2934
I-Butane	58.12	0.5278
N-Butene	56.11	0.3116
N-Pentane	72.15	0.2762
I-Pentane	72.15	0.4208
N-Pentene	70.14	0.0102
I-Pentene	70.14	0.2273
Cyclopentane	70.14	0.0129
N-Hexane	86.18	0.1136
I-Hexane	86.18	0.1843
N-Hexene	84.16	0.0046
O-Hexene	84.16	0.0362
Methylcyclopentane	84.16	0.0460
Cyclohexane	84.16	0.0009
Benzene	78.11	0.0415
N-Heptane	100.21	0.0542
I-Heptane	100.21	0.0894
N-Heptene	98.19	0.0045
I-Heptene	98.69	0.0357
Demethyl-Cyclopentane	98.19	0.0350
Methylcyclohexane	98.19	0.0082
Toluene	92.14	0.1307
N-Octane	114.23	0.0183
I-Octane	114.23	0.0310
N-Octene	112.22	0.0073
I-Octene	112.21	0.0573
C8-N5	112.22	0.0232
C8-N6	112.24	0.0054
P-Xylene	106.17	0.1090
O-Xylene	106.17	0.0347
Ethylbenzene	106.17	0.0471
N-Nonane	128.26	0.0054
I-Nonane	128.26	0.0180
N-Nonane	126.24	0.0034
I-Nonene	126.24	0.0268
C9-N5	126.24	0.0057

Table 43 (Cont'd)

Second Stage ZSM-5Reactor Yields

<u>Components</u>	<u>Mol.-Wt.</u>	<u>Lb-Mol</u>
C9-N6	126.27	0.0013
N-Propylbenzene	120.20	0.0039
Methyl-Ethyl-Benzene	120.20	0.0658
Trimethyl-Benzene	120.20	0.0483
I-Decane	142.28	0.0054
N-Decene	140.27	0.0010
I-Decene	140.27	0.0080
C10-N5	140.30	0.0017
C10-N6	140.30	0.0004
I-Butylbenzene	134.22	0.0214
Tetramethylbenzene	134.22	0.0062
Diethylbenzene	134.22	0.0025
C11-Alkylbenzene	148.25	0.0298
C12-Paraffin	170.38	0.0087
C12-Alkylbenzene	162.30	0.0183
C13-Paraffin	184.41	0.0040
C13-Alkylbenzene	176.33	0.0084
<hr/>		
Lb-Mol per 100 Lb-Mol Feed		48.4664

3. Reactor Conditions

The process design conditions for the first- and second-stage reactors are shown below.

	First-Stage SFT	Second-Stage ZSM-5
Inlet Pressure, Psia	250	235
Inlet Temperature, °F	440	700
Outlet Temperature, °F	500	767
H ₂ /CO Ratio, Molar	0.67 ⁽¹⁾	N/A
Space Velocity	2.75 ⁽²⁾	1.65 ⁽³⁾
Catalyst	Fe/Cu/K ₂ CO ₃	ZSM-5 Class
Heat of Reaction Btu/Mol (H ₂ +CO)	23,000	520
In SFT Feed		

4. Material Balances

The overall design material balance for the battery limits plant in this study is shown below:

	<u>Lb/Hr</u>	<u>Sp. Gr. (Mol. Wt.)</u>	<u>BPSD (SCFD X10⁶)</u>
Feeds			
Synthesis Gas	2,111,070	(19.8)	(973.5)
Steam	121,351	(18.0)	(0.6)
I-butanes	<u>10,671</u>	(58.1)	1,299
	2,243,092		
Products			
Offgas	392,634	(15.7)	(227.4)
Propane LPG	22,528	0.501	3,087
Mixed Butanes	7,524	(0.584)	883
10 RVP Gasoline	274,380	0.701	26,869
Distillate	3,926	0.753	357
Wax	30,260	(389.1)	2,400
Waste Water	16,314	1.0	1,126
Carbon Dioxide	<u>1,495,526</u>	(44.0)	(291)
	2,243,092		

(1) Assumed attained after the shift.

(2) In NL/gFe-hr.

(3) In WHSV based on hydrocarbons in feed.

Detailed material balances for the reactor and product recovery sections are shown on Tables 44 and 45.

5. Product Quality

The estimated finished 10 RVP gasoline (including alkylate) properties are summarized below:

Research Octane, Clear	89
Motor Octane, Clear	83
RVP, Psia	10
Distillation, °F	<u>ASTM</u>
10 Vol. %	109
30 " %	139
50 " %	199
70 " %	240
90 " %	286
PONA (Vol. %)	67/13/4/16

6. Process Flow Scheme

All process flow diagrams are summarized in Appendix G. Figure G-1 (DWG. B-00242-60-0107) is a block flow diagram of the entire process plant. The process schemes for the reactor and product recovery sections are shown on Figures G-2 (DWG. B-00242-60-0104) and G-3 (DWG. 2B-00242-60-0106), respectively.

D. Plant Description

The plant consists of two main sections: (1) the reactor section and (2) the product recovery section.

1. Reactor Section

The reactor section encompasses the two stages, slurry F-T reactors followed by fixed-bed ZSM-5 reactors. In addition, special functions such as slurry filtration, catalyst activation and ZSM-5 catalyst regeneration are accomplished in smaller processing facilities that operate in a batch mode.

The clean synthesis gas is heated by the second-stage reactor effluent in heat exchanger E-3 and combined with steam before entering the SFT reactor (see Figure G-2). The synthesis gas is converted to hydrocarbons by the F-T catalyst suspended in the liquid phase. The heat of reaction in each slurry F-T reactor is removed by steam generation. The overhead reactor effluent stream includes carbon dioxide, hydrocarbon vapor products and the unconverted synthesis gas. Small amounts of high molecular weight waxy liquid hydrocarbon remain in the

Table 44
Slurry Fischer-Tropsch/ZSM-5 Process
Reactor Section Material Balance

<u>Stream</u>	<u>1 Clean Syn-Gas</u>	<u>2 Steam</u>	<u>3 HC Vapor</u>	<u>4 HC Liquid</u>	<u>5 Process Water</u>	<u>6 Waxy Liquid</u>
BPSD						2,386
Lb/Hr	2,111,070	121,351	2,081,460	104,340	16,314	30,260
MW	19.77	18.01	33.7	96.7	18.01	389.1
<u>Component</u>	<u>MW</u>					
CO ₂	44.01	2360.0	34392.9	79.2		
C ₂ H ₄	28.05	26.0	171.5	0.5		
CO	28.01	64319.0	5777.9	1.7		
H ₂	2.01	31841.0	7791.3	1.1		
CH ₄	16.04	7490.0	9293.3	7.9		
C ₂ H ₆	30.07	341.9	727.5	3.3		
N ₂	28.01	365.0	365.0	0.1		
H ₂ O	18.01	6738.0	19.7	0.1	905.5	
C ₃ H ₆	42.08		354.0	4.7		
C ₃ H ₈	44.09		432.8	6.5		
i-C ₄ H ₁₀	58.12		491.4	17.0		
C ₄ H ₈	56.10		287.7	12.4		
n-C ₄ H ₁₀	58.12		269.1	13.5		
C ₅ ⁺	79.79		1296.6	930.7		
C ₆ ⁺						77.8
Total Lb-Mol/Hr	106,742.9	6,738.0	61,670.7	1078.7	905.5	77.8

Table 45
Slurry Fischer-Tropsch/ZSM-5 Process
Product and Recovery Section Material Balance

	7 HC Vapor From CO ₂ Removal Unit	8 CO ₂	9 Fuel Gas	10 Alkyl. Feed	11 Lt. Gasoline	12 Hvy. Gasoline	13 Dist. Blend Stock	14 Purchased i-C ₄	15 Total Propanes	16 Total Butanes	17 Alkylate
BPSD					15,739	3,224	357	1,229	3,087	1,950	6,839
Lb/Hr	585,976	1,495,526	392,634	97,253	156,435	40,073	3,926	10,671	22,528	16,613	68,783
MW	20.9	44.0	15.9	51.5	83.4	125.8	167.7	57.4	43.4	58.6	103.3
<u>Component</u>											
CO ₂	411.4	33,981.5	490.6								
C ₂ H ₄	171.5		172.1								
CO	5,777.9		5,779.7								
H ₂	7,791.3		7,792.3								
CH ₄	9,293.4		9,301.2								
C ₂ H ₆	727.5		702.7	28.1				28.1			
N ₂	365.0		365.1								
H ₂ O			19.1								
C ₃ H ₆	354.1		22.7	336.1							
C ₃ H ₈	432.8		13.2	426.2			9.3	485.6			
i-C ₄ H ₁₀	491.4			499.9	8.5		159.8	4.5	13.5	8.0	
C ₄ H ₈	287.7		296.1	296.1	4.0						
n-C ₄ H ₁₀	269.1			278.3	4.3		16.7	0.2	261.2	33.6	
i-C ₅ H ₁₂				17.1					8.4		
C ₅ H ₁₀				4.4					0.6		
n-C ₅ H ₁₂				0.4							
C ₅ ⁺	1,296.6			1,863.4					624.0		
C ₈ ⁺					318.6	23.4					
Total Lb-Mol/Hr	27,669.5	33,981.5	24,658.7	1,886.5	1,880.2	318.6	23.4	185.8	518.4	283.7	665.6

slurry reactor at the reaction condition. This excess reactor-wax is continuously removed from the reactor, separated from residual catalyst and stored.

Effluent from the slurry reactor is heated against the second-stage reactor effluent in heat exchanger E-1 and then enters the second-stage reactor where an exit temperature of 767°F is attained. After preheating the second-stage reactor feed, the second-stage reactor effluent is further cooled by generating 450 psig steam, then preheating the SFT reactor feed and by cooling water before entering the product separator. Three-phase separation of the hydrocarbon liquid, water and vapor occurs in this vessel. The water phase is sent to a waste water treatment plant outside the plant battery limit.

a. SFT Reactor

For the purpose of this study, the SFT reactors adopted are fourteen feet in diameter by thirty-five feet in length. To remove the heat generated by the reaction, the internal configuration of the reactor is similar to the Rheinpreussen-Koppers demonstration reactor. The selection of fourteen feet diameter for the SFT reactor is based on mechanical considerations foreseen in the construction of larger vessels, particularly in the design of the internal heat transfer components.

At the design feed gas rate of 2,111,070 lb/hr and a gas linear velocity of 0.3 ft/s, a total of forty SFT reactors are required.

The heat of reaction is removed by steam generation at approximately 2.5-3.0 million pounds of 450 psig steam per hour. The heat exchange elements of each SFT reactor are connected to steam drums.

To minimize the use of valves and piping, the reactors are grouped in 'clusters' of five reactors which function as a single reactor unit during normal operation. Each cluster can be taken off-line as a unit for catalyst replacement. Furthermore, the SFT reactors are arranged into two parallel trains of twenty reactors each. Figure G-4 in Appendix G shows the equipment and arrangement in the reactor section.

b. Reactor-Wax Withdrawal

A small fraction of the products in the first-stage reactor consist of high molecular weight compounds (reactor-wax) which remain in the slurry reactor. As a result, there is a continuous increase in the slurry inventory in the reactors which must be controlled without losing much of the dispersed catalyst. This is accomplished by withdrawing slurry from the reactor and

circulating it through a catalyst/reactor-wax separation unit where the slurry feed is separated into two streams. The stream with high catalyst concentration is returned to the reactor. The other stream, containing 0.5-1.0 wt % of solids, is removed from the reactor for further catalyst removal in the filtration system. The five reactors in a cluster share a common catalyst/reactor-wax separation system which consists of a circulation pump and the catalyst/reactor-wax separation unit. Figure G-5 in Appendix G is a schematic diagram of the SFT reactor clusters.

The reactor-wax filtration system consists of a holding vessel to provide surge for the catalyst-containing reactor-wax from the catalyst/reactor-wax separation unit. This vessel is equipped with an agitator to prevent settling and agglomeration of the catalyst, heating coils to maintain adequate temperature control and a overhead vapor condenser and an accumulator to recover lighter hydrocarbons flashing from the reactor-wax. The reactor-wax is then pumped through a vertical leaf type filter to remove the suspended catalyst and the clear product is sent to storage. Auxiliary equipment for filter precoating and filter cake handling are also part of the filtration system. The plant is equipped with two filtration systems, one for each train of the SFT reactors.

c. F-T Slurry Preparation and Activation

Deactivation of the F-T catalyst requiring periodic replacement of the slurry. At the end of the catalyst life, which is assumed to be 60-70 days, the slurry from each cluster of SFT reactors is transferred to a surge tank for later filtration and reactor-wax recovery. The reactors are then loaded with new slurry which has been preactivated in the slurry preparation and activation system. This system consists of an agitated and heated vessel to prepare the mix of catalyst powder with reactor-wax from storage. The slurry is then transferred to the activation vessel which is a SFT reactor equipped with a heating and cooling system using Mobiltherm-600 fluid. Once in the activation vessel, the slurry is heated to 540°F while maintaining hot nitrogen injection through the bottom to keep the catalyst in suspension and to improve the heat transfer. The hot nitrogen is supplied by a closed circuit nitrogen circulation system. On reaching 540°F the nitrogen flow is replaced by synthesis gas from the feed header to initiate the activation step. The activation is characterized by gradual increase in synthesis gas conversion. The removal of the heat of reaction is accomplished using the Mobiltherm-600 system in the cooling mode. During the activation, the effluent gas is combined with the effluent from the SFT reactors. This step lasts approximately 15-20 hours and once completed, the activated slurry is transferred to the SFT reactor cluster to start production at the normal conditions. Figure G-5 in Appendix G also shows a

schematic diagram of the reactor-wax liquid filtration, slurry activation and nitrogen circulation systems.

The effluent gas from the two trains of SFT reactors merge in a common header that provides the feed to the second-stage ZSM-5 reactors.

d. Fixed-Bed ZSM-5 Reactors

The ZSM-5 reactors are fixed-bed, downflow, adiabatic type reactors. There are four reactors on stream and sized for a WHSV of 1.65 l/hr (based on hydrocarbons) and a mass flow rate of 2500-3500 lbs/hr-ft² for a good flow distribution and low pressure drop. A fifth reactor permits the periodic removal of one reactor for catalyst regeneration.

The feed to the ZSM-5 reactor is preheated by exchange with its effluent since the adiabatic temperature rise provides a difference larger than 200°F between the SFT and the ZSM-5 reactors effluents. Further heat is removed from the effluent in a series of heat exchangers and coolers described previously.

e. ZSM-5 Catalyst Regeneration

Due to coke deposition on the catalyst, the ZSM-5 catalyst undergoes deactivation which requires a progressively higher reactor feed temperature to maintain the yield structure. When the inlet temperature has reached the design limit, the reactor is taken out of line for catalyst regeneration and another reactor with regenerated catalyst replaces it.

For the purpose of this conceptual design, the catalyst cycle between regeneration is thirty days and the regeneration time allowed is three days. In preparation for regeneration, the reactor is purged with nitrogen to minimize the hydrocarbons content in the bed and then is heated to combustion temperature (approximately 700-900°F) using hot nitrogen in a closed circuit. Air added to the hot recycle regenerating gas so that the combined stream contains less than 1 vol % oxygen. This limits the temperature rise in the catalyst.

The regeneration system consists of a gas circulator, regeneration gas heater, heat exchangers and compressor suction vessel.

2. Product Recovery Section

The product recovery section consists of a conventional distillation train to produce the gasoline product. Included in this section also are the carbon dioxide removal and the alkylation units. The vapor phase from the product separator is composed mostly of carbon dioxide, hydrocarbons, and unconverted

carbon monoxide and hydrogen. To increase the efficiency of the hydrocarbon recovery system, carbon dioxide is removed and discharged to atmosphere. A hot potassium carbonate absorption system is used for carbon dioxide removal. The hydrocarbon vapor is then cooled and compressed to combine with the deethanizer tower overhead stream.

A lean oil absorption type gas plant with a sponge absorption tower is required to maximize the propylene recovery.

The hydrocarbon liquid from the product separator is pumped to the deethanizer tower. A light lean oil stream is combined with the deethanizer overhead vapor stream cooled by water and separated. The liquid from the accumulator is refluxed to the tower, while the vapor stream is combined with the hydrocarbon vapor from the carbon dioxide removal unit. This stream is further cooled by process streams and refrigeration and is then flashed. The liquid effluent is heated by a heat exchange and enters the deethanizer tower. The vapor stream from the flash drum enters the sponge absorption tower.

A heavy sponge oil from the gasoline splitter tower bottom is cooled and enters on the top tray of the sponge absorption tower. The vapors from the sponge tower is the fuel gas stream composed mostly of carbon monoxide, hydrogen and methane. The sponge tower bottom stream is heated and enters the deethanizer tower with the hydrocarbon liquids from the reactor section separator.

The bottom stream from the deethanizer tower is the stabilizer feed. The overhead liquid stream is the feed to the Alkylation unit. The stabilizer bottom stream is split to provide a lean oil to the deethanizer and a gasoline splitter feed.

Overhead liquid stream from the gasoline splitter is sent to gasoline blending. The bottom stream is split to provide the lean oil to the sponge tower and the gasoline fractionator tower feed. The gasoline fractionator is used to eliminate a small fraction of high boiling range hydrocarbons that will otherwise interfere with the gasoline boiling range specifications.

Stabilizer overhead liquid hydrocarbon stream enters the Alkylation process. A small amount of i-butanes is imported to supplement a requirement for alkylation. Alkylation yields used reflect typical commercial experience.

3. List of Major Equipment

Lists of major equipment for the reactor section and the product recovery section are given in Tables 46 and 47, respectively.

E. Operating Requirements

1. Utilities

<u>Unit</u>	<u>Reactor Section</u>	<u>CO₂ Removal Unit</u>	<u>Compre- sion</u>	<u>Product Sep.</u>	<u>Alkylation</u>	<u>Total</u>
Steam Prod. (Consump.) Mlb/Hr						
	2,812					2,218
Sat. 450 Psig	(221)		(217) ⁽¹⁾	(225)	(146)	(809)
Sat. 50 Psig		(1,100)				(1,100)
BFW Lb/Hr	2,953					2,953
Cooling Water GPM	27,000	43,000	18,000	3,500	12,200	103,700
Power KW	252	8,950		1,450	400	11,052
Fired HTR Fuel MMBtu/Hr	327			260		587
Demin. Water Lb/Hr	300					300

(1) Assumed available as superheated at 690° in the complex.

Table 46

List of Major Equipment - Reaction Section

<u>Service</u>	<u>No.</u>	<u>Description</u>
SFT Reactors	41	14'-0" \varnothing x 35'-0" T-T
ZSM-5 Reactors	5	15'-0" \varnothing x 16'-6" T-T
Product Separator	1	17'-0" \varnothing x 20'-0" T-T
Steam Drum (Second Stage)	1	8'-6" \varnothing x 20'0" T-T
Steam Drum (First Stage)	2	12'-0" \varnothing x 54'-0" T-T
ZSM-5 Rx Fired/Effluent Exch.	4	42.0 MM BTU/HR each
ZSM-5 Rx Effluent/Steam Gen.	4	14.0 " " "
" " " /Syn.Gas Feed	4	73.0 " " "
" " " /Cooler Condensers	4	8.0 " " "
Slurry Filtration System	2	System includes: Surge Vessel, Filtration Equipment and Filter Cake Handling Facilities
Slurry Activation System	1	System includes: Slurry Preparation Vessel, Activation Reactor (SFT), Mobiltherm System
Nitrogen Circulation System	1	System includes: Nitrogen Circulator, Fired Heater Exchangers and Separator Vessel
ZSM-5 Catalyst Regeneration	1	System Includes: Air Compressor, Regen. Gas Circulator, Fired Heater, Exchangers and Separator

Table 47

List of Major Equipment - Product Recovery Section

<u>Service</u>	<u>No.</u>	<u>Description</u>
Carbon Dioxide Removal	1	Four parallel Trains of Potassium Carbonate Absorption Towers with Associated Regeneration
Compressor	1	Centrifugal compressor 16,000 HP
Deethanizer Absorber	1	7'-6" ϕ x 16'0" ϕ x 120' T-T With Fired Reboiler and Overhead Condenser
Sponge Absorber	1	9'-6" ϕ x 60' T-T
Stabilizer Tower	1	12'-6" ϕ x 105' T-T With Steam Reboiler and Water Cooled Overhead Condenser
Gasoline Splitter Tower	1	14'-6" ϕ x 65' T-T With Steam Reboiler and Water Cooled Overhead Condenser
Gasoline Fractionator Tower	1	7'-6" ϕ x 60' T-T With Fired Reboiler and Air Cooled Overhead Condenser
Alkylation Plant	1	6900 BPSD Alkylate Unit

2. Initial Catalyst and Chemicals Requirements

F-T Catalyst, Lbs.	1,000,000
ZSM-5 Catalyst, Lbs.	400,000
Potassium Carbonate Solution, Gal.	500,000

3. Operating Manpower

	<u>Total</u>
SFT/ZSM-5 Reactor Section	32
Carbon Dioxide Removal, Gas Plant and Alkyl. Unit	19
TOTAL	<u>51</u>

F. Scoping Cost Estimate

The cost of the battery limits facilities is estimated to be 700 million dollars based on July 1983 and Wyoming location. This estimate does not include coal gasification and gas cleanup facilities, utilities and offsites, SFT catalyst manufacture facilities, and catalyst fills and royalties.

The facilities included are the following:

- SFT and ZSM-5 reactor section
- Carbon dioxide removal unit
- Alkylation unit
- Product recovery section
- SFT catalyst slurry filtration system
- SFT catalyst slurry activation system
- ZSM-5 catalyst regeneration and nitrogen circulation systems

The cost contribution of each plant section as percent of the total investment is approximately as follows:

	<u>Percent</u>
Reactor section	70
Carbon dioxide removal	20
Alkylation	5
Product recovery	5

Included in the 700 million dollars are equipment, bulk materials, labor, field indirects, contractor engineering and fees, owners engineering and project management costs and capitalized spares. Because of the Wyoming location, an allowance for a construction workers' camp is also included. The investment estimate has been developed using the Rand Corporation guidelines (Merrow, et al., 1980) for calculating project cost growth factors. The cost growth factor is estimated at 0.59. This is equivalent to a 69% cost increase as a contingency for a first-of-a-kind plant.

The effects of design conditions and yields structure changes on the investment were investigated to develop a qualitative understanding of their impact. The results are summarized below:

- A decrease of approximately twenty percent in the yield of the methane and ethane in favor of either higher reactor-wax or higher gasoline range products will not result in appreciable changes in plant investment.
- Elimination of the F-T slurry catalyst activator and its related equipment will result in a reduction of less than ten percent of the total investments.
- Larger SFT reactors (i.e., 20-25 ft ID) will decrease significantly the number of reactors required. However, the total investment for reactors could be higher if they have to be field-fabricated. In addition, the designs and fabrication methods for the internal heat transfer elements are not well studied.
- Higher operating pressure (i.e., 350 psig) in the SFT reactor section is expected to cause an increase of less than ten percent of the total investment as a result of increased material cost for the section. The number of reactors required is reduced proportionally to the pressure increase; however, the height must be increased to accommodate larger heat transfer area requirements. The possibility of increasing the heat transfer area per reactor volume was not investigated.

XII. Recommendation for Further Study

Based on studies carried out in this Contract, areas of major importance have been identified. Many of those areas are recommended for further study to improve the process economics, the product flexibility, and the scaleup of the slurry F-T reactor. For convenience, these areas of interest are summarized below into four groups:

Slurry F-T Operation

- Low methane + ethane operation.
- Scaleup factors of slurry F-T reactor, including type, maximum size, internals, and hydrodynamics.
- Steam co-feeding to slurry F-T reactor to allow use of a synthesis gas of H_2/CO ratio lower than the usage ratio.
- Higher pressure operation and its effect on process performance.
- Slurry F-T catalyst activation.
- Effect of varying catalyst loading in SFT reactor on the reactor performance.
- Continuous removal and replacement of F-T catalyst to maintain a constant activity in the F-T reactor.

F-T Product Upgrading

- F-T catalyst/reactor-wax separation.
- Means to upgrade F-T reactor-wax into high quality distillate and gasoline.
- Effect of low methane + ethane mode operation on the performance of the second-stage ZSM-5 reactor.

Process Optimization

- Carbon dioxide removal schemes and their utility integration with other part of the plant.
- Schemes for further conversion of unconverted H_2+CO .

- Schemes for recycle of C₁+C₂ hydrocarbons to the slurry F-T reactor via a steam reformer or a partial oxidation unit.
- Schemes for further conversion of unconverted light olefins.
- Alternate distillation schemes for more efficient separation of heavier boiling hydrocarbons in the gasoline.
- Examining benefits or penalties of lower single-pass H₂+CO conversion with recycle to the slurry F-T reactor or with the use of multi-staged F-T reactors.

Process Economics

- Performing conceptual process design and scoping cost estimate of maximum distillate + gasoline mode operation.
- Detailed economic comparison of this technology against the best alternative.

Further discussions of some of these areas are given below.

Low methane + ethane mode operation is aimed at maximizing the liquid fuel yield and is therefore worthy of further investigation. The high F-T reactor-wax yield from this operation provides a possibly new route for distillate production. Such a route was proposed by M. E. Dry of SASOL (Dry, 1982). He reported that a high yield (80 wt %) of high quality diesel (65 cetane number) was obtained by mild hydrocracking of a F-T wax obtained from SASOL's fixed-bed tubular F-T reactor (Arge Process). The light hydrocarbon (C₁ to C₄) yield was only 5 wt %. Because of the expected high reactor-wax yield, the separation of the reactor-wax from the F-T catalyst is apparently an important problem.

Another area of major importance is the commercial scaleup of the slurry F-T reactor. The factors that need to be evaluated include the type and size of the reactor, its internals (buffers and/or heat transfer tubes), feed-gas distributor; gas bubble size, gas holdup, and the liquid- and gas-phase back-mixing. Although a high synthesis gas conversion was demonstrated by the well-known Rheinpreussen-Koppers demonstration plant (1.55 m ID x 8.6 m height with internal steam-generation tubes), simulation of such a performance by examining the important hydrodynamic factors in a large-diameter hot-flow reactor model is highly desirable.

Various process optimization schemes need to be examined. In any coal-to-hydrocarbon plant, the amount of carbon dioxide to be removed is directly proportional to the inefficiency of the plant. The amount of carbon dioxide to be removed in the two-stage slurry F-T/ZSM-5 plant is expected to be relatively small because of its high thermal efficiency. However, the investment associated with the carbon dioxide removal is still quite substantial. Examination of other removal schemes and their utility integration with other parts of the plant is warranted. Other possible optimization schemes are further conversion of unconverted H_2+CO and light olefins, and the recycle of methane + ethane to the slurry F-T reactor via a steam reformer or a partial oxidation unit. All these schemes will contribute to higher liquid hydrocarbon yield.

With maximum distillate + gasoline mode operation, an additional investment will be required for the upgrading of the reactor-wax. However, the final product value is also expected to be higher. Therefore, the conceptual process design and scoping cost estimate for this operation must be updated. Finally, to determine the priority on the development of various routes of coal-to-liquid fuel projects, a detailed economic comparison of this technology against the best alternate route of making similar products should be conducted.

XIII. Nomenclature

a_c	Catalyst particle external surface area per slurry volume, $6C_c(1-v_c)/\rho_c d_c$, (cm^2 solid-liquid area/ cm^3 slurry)
a_g	Gas bubble interfacial area, $6\epsilon_g/d_B$, (cm^2 gas-liquid area/ cm^3 expanded slurry)
a_i	Coefficients, $i=1,2,\dots, 2(N+2)$, given in Equation (27)
B_1	A function of P_e and B_2 , defined as Equation (20)
B_2	R_k/R_d
C	Concentration, (mol/cm^3 liquid or gas)
C^*	Concentration at gas-liquid interface, (mol/cm^3)
C_c	Catalyst loading, (gCat/cm^3 liquid)
\bar{C}_c	Dimensionless catalyst loading, C_c/C_{ca}
C_{ca}	Average catalyst loading, (gCat/cm^3 slurry)
C_{Fe}	Iron loading, (gFe/cm^3 liquid)
\bar{C}_g	C_g/C_{gl}^i
C_{Hs}	Liquid phase H_2 concentration inside catalyst, (mol/cm^3 liquid)
\bar{C}_L	$C_L K/C_{gl}^i$
d_B	Bubble diameter, (cm)
d_c	Catalyst particle diameter, (cm)
d_R	Reactor diameter, (cm)
E	Axial dispersion coefficient, (cm^2/s)
f	Molar H_2/CO ratio at reactor inlet
f_{Fe}	Weight fraction of Fe in catalyst
g	Gravitational constant, 981, (cm/s^2)
I	Carbon number

K	Solubility coefficient C_g^*/C_L^* , (cm^3 liquid/ cm^3 gas)
k_1, k_2	Intrinsic kinetic rate constants for F-T and water-gas shift reactions, respectively, used in Equations (29) and (31), (cm^3 liquid/s-gFe)
\bar{k}_2	$k_2 K_1 / K_4$, (cm^3 liquid/gFe-s)
k_3, k_4	Constants used in the rate expressions (29) and (31)
\bar{k}_3	$k_3 K_2 / K_4$
\bar{k}_4	$k_4 K_1 K_3 / K_2 K_4$
k_c	Liquid-particle mass transfer coefficient, (cm/s)
k_g	Gas side mass transfer coefficient, (cm/s)
k_H''	Intrinsic kinetic rate constant for H_2 conversion, $r_H / (1 - \epsilon_g) (1 - v_c) C_{HL} C_{Fe}$, (cm^3 liquid/s-gFe)
k_L	Liquid side mass transfer coefficient, (cm^3 liquid/s-(cm^2 gas-liquid area))
L	Bubble-column height, (cm)
M_I	Weight fraction of the I carbon-number hydrocarbon
m	Average H/C atomic ratio of F-T products
N	Number of interior collocation points
P	Pressure, (Pa)
$P_j(\bar{z})$	Jacobi polynomials, $j=1, 2, \dots$, defined as Equation (24)
R_c	H_2 transport resistance, from bulk liquid phase to liquid-solid interface, $K_H / k_c a_c (1 - \epsilon_g)$
R_d	H_2 transport resistance from gas-liquid interface to bulk liquid phase, $K_H / k_L a_g$, ($\text{s} \cdot \text{cm}^3$ expanded slurry/ cm^3 gas)
R_G	Gas law constant, 8.2, ($\text{MPa} \cdot \text{cm}^3$)/(mol \cdot $^\circ\text{K}$)
R_g	H_2 transport resistance, from bulk gas phase to gas-liquid interface, $(k_g a_g)^{-1}$, (s)
R_k	Kinetic resistance, $K_H / k_H'' C_{Fe} (1 - \epsilon_g) (1 - v_c)$ for single component model, $K_1 / \bar{k}_j C_{Fe} (1 - \epsilon_g) (1 - v_c) \bar{C}_c$ ($j=1, 3$) for multi-component model, ($\text{s} \cdot \text{cm}^3$ expanded slurry/ cm^3 gas)

r_H	H_2 conversion rate, (mol/s-gFe)
r_1	Kinetic rate of F-T reaction, given as Equation (29), (mol/s-gFe)
r_2	Kinetic rate of water-gas shift reaction, given as Equation (31), (mol/s-gFe)
\bar{r}_1	$\bar{C}_{L1}\bar{C}_{L2}/(\bar{C}_{L2} + \bar{k}_3\bar{C}_{L4})$
\bar{r}_2	$(\bar{C}_{L2}\bar{C}_{L4} - \bar{C}_{L1}\bar{C}_{L3}/\bar{k}_4)(\bar{C}_{L2} + \bar{k}_3\bar{C}_{L4})$
s_{ij}	Elements of stoichiometric matrix, $i = 1, \dots, 4$; and $j = 1, 2$
T	Temperature, ($^{\circ}$ C)
U	Molar H_2 /CO usage ratio
u	Superficial velocity, (cm/s)
u_{cs}	Catalyst settling velocity in a catalyst swamp, (cm/s)
u_{ct}	Single catalyst particle settling velocity, (cm/s)
\bar{u}_g	u_g/u_g^i
v_c	Volumetric fraction of catalysts in slurry, $\rho_L w_c/\rho_s + w_c(\rho_L - \rho_s)$, (cm^3 catalyst/ cm^3 slurry)
v_c^*	v_c as $C_c = 0.1$ gCat/cm ³ slurry, (cm^3 catalyst/ cm^3 slurry)
w_c	Weight fraction of catalyst in slurry, (gCat/g slurry)
w_{Fe}	Weight fraction of Fe in slurry, (gFe/g slurry)
x_H	H_2 conversion
x_{H2+CO}	Molar H_2+CO conversion
\bar{x}	Dimensionless liquid-phase H_2 concentration, $K_H C_{HL}/C_{Hg}^i$
y	$(1 - \bar{x})/(1 + \alpha^* \bar{x})$
Y	Gas-phase H_2 mole fraction
\bar{y}	Dimensionless gas-phase H_2 mole fraction, y/y^i
z	x_H^e/St_k
z	Axial reactor distance, (cm)
\bar{z}	Dimensionless axial reactor distance, z/L

Greek Letters

α	Contraction factor, molar contraction per mole of H_2^{1CO} converted, defined in Equation (13)
α'	Probability of the chain-growth
α^*	$\alpha f(1+U)/U(1+f)$
γ_{ij}	Coefficients for Jacobi polynomials, $i, j = 1, 2, \dots$, defined by Equation (25)
ϵ_g	Gas holdup, (cm^3 gas/ cm^3 expanded slurry)
ρ	Density, (g/cm^3)
ρ_c	Catalyst particle density, ($gCat/cm^3$ catalyst particle)
ρ_s	Catalyst solid density, ($gCat/cm^3$ catalyst solid)
μ	viscosity, ($g/s\cdot cm$)

Dimensionless Numbers

Ar	Archimedes number, $\rho_L(\rho_c - \rho_L)gd_c/\mu_L^2$
Fr	Froude number, $u_{gm}/(gd_R)^{0.5}$
Pe _c	Axial Peclet number (catalyst particle), $u_{cs}L/E_c$
Pe _L	Axial Peclet number (liquid), $u_g^{iL}/E_L(1-\epsilon_g)(1-v_c)$
Re _c	Reynolds number (catalyst particle), $u_{ct}d_c\rho_L/\mu_L$
Sc	Schmidt number (liquid), $\mu_L/\rho_L D_L$
Sh	Sherwood number (liquid), $k_c d_c/D_L$
St _d	Stanton number (diffusion resistance), $L/u_g^{iR_d}$
St _k	Stanton number (kinetic resistance), $L/u_g^{iR_k}$

Acronyms

AD	Axially Dispersed liquid phase model
BPSD	Barrels Per Stream Day
BSU	Bench-Scale Unit
DOS	Days on Stream
DP	Differential Pressure
F-T	Fischer-Tropsch
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity
FS-GC	Fused Silica capillary Gas Chromatography
HOS	Hours on Stream
LC	Liquid Chromatography
MS	Mass Spectrometry
MTG	Methanol-To-Gasoline
NM	axially Non-Mixed liquid phase model
PM	axially Perfectly-Mixed liquid phase model
SASOL	South African Coal, Oil and Gas Corporation, Ltd.
SCFD	Standard Cubic Feet per Day
SFT	Slurry Fischer-Tropsch
STP	Standard Temperature and Pressure
STY	Space-Time-Yield, (gMol H ₂ +CO converted/hr-cm ³ expanded slurry)
SV	Space Velocity, (NL/gFe-hr)
WHSV	Weight Hourly Space Velocity, (l/hr)

Superscripts

i At reactor inlet
e At reactor exit

Subscripts

c Catalyst
esl Expanded slurry
g Gas
H Hydrogen
i Components, $i = 1, 2, 3, 4$ for H_2 , CO, CO_2 , H_2O , respectively
L Liquid
m Arithmetic mean value of that at reactor entrance and that at reactor exit
sl Slurry

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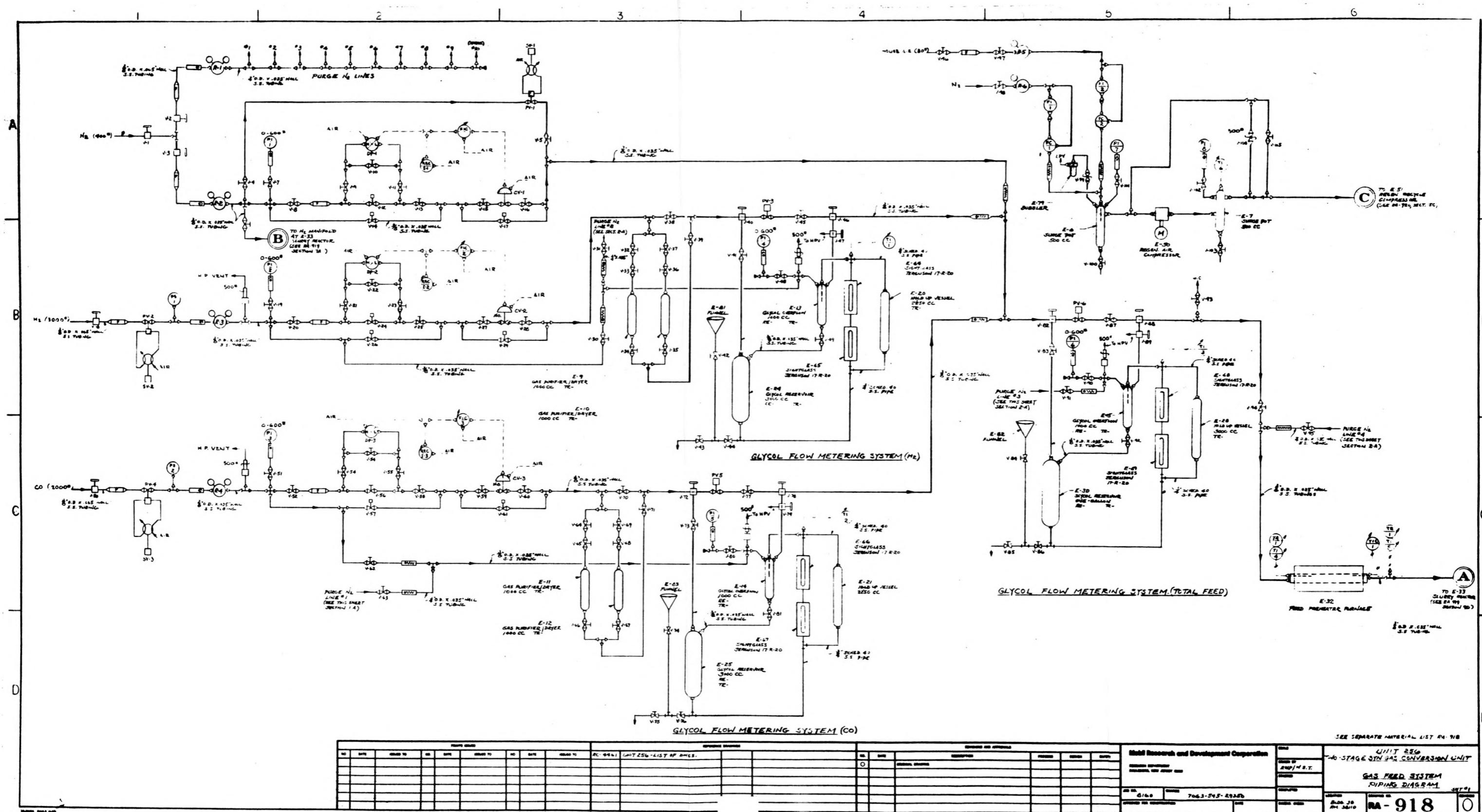
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A P P E N D I X A

DRAWINGS FOR TWO-STAGE BENCH-SCALE PILOT PLANT

FIGURE A-1



— A —

FIGURE A-2
ENGINEERING FLOW, AND PIPING AND INSTRUMENTATION DIAGRAM:
SLURRY F-T REACTOR SECTION

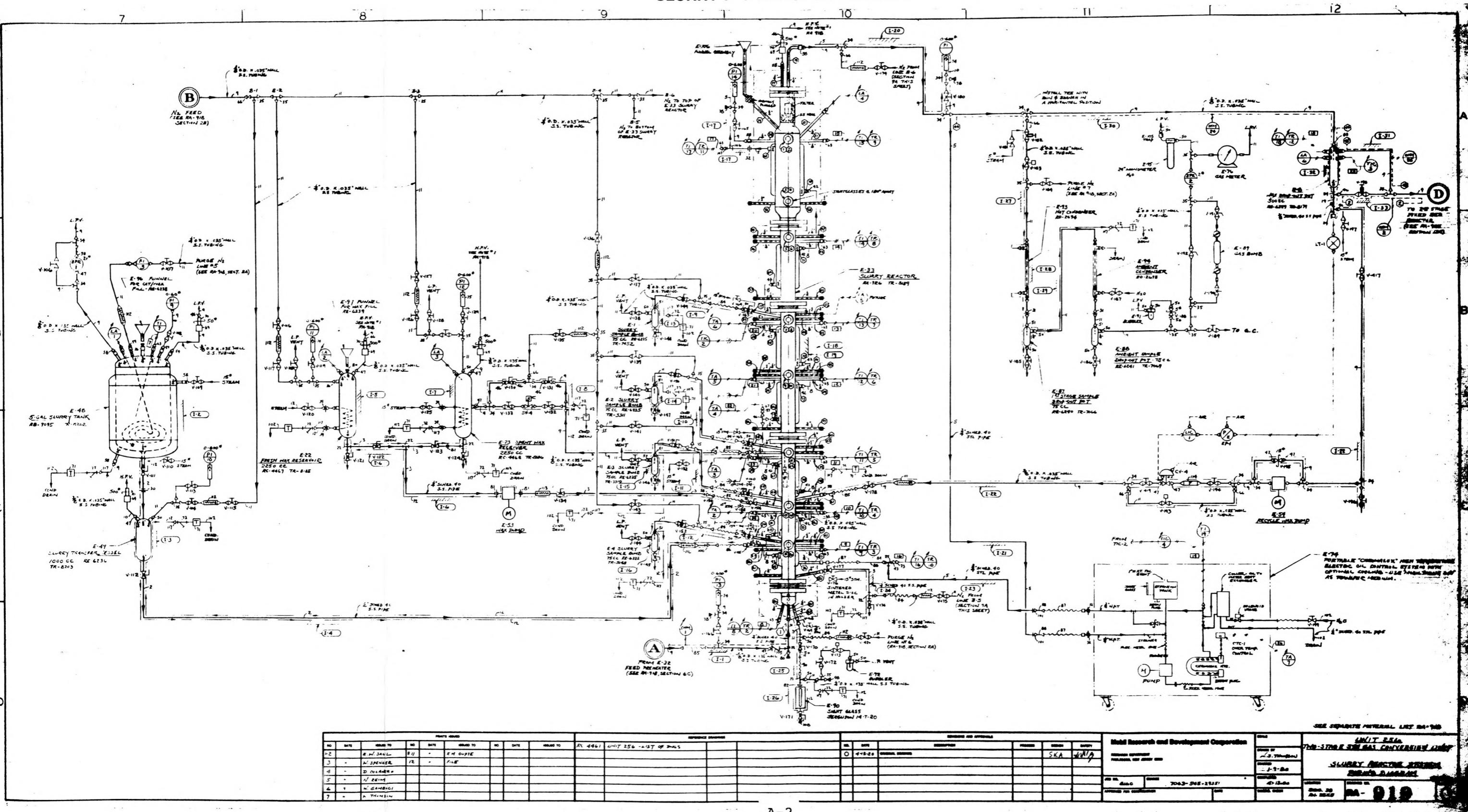


FIGURE A-3

ENGINEERING FLOW, AND PIPING AND INSTRUMENTATION DIAGRAM:
ZSM-5 FIXED-BED REACTOR AND PRODUCT RECOVERY SECTION

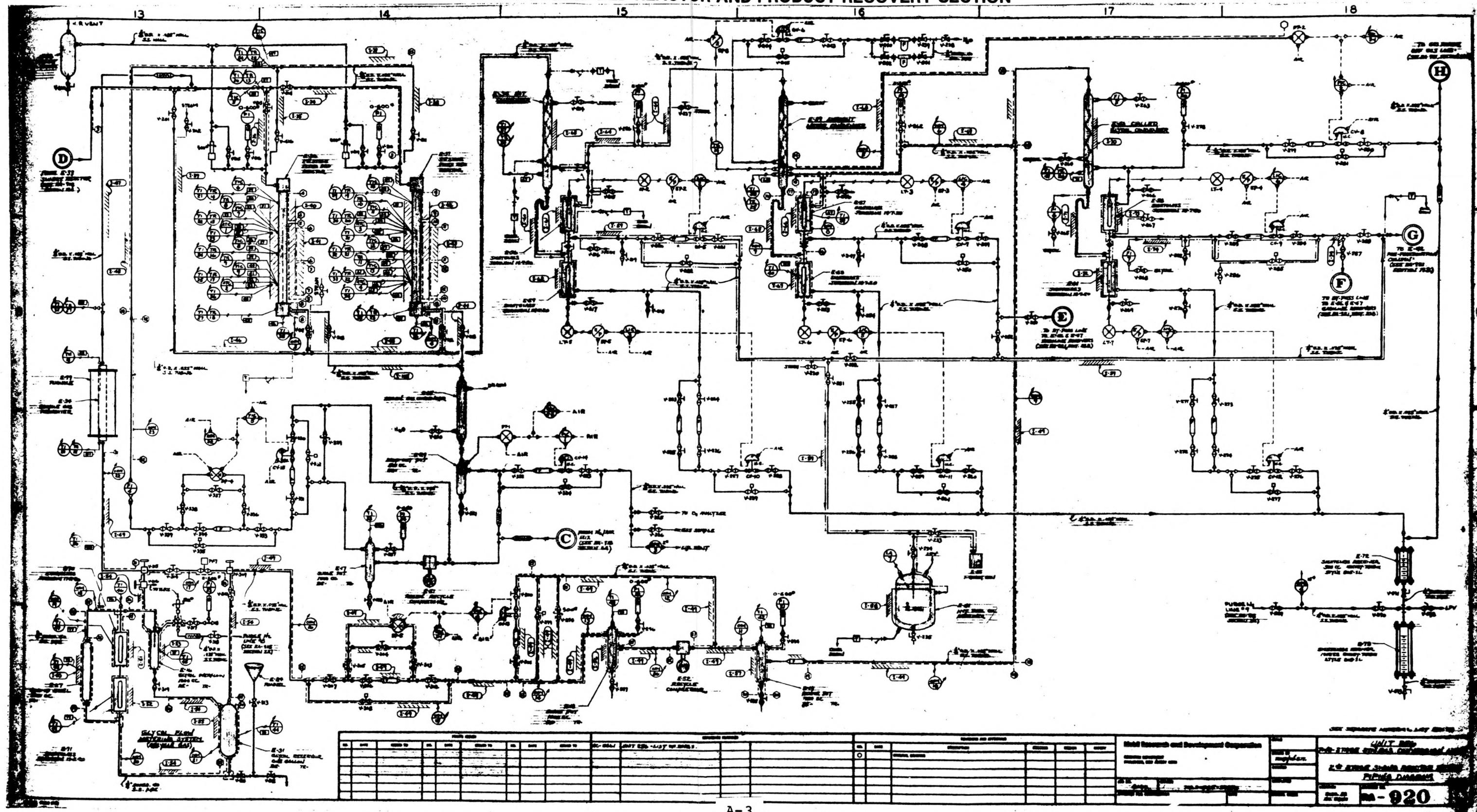


FIGURE A-4

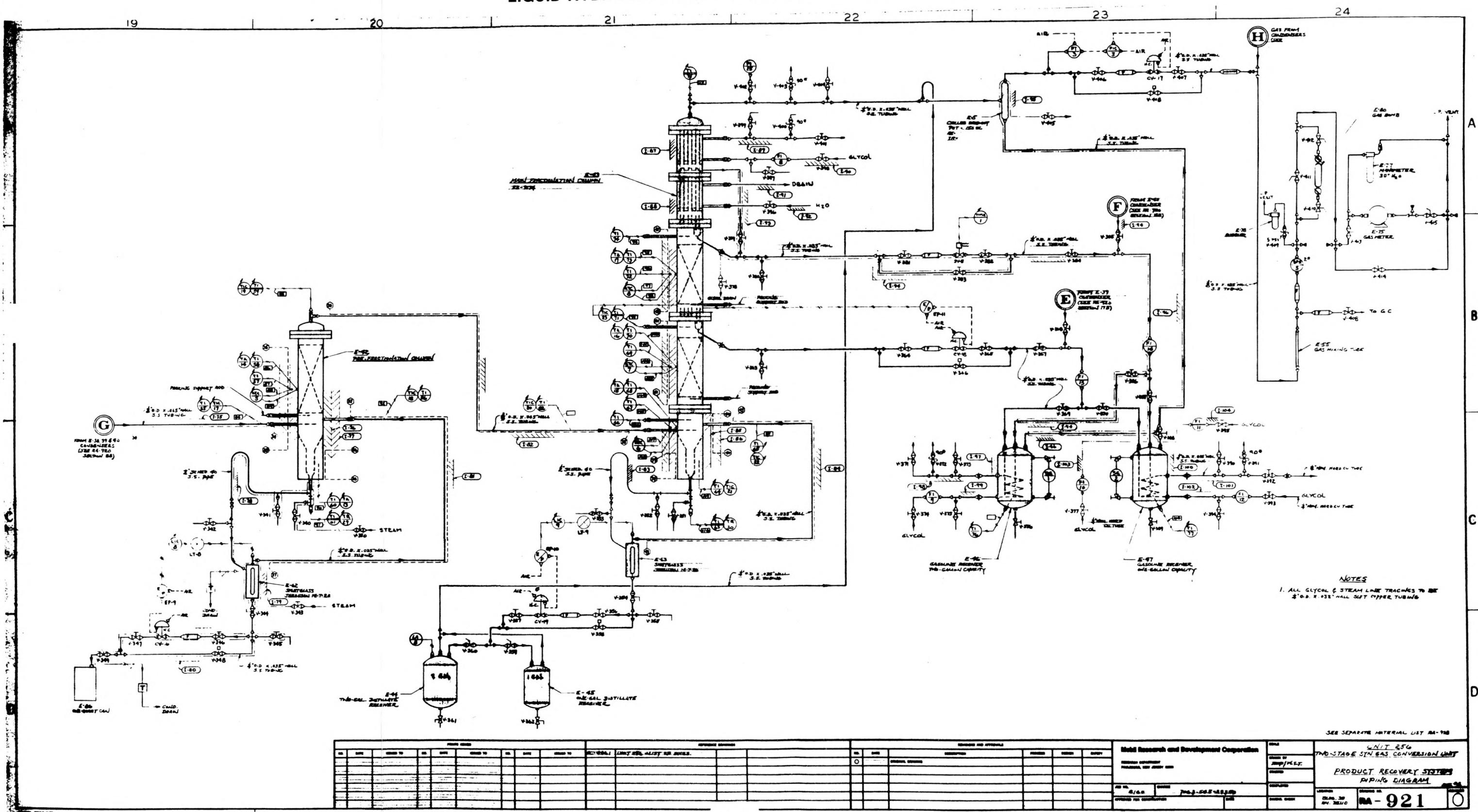
ENGINEERING FLOW, AND PIPING AND INSTRUMENTATION DIAGRAM:
LIQUID HYDROCARBON PRODUCT DISTILLATION SECTION

FIGURE A-5

SLURRY F-T REACTOR ASSEMBLY AND DETAILS

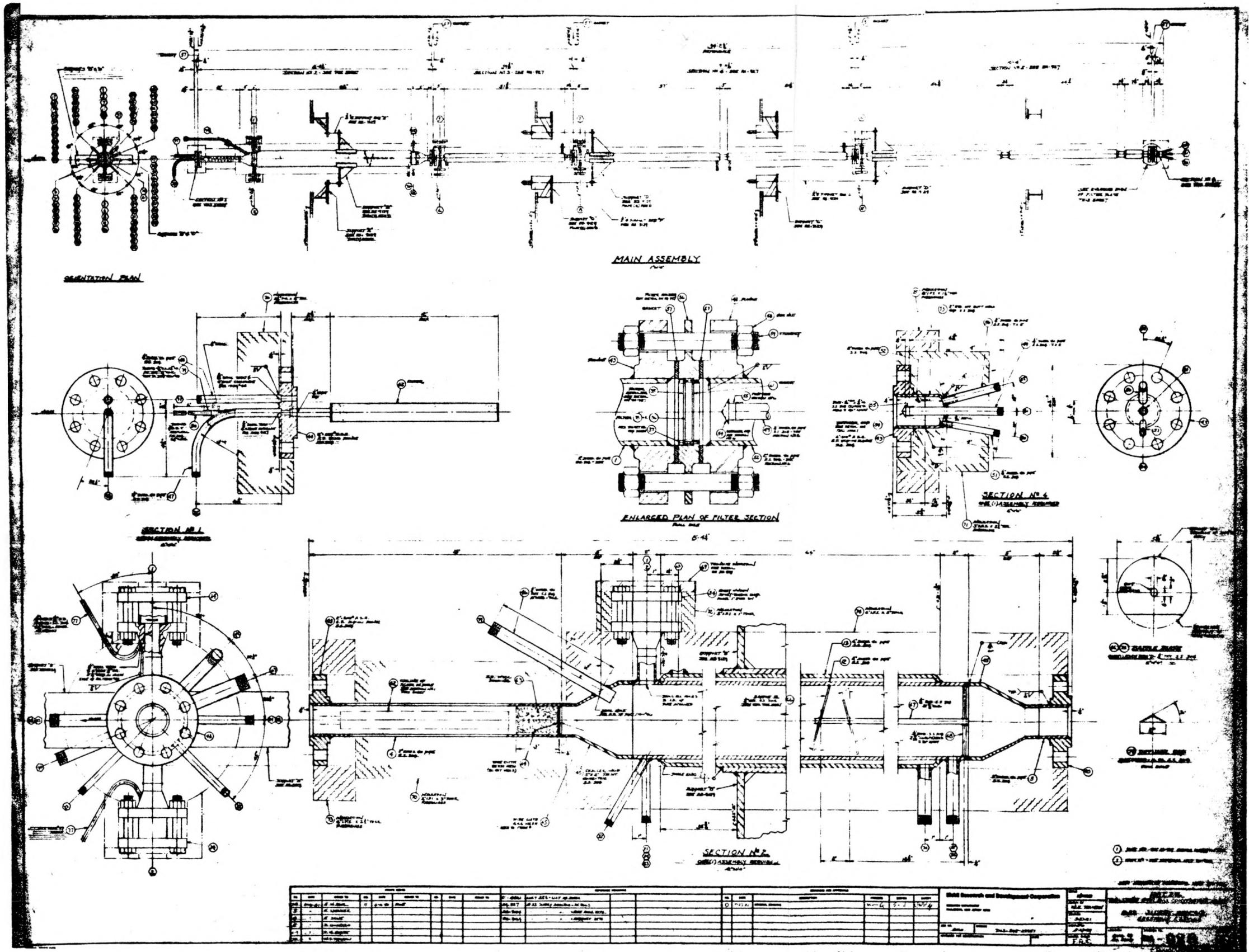


FIGURE A-6

SLURRY F-T REACTOR DETAILS

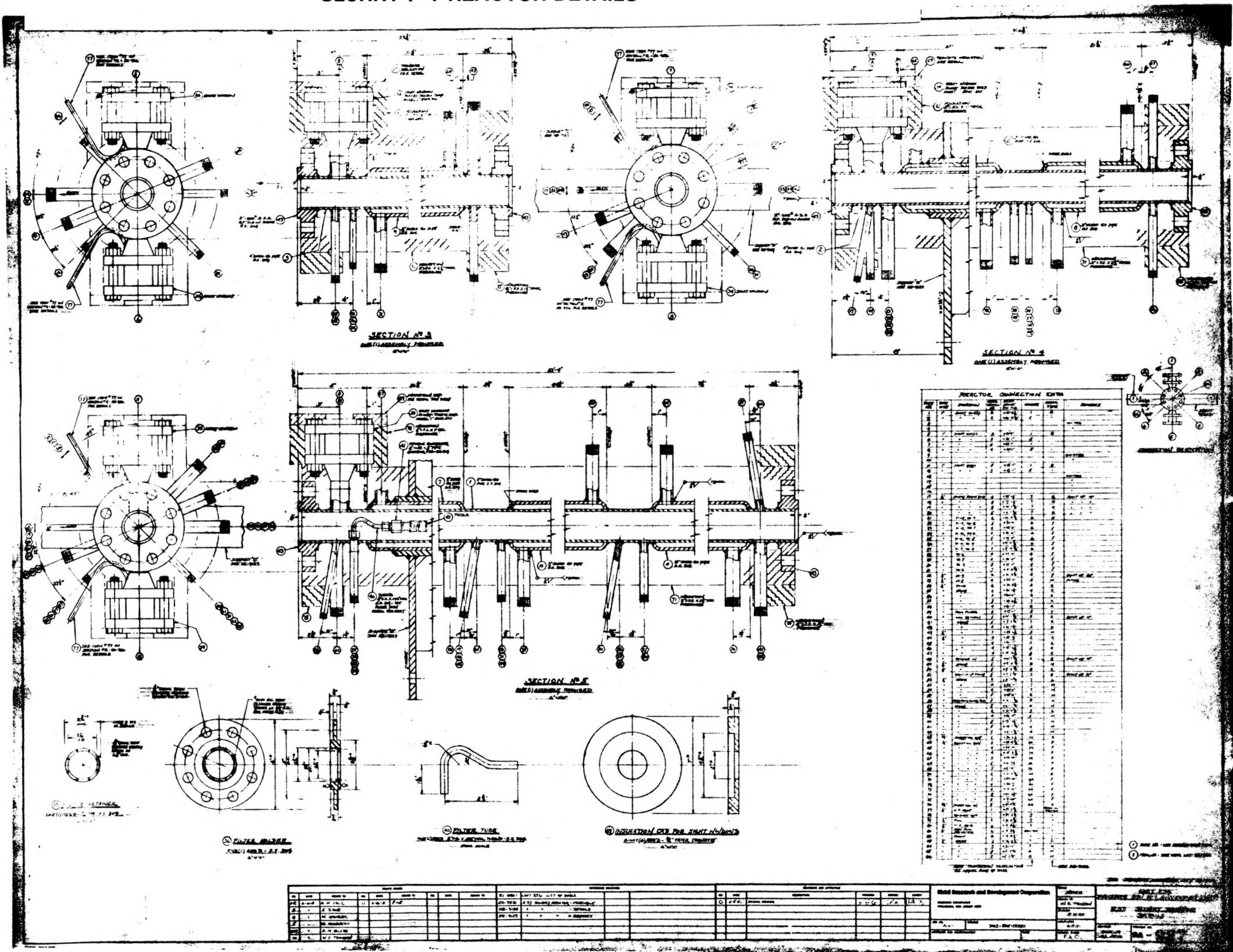


FIGURE A-7: SECOND-STAGE FIXED-BED REACTOR ASSEMBLY AND DETAILS

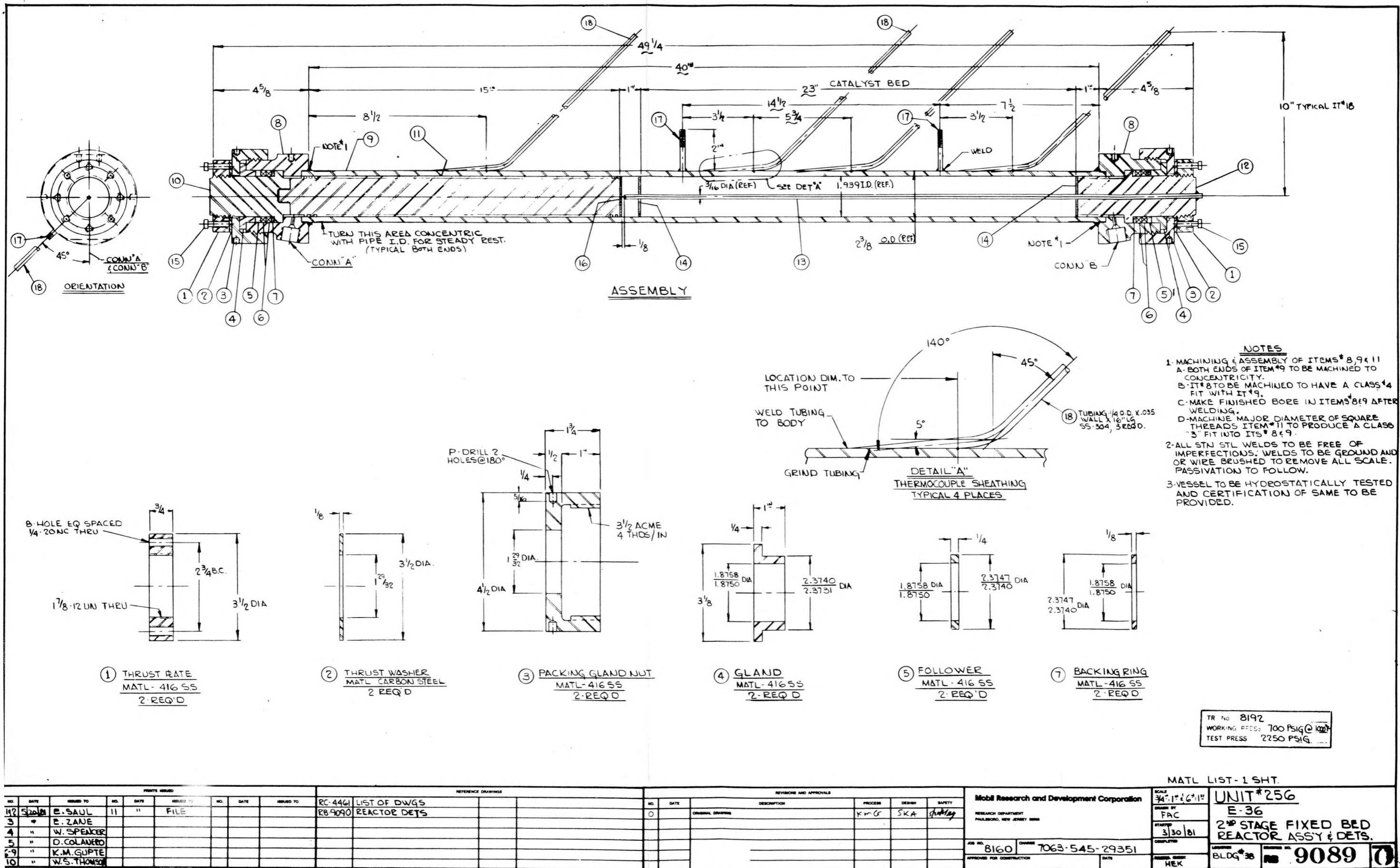


FIGURE A-8
ELEVATION VIEWS OF THE BENCH-SCALE PILOT PLANT

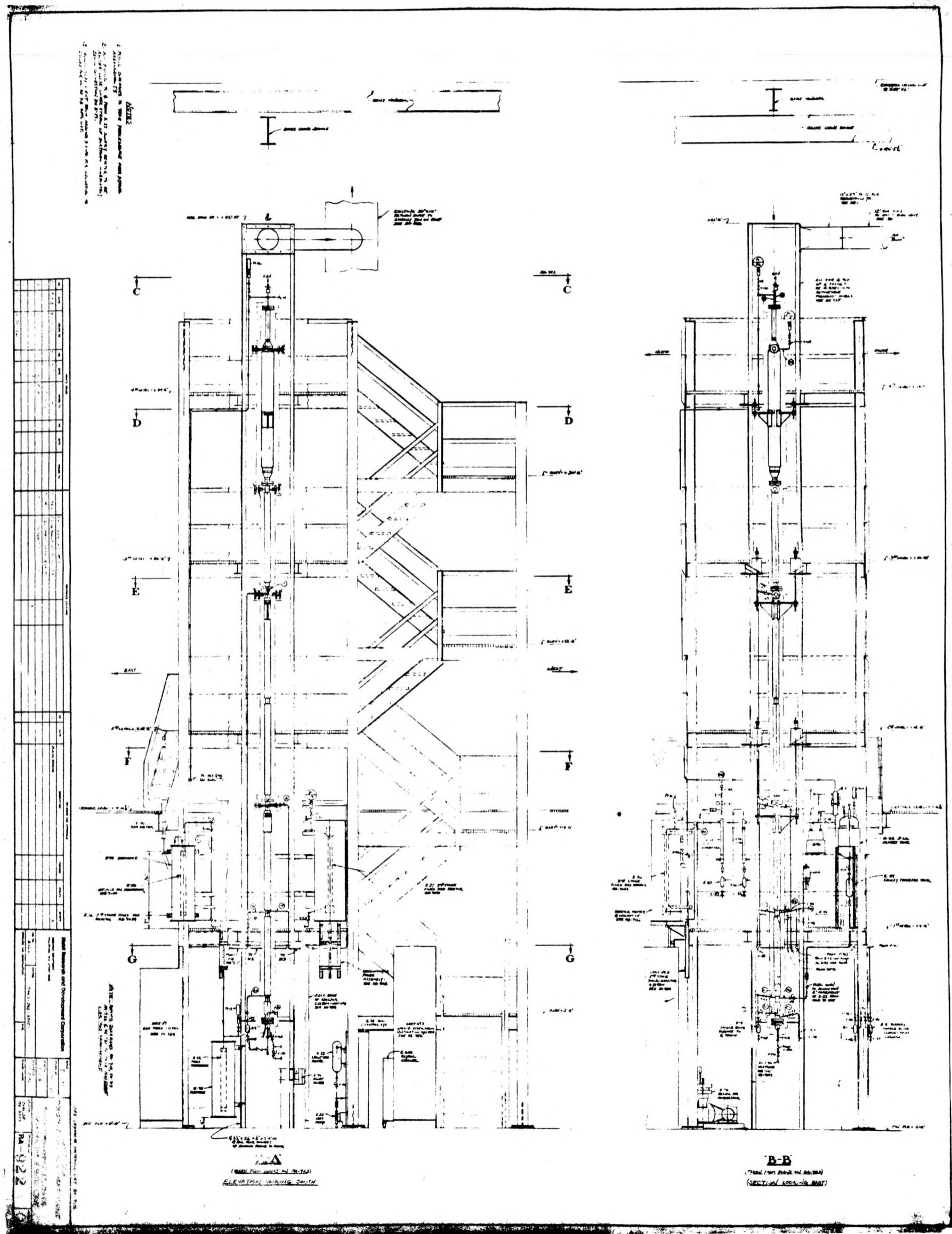


Table B-1
First-Stage Fischer-Tropsch Slurry Reactor
Operating Conditions and Material Balances
(Second-Stage Not-Operative)
(Run CT-256-1)

(Nitrogen-Free Basis)

M.B. No.	1- 1	1- 2	1- 3	1- 4	1- 6
Days On-stream	2.3	3.3	4.4	5.4	11.8
First-Stage Conditions:					
Charge H ₂ /CO (Molar)	0.719	0.734	0.752	0.627	0.603
Temperature, °C	260	260	260	260	265
Pressure, MPa	1.136	1.136	1.136	1.136	1.136
Feed Sup. Vel., cm/s	2.250	2.250	2.250	2.060	1.767
Space Vel., NL/gFe-hr	8.54	9.12	9.20	8.42	9.96
N ₂ in Feed, Mol %	11.0	11.3	11.6	12.6	14.6
Conversions, Mol % :					
H ₂	49.95	44.39	45.57	47.86	38.51
CO	68.14	60.35	54.00	53.34	44.81
H ₂ +CO	60.53	53.59	50.38	51.23	42.44
Yields, Wt % of Products :					
Hydrocarbons (1)	17.81	16.12	14.54	13.24	11.04
CO ₂	47.09	41.85	39.31	38.72	31.26
H ₂ O (1)	0.85	1.00	0.66	0.62	0.31
H ₂	2.58	2.84	2.74	2.28	2.65
CO	31.67	38.20	42.75	45.14	54.74
Total	100	100	100	100	100
Bal Recovery, Wt % of Charge:	95.58	98.53	102.05	98.84	96.55
gHC/Nm ³ (H ₂ +CO) conv.:	214	224	221	204	203
(H/C) Atomic Ratio in HC :	2.19	2.20	2.21	2.22	2.13
Selectivities, Wt % of HC :					
Methane	5.69	5.79	6.54	6.62	8.64
Ethene	3.39	3.57	3.77	4.05	4.65
Ethane	1.48	1.39	1.42	1.47	1.59
Propene	5.97	6.05	6.59	6.90	7.84
Propane	0.85	0.87	0.95	1.03	1.31
Butenes	4.93	5.06	5.54	5.92	6.60
i-Butane	0.06	0.07	0.06	0.06	0.05
n-Butane	0.92	0.95	1.05	1.11	1.43
C5 - C11	23.72	25.18	29.65	32.87	14.68
C12+ (Excl. Rx. Wax)	16.57	20.73	18.63	18.17	0.00
Light Hydrocarbons (3)	0.00	0.00	0.00	0.00	28.42
Heavy Hydrocarbons (4)	0.00	0.00	0.00	0.00	17.79
Slurry Rx.-Wax	33.00	25.00	19.00	14.00	7.00
Total	100	100	100	100	100
C5 - C11 PONA, Wt % :					
Paraffins	21.89	22.62	22.15	19.72	(2)
Olefins	78.11	77.38	77.85	80.28	(2)
Naphthenes	0.00	0.00	0.00	0.00	(2)
Aromatics	0.00	0.00	0.00	0.00	(2)

(1) Including Oxygenates

(2) Not Available

(3) Collected in Chilled and Ambient Condensers

(4) collected in Hot Condenser

Table B-2
 First-Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances
 (Based On Inter-Reactor Sample)
 (Run CT-256-1)

(Nitrogen-Free Basis)					
M.B. No.	1- 30	1- 31	1- 34	1- 41	1- 43
Days On-stream	41.4	42.4	45.4	52.4	54.3
First-Stage Conditions:					
Charge H ₂ /CO (Molar)	0.672	0.679	0.669	0.656	0.651
Temperature, °C	267	269	269	267	268
Pressure, MPa	1.48	1.48	1.48	1.48	1.48
Feed Sup. Vel., cm/s	1.737	1.761	1.767	1.691	1.666
Space Vel., NL/gFe-hr	5.244	5.318	5.335	5.260	5.183
N ₂ in Feed, Mol %	13.0	13.0	13.0	10.8	11.4
Conversions, Mol % :					
H ₂	59.76	60.29	63.21	65.07	62.04
CO	46.70	49.99	72.45	72.88	67.29
H ₂ +CO	51.95	54.15	68.74	69.79	65.22
Yields, Wt % of Products :					
Hydrocarbons (1)	11.75	13.66	18.01	18.45	15.80
CO ₂	35.13	34.53	54.94	54.58	53.82
H ₂ O (1)	0.00	0.00	0.00	0.00	0.00
H ₂	1.88	1.94	1.64	1.55	1.57
CO	51.24	49.88	25.42	25.42	28.81
Total	100.00	100.00	100.00	100.00	100.00
Bal Recovery, Wt % of Charge:					
gHC/Nm ³ (H ₂ +CO) conv.:	186	199	220	221	215
(H/C) Atomic Ratio in HC :	2.23	2.22	2.24	2.23	2.26
Selectivities, Wt % of HC :					
Methane	8.50	7.62	8.33	7.92	9.70
Ethene	4.31	3.62	3.64	4.37	5.08
Ethane	1.56	1.34	2.14	1.89	2.21
Propene	7.08	5.82	7.84	7.59	9.03
Propane	1.57	1.32	1.71	1.71	2.08
Butenes	5.94	4.84	6.82	6.32	7.71
i-Butane	0.07	0.07	0.08	0.11	0.00
n-Butane	1.52	1.28	1.66	1.61	2.03
C ₅ - C ₁₁ (2)	11.19	8.45	17.30	14.87	17.92
Light Hydrocarbons (3)	25.44	30.41	21.95	24.37	19.18
Heavy Hydrocarbons (4)	26.82	29.23	22.53	23.24	18.15
Slurry Rx.-Wax	6.00	6.00	6.00	6.00	6.00
Total	100.00	100.00	100.00	100.00	100.00

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condensers

(4) Collected in Hot Condenser

Table B-3
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor
(Run CT-256-1)

M. B. No. Days On-stream	1-1 2.3	1-2 3.3	1-3 4.4	1-4 5.4	1-6 11.8	(1) 41.4	(1) 42.4	(1) 45.4	(1) 52.4	(1) 54.3
METHANE	5.69	5.79	6.54	6.62	8.64	8.50	7.62	8.33	7.92	9.70
ETHENE	3.39	3.57	3.77	4.05	4.65	4.31	3.62	3.64	4.37	5.08
ETHANE	1.48	1.39	1.42	1.47	1.59	1.56	1.34	2.14	1.89	2.21
PROPENE	5.97	6.05	6.59	6.90	7.84	7.08	5.82	7.84	7.59	9.03
PROPANE	0.85	0.87	0.95	1.03	1.31	1.57	1.32	1.71	1.71	2.08
BUTENES	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
I-BUTANE	0.06	0.07	0.06	0.06	0.05	0.07	0.07	0.08	0.11	0.00
1-BUTENE+2-METHYLPROPENE	4.73	4.86	5.35	5.69	6.41	5.81	4.77	6.58	6.14	7.51
N-BUTANE	0.92	0.95	1.05	1.11	1.43	1.52	1.28	1.66	1.61	2.03
TRANS-2-BUTENE	0.07	0.07	0.06	0.06	0.05	0.03	0.07	0.09	0.06	0.07
CIS-2-BUTENE	0.13	0.13	0.13	0.14	0.13	0.10	0.00	0.15	0.12	0.13
PENTENES	0.18	0.02	0.03	0.45	0.00	0.00	0.00	0.00	0.00	0.00
3-METHYL-1-BUTENE	0.30	0.30	0.32	0.34	0.33	0.29	0.21	0.36	0.44	0.50
I-PENTANE	0.11	0.13	0.15	0.14	0.13	0.04	0.09	0.29	0.24	0.39
1-PENTENE	3.54	3.75	4.25	4.51	4.92	4.13	3.31	5.02	4.24	5.33
2-METHYL-1-BUTENE	0.17	0.18	0.18	0.19	0.20	0.13	0.13	0.19	0.18	0.20
N-PENTANE	0.72	0.76	0.87	0.92	1.07	1.07	0.88	1.27	1.18	1.49
TRANS-2-PENTENE	0.07	0.05	0.05	0.06	0.07	0.00	0.00	0.08	0.04	0.05
CIS-2-PENTENE	0.07	0.07	0.08	0.08	0.07	0.04	0.00	0.09	0.06	0.07
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.02
HEXENES + ISO-HEXANES	0.42	0.44	0.43	0.47	0.51	0.35	0.26	0.78	0.74	0.96
ISO-HEXANES	0.01	0.02	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00
ISO-HEXENES	0.29	0.06	0.09	0.58	0.00	0.00	0.00	0.00	0.00	0.00
1-HEXENE	2.72	3.20	3.74	3.76	3.44	2.55	1.91	3.35	2.81	3.47
C-2-HEXENE	0.01	0.02	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00
T-2-HEXENE	0.01	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
N-HEXANE	0.62	0.75	0.87	0.86	0.76	0.67	0.53	0.91	0.81	1.03
HEPTENES + ISO-HEPTANES	0.24	0.23	0.25	0.21	0.18	0.12	0.00	0.53	0.43	0.55
1-HEPTENE	1.99	2.65	3.31	3.11	1.78	1.05	0.72	1.79	1.42	1.85
C-2-HEPTENE	0.03	0.04	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00
T-2-HEPTENE	0.02	0.03	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00
ISO-HEPTANES	0.04	0.05	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00
ISO-HEPTENES	0.50	0.21	0.28	0.92	0.00	0.00	0.00	0.00	0.00	0.00
N-HEPTANE	0.50	0.66	0.83	0.79	0.42	0.30	0.18	0.50	0.44	0.59
C8-OLEFINS + ISO-P	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.28	0.21	0.29
1-OCTENE	1.35	2.27	2.90	2.61	0.57	0.20	0.00	0.66	0.52	0.68
C-2-OCTENE	0.06	0.08	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.00
T-2-OCTENE	0.04	0.06	0.08	0.07	0.00	0.00	0.00	0.00	0.00	0.00
ISO-OCTANES	0.10	0.09	0.11	0.16	0.00	0.00	0.00	0.00	0.00	0.00
ISO-OCTENES	0.75	0.39	0.48	1.29	0.00	0.00	0.00	0.00	0.00	0.00
N-OCTANE	0.76	0.71	0.90	0.81	0.16	0.00	0.00	0.23	0.19	0.23
C9-OLEFINS + ISO-P	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.06
1-NONENE	1.50	1.91	2.37	2.13	0.06	0.00	0.00	0.17	0.16	0.16
C-2-NONENE	0.08	0.09	0.11	0.10	0.00	0.00	0.00	0.00	0.00	0.00
T-2-NONENE	0.07	0.08	0.10	0.09	0.00	0.00	0.00	0.00	0.00	0.00
ISO-NONANES	0.13	0.09	0.11	0.18	0.00	0.00	0.00	0.00	0.00	0.00
ISO-NONENES	0.82	0.41	0.52	1.27	0.00	0.00	0.00	0.00	0.00	0.00
N-NONANE	0.52	0.67	0.82	0.71	0.00	0.00	0.00	0.00	0.00	0.00
N-DECANE	0.64	0.77	0.84	0.70	0.00	0.00	0.00	0.03	0.03	0.00
1-DECENE	1.33	1.60	1.91	1.62	0.00	0.00	0.00	0.03	0.06	0.00
C-2-DECENE	0.10	0.11	0.12	0.11	0.00	0.00	0.00	0.00	0.00	0.00
T-2-DECENE	0.07	0.09	0.10	0.09	0.00	0.00	0.00	0.00	0.00	0.00
ISO-DECANES	0.15	0.10	0.11	0.14	0.00	0.00	0.00	0.00	0.00	0.00
ISO-DECENES	0.72	0.32	0.40	1.00	0.00	0.00	0.00	0.00	0.00	0.00
N-UNDECANE	0.38	0.45	0.43	0.42	0.00	0.00	0.00	0.00	0.00	0.00
1-UNDECENE	0.77	0.86	0.88	0.85	0.00	0.00	0.00	0.00	0.00	0.00
C-2-UNDECENE	0.06	0.06	0.06	0.06	0.00	0.00	0.00	0.00	0.00	0.00
T-2-UNDECENE	0.04	0.05	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00
ISO-UNDECANES	0.09	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00
ISO-UNDECENES	0.58	0.26	0.27	0.64	0.00	0.00	0.00	0.00	0.00	0.00
N-DODECANE	0.12	0.15	0.16	0.13	0.00	0.00	0.00	0.00	0.00	0.00
1-DODECENE	0.20	0.17	0.21	0.22	0.00	0.00	0.00	0.00	0.00	0.00
C-2-DODECENE	0.02	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
T-2-DODECENE	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ISO-DODECANES	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ISO-DODECENES	0.20	0.01	0.00	0.25	0.00	0.00	0.00	0.00	0.00	0.00
N-TRIDECANE	0.03	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
1-TRIDECENE	0.04	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00
C-2-TRIDECENE	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
ISO-TRIDECENES	0.03	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN LITE HYDRO-CARB LIQ (2)	0.00	0.00	0.00	0.00	28.42	25.44	30.41	21.95	24.37	19.18
UNKNOWN HVY HYDRO-CARB LIQ (3)	0.00	0.00	0.00	0.00	17.79	26.82	29.23	22.53	23.24	18.15
UNKNOWN C12+	15.90	20.38	18.26	17.39	0.00	0.00	0.00	0.00	0.00	0.00
SLURRY REACTOR-WAX	33.00	25.00	19.00	14.00	7.00	6.00	6.00	6.00	6.00	6.00

(1) Based on Inter-Reactor Sample

(2) Collected in Chilled and Ambient Condensers

(3) Collected in Hot Condenser

Table B-4
Composition of Fischer-Tropsch
Hydrocarbon Phase Oxygenates
(Run CT-256-1)

M.B. No.	1-1	1-2	1-3	1-4
Days On-stream	2.2	3.3	4.4	5.4
Component, Wt %				
METHANOL	0.10	0.12	0.21	0.29
ETHANOL	0.64	0.71	1.12	1.49
ACETONE	0.05	0.07	0.13	0.15
N-PROPANOL	0.60	0.61	0.91	1.16
N-BUTANONE	0.05	0.05	0.09	0.12
N-BUTANOL	0.68	0.64	0.94	1.15
N-2-BUTANOL	0.02	0.02	0.02	0.02
OTHER BUTANOLS	0.02	0.02	0.03	0.04
C5-N-METHYL KETONE	0.06	0.06	0.12	0.13
N-1-PENTANOL	0.54	0.49	0.68	0.77
N-2-PENTANOL	0.02	0.02	0.03	0.04
OTHER PENTANOLS	0.05	0.04	0.06	0.07
C6+ ALKANOLS	4.96	6.30	7.40	7.50
Total, Wt %	7.8	9.2	11.7	12.9
Yield per HC Produced, g/100g	3.4	5.3	6.8	7.8

Table B-5
Composition of Fischer-Tropsch
Aqueous Phase Organic Oxygenates
(Run CT-256-1)

M.B.No. Days On-stream	1-1 2.3	1-2 3.3	1-3 4.4	1-4 5.4
Component, Wt %				
METHANOL	3.15	3.29	4.22	4.50
ETHANOL	8.45	12.34	15.64	16.31
ACETONE	0.42	0.74	1.02	1.04
N-PROPANOL	2.18	3.42	4.52	4.62
N-BUTANONE	0.09	0.20	0.30	0.31
N-BUTANOL	0.80	1.29	1.78	1.85
N-2-BUTANOL	0.02	0.04	0.05	0.05
OTHER BUTANOLS	0.03	0.06	0.09	0.09
I-PENTANONE	0.01	0.01	0.01	0.01
C5-ESTERS	0.03	0.03	0.09	0.10
C5-ESTERS + I-PENTANONE	0.03	0.10	0.17	0.19
N-1-PENTANOL	0.25	0.40	0.56	0.59
N-2-PENTANOL	0.00	0.00	0.02	0.01
OTHER PENTANOLS	0.03	0.05	0.09	0.09
C6-N-METHYL KETONE	0.02	0.02	0.08	0.09
N-1-HEXANOL	0.05	0.08	0.12	0.13
N-1-HEPTANOL	0.01	0.01	0.02	0.03
C8+ ALKANOLS	0.04	0.11	0.22	0.33
Total, Wt %	15.61	22.19	29.30	30.34
Yield per HC Produced, g/100g	1.01	1.83	1.80	1.83

Table B-6
Composition of Fischer-Tropsch Reactor-wax
(Run CT-256-1)

Days On-stream	1.9	3.0	6.8	34	41	56
Carbon No.	Weight %					
13	0.04	0.04	0	0	0	0
14	0.04	0.09	0.13	0	0	0
15	0.08	0.18	0.21	0	0	0
16	0.08	0.35	0.27	0	0	0
17	0.13	0.87	0.36	0.05	0	0
18	0.24	0.66	0.59	0.11	0	0.33
19	0.52	0.88	0.72	0.24	0.08	0.61
20	0.67	1.11	1.13	0.29	0.10	0.41
21	0.70	0.96	1.15	0.41	0.10	0.95
22	0.80	1.06	1.40	0.51	0.12	1.26
23	0.99	1.29	1.55	0.61	0.31	1.52
24	1.35	1.48	1.82	0.73	0.57	1.81
25	2.68	2.04	2.28	0.90	1.82	2.95
26	4.79	3.96	4.16	1.55	1.60	3.16
27	10.86	10.02	9.87	3.41	2.50	3.79
28	6.44	6.06	5.15	4.89	4.27	5.20
29	1.78	1.81	2.14	3.35	3.07	4.37
30	1.80	1.81	2.42	5.17	4.15	4.79
31	1.34	2.29	2.90	4.44	4.58	5.09
32	3.77	3.69	4.06	6.49	5.02	5.41
33	6.15	6.05	6.62	8.67	6.52	6.02
34	9.75	10.01	10.24	11.12	8.20	7.94
35	12.35	12.85	10.67	9.31	8.97	6.00
36	4.77	4.19	4.89	4.76	4.64	3.99
37	2.14	2.56	2.24	3.35	3.46	3.05
38	2.27	1.74	2.05	2.98	2.82	2.52
39	2.58	2.49	1.89	2.64	2.82	2.42
40	2.91	3.02	2.29	3.05	2.57	2.24
41	2.76	2.05	2.25	2.84	2.63	2.22
42	2.42	2.31	1.80	2.31	2.23	1.94
43	1.76	1.55	1.31	1.79	1.76	1.70
44	0.99	0.93	0.96	1.36	1.71	1.39
45	0.81	0.71	0.87	1.15	1.56	1.35
46	0.75	0.76	0.81	1.08	1.55	1.32
47	0.68	0.70	0.78	0.98	1.54	1.35
48	0.63	0.67	0.70	0.89	1.56	1.22
49	0.65	0.61	0.63	0.80	1.46	1.16
50	0.59	0.56	0.63	0.75	1.61	1.31
51	0.53	0.48	0.57	0.70	1.45	1.22
52	0.55	0.47	0.56	0.64	1.35	1.18
53	0.49	0.43	0.52	0.53	1.36	0.90
54	0.41	0.38	0.49	0.48	1.31	0.99
55	0.36	0.40	0.42	0.45	0.86	0.76
56	0.35	0.35	0.40	0.43	1.03	0.60
57	0.39	0.35	0.39	0.39	0.80	0.58
58	0.34	0.34	0.38	0.35	0.69	0.44
59	0.30	0.31	0.32	0.30	0.63	0.35
60	0.27	0.26	0.31	0.28	0.67	0.47
61	0.28	0.26	0.32	0.26	0.60	0.42
62	0.26	0.23	0.25	0.26	0.66	0.39
63	0.24	0.23	0.24	0.26	0.56	0.63
64	0.23	0.26	0.26	0.25	0.48	0.26
65	0.21	0.12	0.21	0.20	0.37	0
66	0.21	0.22	0.16	0.17	0.31	0
67	0.19	0.15	0.16	0.16	0.21	0
68	0.19	0.15	0.12	0.15	0.18	0
69	0.02	0.17	0	0.16	0.19	0
70	0.02	0.06	0	0.17	0.16	0
71	0.08	0.03	0	0.11	0.18	0
72	0.01	0	0	0.13	0	0
73	0	0	0	0.07	0	0
74	0	0	0	0.04	0	0
Total	100	100	100	100	100	100

Table B-7
Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
(Run CT-256-1)

(Nitrogen-Free Basis)										
M.B. No.	1- 7	1- 9	1- 10	1- 13	1- 14	1- 15	1- 16	1- 17	1- 18	
Days On-stream	13.5	17.1	19.1	22.2	22.6	23.6	24.6	25.6	27.6	
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.631	0.666	0.656	0.669	0.641	0.669	0.672	0.678	0.643	
Temperature, °C	265	268	268	268	268	267	268	268	271	
Pressure, MPa	1.14	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	
Feed Sup. Vel., cm/s	1.746	1.656	1.668	1.712	1.786	1.767	1.768	1.763	1.789	
Space Vel., NL/gFe-hr	9.786	12.009	12.096	12.415	12.952	12.813	12.821	12.784	12.973	
N ₂ in Feed, Mol %	14.9	12.5	11.5	12.8	12.8	12.7	12.4	12.7	12.7	
Second-Stage Conditions:										
Temp., Inlet, °C	371	344	330	333	329	330	328	330	327	
Outlet, °C	395	376	366	352	359	359	361	361	361	
Pressure, MPa	1.067	1.411	1.411	1.398	1.384	1.391	1.398	1.398	1.398	
GHSV, 1/hr	963	1142	1132	1212	1212	1203	1201	1201	1175	
Days On-stream	0.9	4.5	6.5	9.5	10.0	11.0	12.0	13.0	15.0	
Conversions, Mol % :										
H ₂	40.66	45.73	47.77	41.26	41.45	42.57	41.77	41.69	45.15	
CO	41.21	45.27	48.05	39.58	43.75	42.77	43.03	41.57	44.33	
H ₂ +CO	41.00	45.45	47.94	40.25	42.85	42.69	42.53	41.62	44.65	
Yields, Wt % of Products :										
Hydrocarbons	11.72	12.98	13.19	10.46	11.68	11.92	11.88	11.82	11.72	
CO ₂	30.28	33.14	35.88	28.73	30.27	30.21	30.16	29.45	30.72	
H ₂ O	0.63	0.97	0.96	0.71	1.01	1.02	0.99	0.96	0.66	
H ₂	2.52	2.41	2.27	2.69	2.62	2.62	2.69	2.69	2.49	
CO	54.86	50.50	47.71	57.41	54.42	54.23	54.28	55.08	54.41	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Bal Recovery, Wt % of Charge:										
gHC/Nm ₃ (H ₂ +CO) conv.:	102.43	103.35	103.92	100.35	98.74	100.62	100.04	101.07	97.72	
(H/C) Atomic Ratio in HC :	2.43	2.31	2.33	2.34	2.32	2.32	2.37	2.35	2.30	
Selectivities, Wt % of HC :										
Methane	9.18	8.87	8.94	10.72	9.41	9.18	9.15	8.87	9.37	
Ethene	0.58	0.49	0.48	0.45	0.44	0.45	0.45	0.44	0.00	
Ethane	2.37	2.44	2.62	2.70	2.63	2.54	2.52	2.38	2.34	
Propene	0.87	0.84	0.85	0.74	0.78	0.78	0.81	0.80	0.82	
Propane	16.87	13.94	14.66	11.13	11.72	11.61	11.80	11.15	11.44	
Butenes	0.73	0.79	0.79	0.84	0.89	0.87	0.89	0.90	0.94	
i-Butane	16.64	15.25	15.61	14.27	14.60	14.48	14.45	13.84	14.24	
n-Butane	8.36	8.66	9.22	8.33	8.76	8.80	8.53	8.33	8.77	
C ₅ - C ₁₁	35.75	39.83	38.98	42.89	43.26	43.75	43.78	45.32	44.82	
C ₁₂₊ (Excl. Rx.-Wax)	1.65	1.89	1.86	1.92	1.52	1.55	1.63	1.96	1.27	
Slurry Rx.-Wax	7.00	7.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
i-C₄/(C₃= + C₄=) Molar										
Olefins, Wt % by C-No. :	8.49	7.73	7.83	7.53	7.32	7.34	7.06	6.78	6.77	
C ₂	19.76	16.59	15.46	14.31	14.46	14.92	15.06	15.58	0.03	
C ₃	4.90	5.68	5.48	6.23	6.20	6.26	6.44	6.70	6.66	
C ₄	2.85	3.18	3.08	3.60	3.67	3.61	3.74	3.91	3.94	
C₅ - C₁₁ PONA, Wt % :										
Paraffins	56.96	39.85	40.98	41.76	41.91	42.06	(2)	(2)	45.79	
Olefins	24.58	13.77	12.38	14.97	13.51	13.33	(2)	(2)	2.57	
Naphthenes	0.53	2.55	3.00	4.23	4.82	5.02	(2)	(2)	6.99	
Aromatics	17.93	43.83	43.64	39.05	39.76	39.59	(2)	(2)	44.65	

(1) Denotes MB adjusted for Inter-Reactor Sampling

(2) Not Available

Table B-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
 (Run CT-256-1)

(Nitrogen-Free Basis)	1- 19	1- 20	1- 22	1- 23	1- 27	1- 28	1- 29	(1)	(1)
M.B. No.	28.8	30.4	33.2	34.4	36.4	37.4	40.4	41.4	42.4
Days On-stream									
First-Stage Conditions:									
Charge H ₂ /CO (Molar)	0.637	0.647	0.629	0.667	0.653	0.680	0.669	0.672	0.679
Temperature, °C	271	270	270	270	270	270	271	267	269
Pressure, MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
Feed Sup. Vel., cm/s	1.789	1.726	1.752	1.802	1.771	1.754	1.755	1.737	1.761
Space Vel., NL/gFe-hr	12.97	12.52	12.71	16.23	6.76	6.69	6.69	5.24	5.32
N ₂ in Feed, Mol %	12.0	12.6	12.3	13.1	13.3	12.3	12.1	13.0	13.0
Second-Stage Conditions:									
Temp., Inlet, °C	328	317	317	317	302	302	301	303	303
Outlet, °C	361	353	354	352	346	346	348	348	350
Pressure, MPa	1.398	1.384	1.391	1.391	1.377	1.370	1.377	1.377	1.377
GHSV, 1/hr	1094	1111	1181	1240	1047	1030	1054	1127	1111
Days On-stream	16.2	17.8	20.5	21.8	23.8	24.8	27.7	28.7	29.7
Conversions, Mol % :									
H ₂	50.66	45.80	39.73	39.27	65.46	50.39	48.20	43.81	48.97
CO	47.96	46.16	45.74	35.14	47.55	53.75	51.66	48.90	49.62
H ₂ +CO	49.01	46.02	43.42	36.79	54.63	52.39	50.27	46.85	49.35
Yields, Wt % of Products :									
Hydrocarbons	11.32	12.90	11.69	8.60	12.61	13.03	12.20	12.53	12.36
CO ₂	30.14	31.01	32.63	25.37	35.27	34.38	33.37	34.99	35.40
H ₂ O	1.16	0.57	1.50	0.10	0.81	0.92	0.86	0.77	0.91
H ₂	2.39	2.49	2.60	2.84	1.54	2.58	2.63	2.62	2.43
CO	54.98	53.04	51.58	63.09	49.76	49.08	50.94	49.10	48.92
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Bal Recovery, Wt % of Charge:	90.44	96.94	100.57	98.04	100.59	89.76	90.49	99.21	98.14
gHC/Nm ³ (H ₂ +CO) conv.:	166	215	216	179	183	173	171	207	191
(H/C) Atomic Ratio in HC :	2.33	2.24	2.34	2.43	2.28	2.29	2.33	2.29	2.32
Selectivities, Wt % of HC :									
Methane	9.41	8.34	9.52	10.45	8.56	8.63	9.27	8.91	9.38
Ethene	0.00	0.43	0.51	0.64	0.45	0.46	0.52	0.51	0.54
Ethane	2.42	1.95	2.14	2.34	1.99	1.90	1.94	1.90	1.96
Propene	0.77	0.72	0.88	1.12	0.77	0.80	0.91	0.93	0.96
Propane	12.25	10.15	11.02	11.76	9.85	9.53	9.29	8.97	9.38
Butenes	0.92	0.88	1.11	1.37	1.01	1.06	1.19	1.26	1.35
i-Butane	14.84	12.90	14.36	15.99	13.30	12.99	12.86	12.85	13.45
n-Butane	9.16	8.39	9.08	9.76	8.55	8.65	8.32	8.16	8.52
C ₅ - C ₁₁	42.74	48.12	44.20	39.84	47.55	48.42	48.22	48.82	47.14
C ₁₂₊ (Excl. Rx.-Wax)	1.49	2.11	1.18	0.70	1.98	1.56	1.48	1.70	1.33
Slurry Rx.-Wax	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
i-C₄/C₃= + C₄=) Molar	7.36	6.75	6.08	5.39	6.32	5.89	5.18	4.96	4.94
Olefins, Wt % by C-No. :									
C ₂	0.00	17.95	19.35	21.51	18.49	19.36	21.25	21.03	21.59
C ₃	5.89	6.63	7.40	8.69	7.26	7.76	8.89	9.39	9.30
C ₄	3.70	3.98	4.50	5.06	4.40	4.68	5.31	5.66	5.78
C₅ - C₁₁ PONA, Wt % :									
Paraffins	49.77	44.71	52.11	62.40	47.67	49.94	(2)	50.41	52.88
Olefins	1.06	1.17	2.02	2.79	3.14	2.21	(2)	2.45	3.26
Naphthenes	6.98	7.28	7.83	8.35	8.16	8.40	(2)	9.52	9.07
Aromatics	42.19	46.85	38.04	26.46	41.03	39.45	(2)	37.62	34.79

(1) Denotes MB adjusted for Inter-Reactor Sampling

(2) Not Available

Table B-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
 (Run CT-256-1)

(Nitrogen-Free Basis)	(1)				
M.B. No.	1- 32	1- 33	1- 34	1- 35	1- 37
Days On-stream	43.4	44.4	45.4	46.4	48.4
First-Stage Conditions:					
Charge H ₂ /CO (Molar)	0.646	0.669	0.669	0.655	0.910
Temperature, °C	272	266	269	270	267
Pressure, MPa	1.48	1.48	1.48	1.48	1.48
Feed Sup. Vel., cm/s	1.758	1.766	1.767	1.783	1.730
Space Vel., NL/gFe-hr	5.308	5.332	5.335	5.383	5.356
N ₂ in Feed, Mol %	13.1	12.9	13.0	12.7	12.5
Second-Stage Conditions:					
Temp., Inlet, °C	302	300	303	304	316
Outlet, °C	351	361	360	363	382
Pressure, MPa	1.370	1.377	1.377	1.377	1.384
GHSV, 1/hr	1104	958	972	982	832
Days On-stream	30.7	31.7	32.7	33.7	35.7
Conversions, Mol % :					
H ₂	49.15	66.50	64.46	62.47	69.27
CO	49.76	75.53	73.70	72.90	95.78
H ₂ +CO	49.52	71.91	69.99	68.77	83.15
Yields, Wt % of Products :					
Hydrocarbons	11.90	16.05	19.40	19.99	26.46
CO ₂	35.54	58.45	54.53	53.09	65.70
H ₂ O	0.94	0.73	0.02	0.00	2.05
H ₂	2.32	1.54	1.59	1.65	1.87
CO	49.28	23.24	24.46	25.26	3.92
Total	100.00	100.00	100.00	100.00	100.00
Bal Recovery, Wt % of Charge:					
gHC/Nm ₃ (H ₂ +CO) conv.:	97.34	100.38	102.49	102.35	101.12
(H/C) Atomic Ratio in HC :	185	175	222	234	224
Selectivities, Wt % of HC :					
Methane	10.08	9.89	8.43	8.19	9.61
Ethene	0.58	0.45	0.38	0.43	0.50
Ethane	2.00	2.63	2.27	2.18	3.85
Propene	1.09	0.90	0.79	0.90	1.12
Propane	9.20	10.35	9.02	8.05	8.88
Butenes	1.54	1.31	1.16	1.37	1.70
i-Butane	13.29	13.88	12.06	11.16	11.08
n-Butane	8.64	9.17	8.08	7.70	7.61
C ₅ - C ₁₁	46.29	43.40	49.37	51.40	47.47
C ₁₂₊ (Excl. Rx.-Wax)	1.30	2.01	2.44	2.61	2.19
Slurry Rx.-Wax	6.00	6.00	6.00	6.00	6.00
Total	100.00	100.00	100.00	100.00	100.00
i-C ₄ /(C ₃ = + C ₄ =) Molar	4.29	5.35	5.26	4.19	3.35
Olefins, Wt % by C-No. :					
C ₂	22.37	14.65	14.44	16.40	11.40
C ₃	10.61	7.97	8.06	10.11	11.20
C ₄	6.54	5.37	5.44	6.75	8.34
C₅ - C₁₁ PONA, Wt % :					
Paraffins	55.19	49.87	46.27	46.36	45.89
Olefins	4.11	3.11	2.49	3.65	3.54
Naphthenes	9.42	7.49	8.35	8.13	8.36
Aromatics	31.29	39.53	42.89	41.87	42.21

(1) Denotes MB adjusted for Inter-Reactor Sampling

(2) Not Available

Table B-8

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

Days On-Stream	16.1	27.1	28.8	36.4	39.1	42.4	47.9	48.4	56.4
Sp. Gr.	0.840	0.801	0.817	0.813	0.804	0.783	0.788	0.778	0.799
Acid No. (Unwashed), mgKOH/g	0.09	0.02	0.01	0.33	0.01	0.30	0.15	0.15	0.68
PONA, Wt %									
Paraffins	15.5	18.2	21.6	21.7	26.9	27.6	31.1	32.3	24.7
Olefins	1.6	0.8	0.9	3.6	1.4	2.8	2.6	4.0	6.2
Naphthenes	1.3	8.6	5.2	11.1	12.	13.5	10.1	10.9	11.1
Aromatics	81.6	72.4	72.3	63.6	59.7	56.1	56.2	52.8	58.0
Octane Numbers:									
R+0	>95	95.9	98.2	96.9	-	96.7	95.6	-	96.0
R+3	104.5	101.1	100.7	100.9	-	101.1	100.5	-	100.5
ASTM Distillation, °C									
IBP	44	44	43	42	34	46	33	33	37
50, Vol %	131	122	130	128	127	127	123	135	129
90, Vol %	179	172	178	177	179	178	172	177	186
95, Vol %	-	191	-	202	214	211	198	208	233
EP	-	-	-	234	230	234	230	249	238
Loss, Vol %	0	0	0	0	0.3	0.7	0.7	0.5	1.9
Residue, Vol %	10.0 ⁽²⁾	6.0 ⁽²⁾	7.5 ⁽²⁾	2.0	2.7	2.3	2.1	1.5	2.1

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

(2) Distillation stopped early due to foaming at the end of distillation.

Table B-9
Composition of Hydrocarbon Products from
Two-Stage Slurry F/T/ZSM-5 Syngas Conversion
(Run CT-256-1)

M. B. No. Days On-stream	1- 7 13.5	1- 9 17.1	1-10 19.1	1-13 22.2	1-14 22.6	1-15 23.6	1-16 24.6	1-17 25.6	1-18 27.6
METHANE	9.18	8.87	8.94	10.72	9.41	9.18	9.15	8.87	9.37
ETHENE	0.58	0.49	0.48	0.45	0.44	0.45	0.45	0.44	0.00
ETHANE	2.37	2.44	2.62	2.70	2.53	2.54	2.52	2.38	2.34
PROPENE	0.87	0.84	0.85	0.74	0.78	0.78	0.81	0.80	0.82
PROPANE	16.87	13.94	14.66	11.13	11.72	11.61	11.80	11.15	11.44
I-BUTANE	16.64	15.25	15.61	14.27	14.80	14.48	14.45	13.84	14.24
1-BUTENE+2-METHYLPROPENE	0.46	0.47	0.48	0.50	0.54	0.53	0.54	0.55	0.58
N-BUTANE	8.36	8.66	9.22	8.33	8.76	8.80	8.53	8.33	8.77
TRANS-2-BUTENE	0.17	0.19	0.18	0.20	0.20	0.20	0.21	0.21	0.22
CIS-2-BUTENE	0.10	0.13	0.12	0.14	0.15	0.15	0.14	0.14	0.15
3-METHYL-1-BUTENE	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
I-PENTANE	7.52	8.60	9.06	9.34	9.33	9.39	8.53	8.51	9.12
1-PENTENE	0.13	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
2-METHYL-1-BUTENE	0.01	0.06	0.06	0.08	0.07	0.07	0.06	0.06	0.07
N-PENTANE	1.77	2.57	2.77	3.33	3.39	3.46	3.02	3.02	3.47
TRANS-2-PENTENE	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.01
CIS-2-PENTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
2-METHYL-2-BUTENE	0.00	0.02	0.02	0.03	0.03	0.03	0.00	0.00	0.03
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5-DIOLEFINS (DIENES)	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.18
CYCLOCOPENTANE	0.02	0.06	0.06	0.06	0.07	0.07	0.00	0.00	0.27
HEXENES + ISO-HEXANES	0.58	0.62	0.62	0.69	0.68	0.67	0.67	0.68	0.04
2,3-DIMETHYLBUTANE	0.01	0.09	0.10	0.10	0.10	0.11	0.00	0.00	0.38
2-METHYL-PENTANE	0.09	0.45	0.54	0.62	0.66	0.69	0.00	0.00	2.41
3-METHYL-PENTANE	0.09	0.37	0.42	0.45	0.47	0.49	0.00	0.00	1.49
HEXENES	0.72	0.02	0.03	0.02	0.03	0.02	0.00	0.00	0.03
1-HEXENE	0.95	1.33	1.35	1.84	1.76	1.79	1.76	1.78	0.00
N-HEXANE	0.86	1.07	1.13	1.44	1.36	1.40	1.08	1.06	0.85
2,4-DIMETHYL-PENTANE	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01
METHYL-CYCLOCOPENTANE	0.04	0.20	0.24	0.33	0.37	0.39	0.00	0.00	0.90
3,3-DIMETHYL-PENTANE	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.01
CYCLOHEXANE	0.00	0.01	0.01	0.02	0.02	0.02	0.00	0.00	0.02
HEPTENES + ISO-HEPTANES	0.38	0.62	0.58	1.15	1.01	1.03	1.03	1.09	0.04
1-HEPTENE	1.36	0.87	0.79	0.67	0.63	0.61	0.62	0.58	0.00
2-METHYL-HEXANE	0.03	0.16	0.21	0.28	0.31	0.33	0.00	0.00	0.61
2,3-DIMETHYL-PENTANE	0.02	0.12	0.13	0.16	0.18	0.18	0.00	0.00	0.21
3-METHYL-HEXANE	0.06	0.26	0.32	0.42	0.45	0.48	0.00	0.00	0.74
1-CIS-3-DIMETHYL-N5	0.01	0.04	0.06	0.10	0.12	0.13	0.00	0.00	0.21
1-TRANS-3-DIMETHYL-N5	0.01	0.07	0.02	0.14	0.16	0.17	0.00	0.00	0.25
1-TRANS-2-DIMETHYL-N5	0.01	0.07	0.09	0.12	0.14	0.15	0.00	0.00	0.22
N-HEPTANE	0.19	0.21	0.22	0.37	0.39	0.35	0.29	0.25	0.27
C7-OLEFINS	0.85	0.02	0.13	0.04	0.04	0.03	0.00	0.00	0.03
METHYL-CYCLOHEXANE	0.03	0.16	0.19	0.29	0.34	0.36	0.00	0.00	0.37
C8-OLEFINS + ISO-P	0.24	0.25	0.24	0.82	0.72	0.70	0.71	0.76	0.05
1-OCTENE	1.75	1.52	1.13	1.31	1.15	1.12	1.13	1.14	0.00
MONOMETHYL-ISO-C8-P	0.05	0.13	0.18	0.29	0.33	0.35	0.00	0.00	0.35
OTHER ISO-C8-P	0.01	0.05	0.06	0.09	0.11	0.11	0.00	0.00	0.10
C8-OLEFINS	1.02	0.02	0.06	0.03	0.03	0.03	0.00	0.00	0.05
C8-NAPHTHENES (N5+N6)	0.06	0.34	0.41	0.62	0.72	0.76	0.00	0.00	0.73
N-OCTANE	0.26	0.00	0.01	0.06	0.06	0.06	0.10	0.05	0.01
C9-OLEFINS + ISO-P	0.49	0.74	0.40	0.37	0.32	0.32	0.37	0.38	0.80
1-NONENE	0.00	0.00	0.00	0.06	0.06	0.05	0.11	0.11	0.00
MONOMETHYL-ISO-C9-P	0.03	0.02	0.03	0.06	0.07	0.08	0.00	0.00	0.08
OTHER ISO-C9-P	0.01	0.04	0.04	0.07	0.08	0.09	0.00	0.00	0.08
C9-OLEFINS	0.84	0.00	0.03	0.01	0.00	0.01	0.00	0.00	0.02
C9-NAPHTHENES (N5+N6)	0.01	0.07	0.08	0.13	0.16	0.17	0.00	0.00	0.17
N-NONANE	0.20	0.01	0.02	0.02	0.02	0.02	0.00	0.00	0.02
ISO-C10-P + O + N5 + N6	8.57	1.08	0.10	0.11	0.12	0.13	0.00	0.00	0.09
BENZENE	0.36	0.82	0.78	0.60	0.60	0.61	0.00	0.00	1.13
TOLUENE	2.37	5.68	5.47	4.79	5.08	4.99	0.00	0.00	5.81
ETHYL-BENZENE	0.04	0.59	0.61	0.72	0.76	0.77	0.00	0.00	0.86
P-XYLENE	0.19	0.00	0.00	0.58	0.00	0.00	0.00	0.00	0.00
M-XYLENE	1.15	4.14	3.98	3.43	4.11	4.13	0.00	0.00	4.47
O-XYLENE	0.49	1.25	1.19	1.17	1.19	1.20	0.00	0.00	1.33
N-PROPYL-BENZENE	0.02	0.04	0.05	0.05	0.05	0.05	0.00	0.00	0.06
1-METHYL-3-ETHYL-BENZENE	0.31	1.10	1.13	1.39	1.46	1.47	0.00	0.00	1.68
1,3,5-TRIMETHYL-BENZENE	0.19	0.21	0.17	0.11	0.09	0.09	0.00	0.00	0.09
1-METHYL-2-ETHYL-BENZENE	0.10	0.24	0.24	0.28	0.28	0.29	0.00	0.00	0.33
ISO-C4-BENZENE	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
1,2,4-TRIMETHYL-BENZENE	0.51	1.27	1.27	1.46	1.50	1.54	0.00	0.00	1.76
1-METHYL-2-ISO-C3-BENZENE	0.00	0.00	0.15	0.13	0.11	0.11	0.00	0.00	0.12
1,3-DIETHYL-BENZENE	0.01	0.03	0.03	0.03	0.03	0.04	0.00	0.00	0.04
1-METHYL-3-N-C3-BENZENE	0.00	0.10	0.11	0.15	0.16	0.16	0.00	0.00	0.19
N-C4-BENZENE	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02
1,2,3-TRIMETHYL-BENZENE	0.00	0.00	0.11	0.09	0.09	0.07	0.00	0.00	0.07
1,2-DIETHYL-BENZENE	0.03	0.02	0.02	0.03	0.04	0.04	0.00	0.00	0.05
C10-ALKYL-BENZENES	0.21	0.44	0.43	0.50	0.50	0.51	0.00	0.00	0.59
1,2,4,5-TETRAMETHYL-BENZENE	0.00	0.07	0.06	0.08	0.08	0.10	0.00	0.00	0.10
1,2,3,5-TETRAMETHYL-BENZENE	0.00	0.01	0.06	0.06	0.06	0.07	0.00	0.00	0.06
C11-ALKYL-BENZENES	0.33	1.28	0.98	1.05	1.01	1.03	0.00	0.00	1.16
NAPHTHALENE	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.01
METHYL-NAPHTHALENEs	0.00	0.14	0.13	0.05	0.00	0.04	0.00	0.00	0.09
UNKNOWNs (HC AROMATICS)	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN LITE HYDRO-CARB LIQ (1)	0.00	0.00	0.00	0.00	0.00	0.00	24.29	25.85	0.00
UNKNOWN C12+	1.65	1.89	1.86	1.92	1.52	1.55	1.63	1.96	1.27
SLURRY REACTOR-WAX	7.00	7.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00

(1) Collected in Chilled and Ambient Condensers.

Table B-9 (cont'd)
 Composition of Hydrocarbon Products from
 Two-Stage Slurry F-T/ISM-5 Syngas Conversion
 (Run CT-256-1)

M.B. No. Days On-stream	1-19 20.8	1-20 30.4	1-22 33.2	1-23 34.4	1-27 36.4	1-28 37.4	1-29 40.4	1-30 41.4	1-31 42.4
METHANE	9.41	8.34	9.52	10.45	8.56	8.63	9.27	8.91	9.38
ETHENE	0.00	0.43	0.51	0.64	0.45	0.46	0.52	0.51	0.54
ETHANE	2.42	1.95	2.14	2.34	1.99	1.90	1.94	1.90	1.96
PROPENE	0.77	0.72	0.88	1.12	0.77	0.80	0.91	0.93	0.96
PROPANE	12.25	10.15	11.02	11.76	9.85	9.53	9.29	8.97	9.38
I-BUTANE	14.84	12.90	14.36	15.99	13.30	12.99	12.86	12.85	13.45
1-BUTENE+2-METHYLPROPENE	0.55	0.55	0.67	0.84	0.63	0.66	0.73	0.75	0.82
N-BUTANE	9.16	8.39	9.08	9.76	8.55	8.65	8.32	8.16	8.52
TRANS-2-BUTENE	0.23	0.20	0.27	0.32	0.23	0.24	0.27	0.30	0.32
CIS-2-BUTENE	0.15	0.13	0.17	0.21	0.15	0.16	0.18	0.21	0.21
3-METHYL-1-BUTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
I-PENTANE	9.61	8.88	9.60	10.83	9.22	9.20	8.45	9.10	9.42
1-PENTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
2-METHYL-1-BUTENE	0.07	0.06	0.10	0.09	0.08	0.09	0.09	0.10	0.13
N-PENTANE	3.61	3.69	4.09	4.42	3.54	4.27	3.76	4.25	4.46
TRANS-2-PENTENE	0.01	0.01	0.01	0.01	0.05	0.01	0.00	0.07	0.07
CIS-2-PENTENE	0.03	0.03	0.06	0.05	0.00	0.06	0.06	0.03	0.03
2-METHYL-2-BUTENE	0.03	0.04	0.04	0.03	0.62	0.05	0.00	0.06	0.06
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.25	0.28
C5-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00
2, 2-DIMETHYLBUTANE	0.15	0.17	0.22	0.27	0.00	0.20	0.25	0.01	0.01
CYCLOPENTANE	0.27	0.26	0.26	0.29	0.21	0.22	0.17	0.22	0.22
HEXENES + ISO-HEXANES	0.04	0.00	0.00	0.00	0.00	0.03	0.03	0.00	0.00
2, 3-DIMETHYLBUTANE	0.39	0.37	0.37	0.43	0.35	0.33	0.25	0.34	0.33
2-METHYLPENTANE	2.49	2.63	2.88	3.04	3.00	3.11	2.17	3.12	3.23
3-METHYLPENTANE	1.52	1.59	1.60	1.69	1.57	1.58	1.05	1.61	1.62
HEXENES	0.02	0.03	0.03	0.04	0.11	0.05	0.00	0.07	0.10
N-HEXANE	0.86	0.98	1.16	1.25	1.22	1.36	0.84	1.47	1.51
2, 4-DIMETHYLPENTANE	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
METHYLCYCLOPENTANE	0.90	0.96	1.03	1.11	0.98	1.01	0.58	1.06	1.09
3, 3-DIMETHYLPENTANE	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
HEPTENES + ISO-HEPTANES	0.02	0.02	0.00	0.01	0.00	0.02	0.00	0.03	0.02
2-METHYLHEXANE	0.60	0.72	0.76	0.77	0.84	0.94	0.37	0.96	0.93
2, 3-DIMETHYLPENTANE	0.20	0.24	0.21	0.19	0.24	0.24	0.04	0.26	0.24
3-METHYLHEXANE	0.73	0.84	0.84	0.79	0.94	1.02	0.37	1.04	1.04
1-CIS-3-DIMETHYL-N5	0.20	0.24	0.29	0.31	0.32	0.34	0.12	0.38	0.36
1-TRANS-3-DIMETHYL-N5	0.24	0.21	0.19	0.14	0.24	0.25	0.00	0.28	0.26
1-TRANS-2-DIMETHYL-N5	0.22	0.28	0.27	0.29	0.29	0.29	0.12	0.32	0.31
N-HEPTANE	0.26	0.29	0.36	0.44	0.34	0.42	0.20	0.50	0.49
C7-OLEFINS	0.03	0.04	0.06	0.04	0.09	0.08	0.00	0.08	0.17
METHYLCYCLOHEXANE	0.35	0.45	0.41	0.35	0.38	0.33	0.04	0.58	0.52
C8-OLEFINS + ISO-P	0.05	0.09	0.14	0.28	0.00	0.17	0.14	0.13	0.13
MONOMETHYL-ISO-C8-P	0.31	0.44	0.43	0.31	0.60	0.65	0.00	0.77	0.67
OTHER ISO-C8-P	0.09	0.13	0.11	0.09	0.15	0.10	0.00	0.19	0.16
C8-OLEFINS	0.04	0.05	0.07	0.06	0.14	0.23	0.00	0.12	0.22
C8-NAPHTHENES (N5+N6)	0.66	0.89	0.81	0.64	1.13	1.28	0.00	1.40	1.19
N-OCTANE	0.01	0.01	0.02	0.03	0.03	0.04	0.00	0.06	0.03
C9-OLEFINS + ISO-P	0.05	0.00	0.11	0.23	0.00	0.10	0.10	0.05	0.05
MONOMETHYL-ISO-C9-P	0.07	0.11	0.08	0.09	0.18	0.20	0.00	0.26	0.22
OTHER ISO-C9-P	0.07	0.11	0.07	0.07	0.14	0.15	0.00	0.20	0.15
C9-OLEFINS	0.02	0.01	0.07	0.02	0.02	0.03	0.00	0.04	0.09
C9-NAPHTHENES (N5+N6)	0.14	0.20	0.20	0.16	0.32	0.32	0.00	0.38	0.31
N-NONANE	0.02	0.03	0.02	0.02	0.03	0.03	0.00	0.04	0.03
ISO-C10-P + O + N5 + N6	0.15	0.22	0.20	0.14	0.26	0.29	0.00	0.42	0.36
N-DECANE	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-DECENE	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BENZENE	1.13	1.16	0.91	0.82	0.86	0.78	0.35	0.75	0.79
TOLUENE	5.43	6.24	4.47	3.12	4.39	4.59	0.71	4.00	3.78
ETHYLBENZENE	1.20	1.43	1.26	1.22	1.12	1.44	0.39	1.33	1.25
P-XYLENE	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
M-XYLENE	3.87	4.98	2.63	1.79	4.56	4.05	0.00	3.90	3.42
O-XYLENE	1.13	1.48	1.06	0.53	1.36	1.19	0.00	1.16	1.01
N-PROPYLBENZENE	0.05	0.06	0.05	0.03	0.08	0.07	0.00	0.08	0.07
1-METHYL-3-ETHYL-BENZENE	1.40	1.93	1.62	0.89	2.23	2.24	0.00	2.39	2.04
1, 3, 5-TRIMETHYL-BENZENE	0.08	0.10	0.05	0.02	0.07	0.05	0.00	0.04	0.04
1-METHYL-2-ETHYL-BENZENE	0.24	0.32	0.23	0.11	0.29	0.27	0.00	0.23	0.20
ISO-C4-BENZENE	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.01
1, 2, 4-TRIMETHYL-BENZENE	1.46	1.95	1.44	0.77	1.90	1.74	0.00	1.75	1.47
1-METHYL-2-ISO-C3-BENZENE	0.10	0.13	0.07	0.03	0.09	0.07	0.00	0.05	0.04
1, 3-DIETHYL-BENZENE	0.04	0.05	0.04	0.02	0.08	0.07	0.00	0.05	0.05
1-METHYL-3-N-C3-BENZENE	0.16	0.22	0.20	0.13	0.26	0.30	0.00	0.36	0.30
N-C4-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
1, 2, 3-TRIMETHYL-BENZENE	0.08	0.11	0.05	0.04	0.09	0.09	0.00	0.07	0.06
1, 2-DIETHYL-BENZENE	0.04	0.05	0.05	0.04	0.08	0.09	0.00	0.11	0.09
1-METHYL-2-N-C3-BENZENE	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
C10-ALKYL BENZENES	0.50	0.68	0.54	0.32	0.74	0.76	0.00	0.81	0.66
1, 2, 4, 5-TETRAMETHYL-BENZENE	0.09	0.12	0.09	0.03	0.07	0.12	0.00	0.12	0.10
1, 2, 3, 5-TETRAMETHYL-BENZENE	0.05	0.07	0.05	0.00	0.01	0.07	0.00	0.06	0.05
1, 2, 3, 4-TETRAMETHYL-BENZENE	0.01	0.00	0.00	0.02	0.21	0.01	0.00	0.15	0.10
C11-ALKYL BENZENES	0.97	1.26	0.89	0.60	1.05	1.07	0.00	0.89	0.83
NAPHTHALENE	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METHYL-NAPHTHALENES	0.00	0.09	0.00	0.00	0.00	0.02	0.00	0.05	0.04
UNKNOWN (HC AROMATICS)	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN LITE HYDRO-CARB LIQ (1)	0.00	0.00	0.00	0.00	0.00	0.00	27.38	0.00	0.00
UNKNOWN C12+	1.49	2.11	1.18	0.70	1.98	1.56	1.48	1.70	1.33
SLURRY REACTOR-WAX	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00

(1) Collected in Chilled and Ambient Condensers.

Table B-9 (cont'd)
 Composition of Hydrocarbon Products from
Two-Stage Slurry F-T/ISM-5 Syngas Conversion
 (Run CT-256-1)

M.B. No. Days On-stream	1-32	1-33	1-34	1-35	1-37
	43.4	44.4	45.4	46.4	48.4
METHANE	10.08	9.89	8.43	8.19	9.61
ETHENE	0.58	0.45	0.38	0.43	0.50
ETHANE	2.00	2.63	2.27	2.18	3.85
PROPENE	1.09	0.90	0.79	0.90	1.12
PROPANE	9.20	10.35	9.02	8.05	8.88
BUTENES	0.00	0.00	0.00	0.00	0.00
1-BUTANE	13.29	13.88	12.06	11.16	11.08
1-BUTENE+2-METHYLPROPENE	0.94	0.80	0.70	0.83	1.02
N-BUTANE	8.64	9.17	8.08	7.70	7.61
TRANS-2-BUTENE	0.36	0.31	0.28	0.32	0.41
CIS-2-BUTENE	0.24	0.20	0.18	0.21	0.27
3-METHYL-1-BUTENE	0.00	0.00	0.00	0.02	0.03
1-PENTANE	9.34	8.58	8.15	7.98	7.47
1-PENTENE	0.00	0.02	0.02	0.02	0.03
2-METHYL-1-BUTENE	0.14	0.13	0.12	0.14	0.18
N-PENTANE	4.55	4.19	4.16	4.20	3.88
TRANS-2-PENTENE	0.11	0.09	0.08	0.10	0.13
CIS-2-PENTENE	0.04	0.04	0.04	0.04	0.06
2-METHYL-2-BUTENE	0.09	0.08	0.10	0.13	0.19
UNKNOWN C5-MONOOLEFINS	0.31	0.27	0.23	0.27	0.00
C5-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.00	0.00	0.01	0.01	0.01
CYCLOPENTANE	0.20	0.12	0.19	0.10	0.20
HEXENES + ISO-HEXANES	0.00	0.01	0.00	0.03	0.31
2,3-DIMETHYLBUTANE	0.31	0.18	0.23	0.23	0.21
2-METHYLPENTANE	3.24	2.52	2.98	3.05	2.60
3-METHYLPENTANE	1.58	1.11	1.40	1.43	1.26
HEXENES	0.11	0.13	0.12	0.23	0.22
N-HEXANE	1.62	1.25	1.48	1.62	1.46
2,4-DIMETHYLPENTANE	0.01	0.01	0.01	0.01	0.01
METHYLCYCLOPENTANE	1.08	0.71	0.95	1.00	0.94
3,3-DIMETHYLPENTANE	0.01	0.00	0.01	0.01	0.01
CYCLOHEXANE	0.03	0.02	0.03	0.00	0.03
HEPTENES + ISO-HEPTANES	0.24	0.12	0.10	0.12	0.06
2-METHYLHEXANE	0.98	0.72	0.93	1.04	0.86
2,3-DIMETHYLPENTANE	0.24	0.16	0.23	0.27	0.24
3-METHYLHEXANE	1.07	0.74	1.01	1.10	0.92
1-CIS-3-DIMETHYL-N5	0.38	0.25	0.34	0.37	0.33
1-TRANS-3-DIMETHYL-N5	0.27	0.20	0.29	0.33	0.32
1-TRANS-2-DIMETHYL-N5	0.31	0.21	0.28	0.29	0.26
N-HEPTANE	0.56	0.37	0.43	0.51	0.49
C7-OLEFINS	0.18	0.13	0.17	0.35	0.26
METHYLCYCLOHEXANE	0.50	0.27	0.29	0.39	0.32
C8-OLEFINS + ISO-P	0.14	0.05	0.02	0.05	0.00
MONOMETHYL-ISO-C8-P	0.73	0.70	0.88	0.94	0.80
OTHER ISO-C8-P	0.17	0.13	0.17	0.28	0.17
C8-OLEFINS	0.25	0.22	0.16	0.27	0.38
C8-NAPHTHENES (N5+N6)	1.25	1.08	1.36	1.36	1.25
N-OCTANE	0.11	0.10	0.08	0.03	0.13
C9-OLEFINS + ISO-P	0.15	0.03	0.00	0.00	0.00
MONOMETHYL-ISO-C9-P	0.27	0.29	0.30	0.35	0.30
OTHER ISO-C9-P	0.20	0.15	0.17	0.20	0.15
C9-OLEFINS	0.13	0.05	0.07	0.15	0.14
C9-NAPHTHENES (N5+N6)	0.36	0.39	0.40	0.34	0.33
N-NONANE	0.03	0.02	0.02	0.03	0.01
ISO-C10-P + O + N5 + N6	0.41	0.42	0.26	0.51	0.48
BENZENE	0.67	0.53	0.74	0.77	0.74
TOLUENE	3.35	3.10	4.18	4.38	4.03
ETHYLBENZENE	1.18	1.14	1.39	1.41	1.20
P-XYLENE	0.00	0.00	1.25	0.00	0.00
M-XYLENE	2.89	3.64	3.35	4.61	4.39
O-XYLENE	0.84	1.10	1.36	1.35	1.31
N-PROPYLBENZENE	0.09	0.11	0.12	0.13	0.14
1-METHYL-3-ETHYL-BENZENE	2.00	2.67	3.06	3.17	3.02
1,3,5-TRIMETHYL-BENZENE	0.03	0.04	0.05	0.04	0.05
1-METHYL-2-ETHYL-BENZENE	0.13	0.20	0.33	0.24	0.20
ISO-C4-BENZENE	0.01	0.01	0.01	0.01	0.02
1,2,4-TRIMETHYL-BENZENE	1.25	1.67	1.94	1.97	1.92
1-METHYL-2-ISO-C3-BENZENE	0.02	0.04	0.05	0.04	0.03
1,3-DIETHYL-BENZENE	0.05	0.07	0.11	0.08	0.12
1-METHYL-3-N-C3-BENZENE	0.34	0.45	0.47	0.52	0.48
N-C4-BENZENE	0.01	0.00	0.00	0.02	0.00
1,2,3-TRIMETHYL-BENZENE	0.04	0.09	0.11	0.09	0.10
1,2-DIETHYL-BENZENE	0.09	0.13	0.15	0.15	0.15
1-METHYL-2-N-C3-BENZENE	0.00	0.00	0.00	0.00	0.00
C10-ALKYL-BENZENES	0.64	0.85	0.94	0.97	0.87
1,2,4,5-TETRAMETHYL-BENZENE	0.08	0.10	0.11	0.12	0.10
1,2,3,5-TETRAMETHYL-BENZENE	0.03	0.06	0.06	0.06	0.04
1,2,3,4-TETRAMETHYL-BENZENE	0.07	0.09	0.18	0.19	0.15
C11-ALKYL-BENZENES	0.66	1.02	1.10	1.16	0.87
NAPHTHALENE	0.00	0.01	0.00	0.00	0.00
METHYL-NAPHTHALENE	0.02	0.04	0.00	0.05	0.00
UNKNOWN (HC PARAFFINICS)	0.12	0.00	0.00	0.00	0.00
UNKNOWN (HC AROMATICS)	0.00	0.00	0.14	0.00	0.11
UNKNOWN C12+	1.30	2.01	2.44	2.61	2.19
SLURRY REACTOR-WAX	6.00	6.00	6.00	6.00	6.00

Table C-1
First-Stage Fischer-Tropsch Slurry Reactor
Operating Conditions and Material Balances
(Based on Inter-Reactor Sample)
(Run CT-256-2)

(Nitrogen-Free Basis)						
M.B. No.	2- 1	2- 2	2- 3	2- 7	2- 15	2- 16
Days On-stream	0.9	1.9	2.9	6.9	14.8	15.8
First-Stage Conditions:						
Charge H ₂ /CO (Molar)	0.687	0.684	0.682	0.683	0.672	0.673
Temperature, °C	260	259	259	258	262	262
Pressure, MPa	1.136	1.136	1.136	1.473	1.480	1.825
Feed Sup. Vel., cm/s	3.266	4.120	4.063	3.612	3.430	3.439
Space Vel., NL/gFe-hr	1.461	1.914	1.906	2.281	2.208	2.705
N ₂ in Feed, Mol %	9.0	5.6	4.6	3.9	4.1	5.0
Conversions, Mol % :						
H ₂	60.56	69.04	75.23	77.32	81.35	84.33
CO	71.57	75.10	87.02	89.17	89.44	89.10
H ₂ +CO	67.09	72.64	82.24	84.36	86.19	87.18
Yields, Wt % of Products :						
Hydrocarbons (1)	17.48	16.87	21.88	20.30	19.87	19.22
CO ₂	52.91	57.85	65.53	67.86	69.27	68.68
H ₂ O (1)	0.00	0.00	0.00	0.89	0.89	1.07
H ₂	1.90	1.46	1.08	1.02	0.79	0.72
CO	27.70	23.82	11.51	9.92	9.19	10.30
Total	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:						
gHC/Nm ³ (H ₂ +CO) conv.:	97.73	99.56	107.37	103.93	109.61	100.88
(H/C) Atomic Ratio in HC :	197	179	222	194	198	174
Selectivities, Wt % of HC :						
Methane	6.69	7.11	6.34	7.24	8.55	7.92
Ethene	3.31	3.01	1.97	1.93	1.75	1.94
Ethane	2.57	2.75	2.66	3.36	3.88	3.48
Propene	8.20	8.57	7.32	8.40	9.32	8.76
Propane	1.33	1.51	1.46	1.96	2.47	2.25
Butenes	6.52	7.02	6.02	6.79	7.57	7.06
i-Butane	0.07	0.06	0.05	0.09	0.00	0.00
n-Butane	1.16	1.41	1.35	1.87	2.28	2.16
C ₅ - C ₁₁ (2)	15.10	16.49	14.08	17.76	12.05	11.68
Light Hydrocarbons (3)	20.49	17.44	21.98	19.06	18.54	19.22
Heavy Hydrocarbons (4)	20.42	25.55	30.14	27.37	31.08	33.47
Slurry Rx.-Wax	13.60	8.43	6.28	3.74	1.78	1.24
Total	100	100	100	100	100	100

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condenser

(4) Collected in Hot Condenser

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

M.B. No. Days On-straem	2-1 0.9	2-2 1.9	2-3 2.9	2-7 6.9	2-15 14.8	2-16 15.8
METHANE	6.69	7.11	6.34	7.24	8.55	7.92
ETHENE	3.31	3.01	1.97	1.93	1.75	1.94
ETHANE	2.57	2.75	2.66	3.36	3.88	3.48
PROPENE	8.20	8.57	7.32	8.40	9.32	8.76
PROPANE	1.33	1.51	1.46	1.96	2.47	2.25
I-BUTANE	0.07	0.06	0.05	0.09	0.00	0.00
1-BUTENE+2-METHYLPROPENE	6.21	6.67	5.63	6.25	6.80	6.44
N-BUTANE	1.16	1.41	1.35	1.87	2.28	2.16
TRANS-2-BUTENE	0.11	0.12	0.15	0.21	0.35	0.25
CIS-2-BUTENE	0.20	0.23	0.25	0.33	0.43	0.37
3-METHYL-1-BUTENE	0.34	0.35	0.26	0.34	0.34	0.31
I-PENTANE	0.18	0.21	0.14	0.21	0.27	0.23
1-PENTENE	4.66	5.17	4.32	4.54	4.73	4.48
2-METHYL-1-BUTENE	0.21	0.21	0.17	0.18	0.21	0.18
N-PENTANE	0.90	1.12	1.08	1.43	1.65	1.51
TRANS-2-PENTENE	0.09	0.10	0.12	0.16	0.21	0.14
CIS-2-PENTENE	0.11	0.13	0.14	0.18	0.20	0.13
2-METHYL-2-BUTENE	0.00	0.00	0.01	0.01	0.00	0.02
HEXENES + ISO-HEXANES	0.71	0.68	0.63	0.75	0.34	0.31
2-METHYLPENTANE	0.00	0.05	0.00	0.00	0.00	0.00
3-METHYLPENTANE	0.00	0.06	0.00	0.00	0.00	0.00
1-HEXENE	3.20	3.61	2.85	2.84	2.40	2.28
N-HEXANE	0.67	0.84	0.78	1.01	0.91	0.84
HEPTENES + ISO-HEPTANES	0.61	0.66	0.54	0.64	0.00	0.24
1-HEPTENE	1.71	1.86	1.42	1.40	0.57	0.63
N-HEPTANE	0.39	0.47	0.44	0.58	0.23	0.24
C8-OLEFINS + ISO-P	0.32	0.24	0.30	0.44	0.00	0.04
1-OCTENE	0.63	0.51	0.48	0.58	0.00	0.04
N-OCTANE	0.18	0.16	0.20	0.34	0.00	0.00
C9-OLEFINS + ISO-P	0.07	0.04	0.11	2.12	0.00	0.05
1-NONENE	0.11	0.04	0.10	0.00	0.00	0.00
DIMETHYL ETHER	0.00	0.00	0.00	0.00	0.31	0.29
ACETONE	0.53	0.65	0.35	0.44	0.15	0.25
I-PROPANOL	0.00	0.00	0.00	0.00	0.28	0.27
UNKNOWN LITE HYDRO-CARB LIQ (1)	20.49	17.44	21.98	19.06	18.54	19.22
UNKNOWN HVY HYDRO-CARB LIQ (2)	20.42	25.55	30.14	27.37	31.08	33.47
SLURRY REACTOR-WAX	13.60	8.43	6.28	3.74	1.78	1.24

(1) Collected in Chilled and Ambient Condensers

(2) Collected in Hot Condenser

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

(Nitrogen-Free Basis)	2- 1	2- 2	2- 3	2- 4	2- 5	2- 6	2- 7
M.B. No.	0.9	1.9	2.9	3.9	4.9	5.8	6.9
Days On-stream							
First-Stage Conditions:							
Charge H ₂ /CO (Molar)	0.687	0.684	0.682	0.753	0.681	0.673	0.683
Temperature, oC	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, oC	284	284	291	295	306	322	330
Outlet, oC	333	332	333	336	343	369	376
Pressure, MPa	1.129	1.129	1.136	1.136	1.136	1.467	1.453
GHSV, 1/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:	97.80	100.39	107.38	111.91	106.47	102.04	103.67
gHC/Nm ₃ (H ₂ +CO) conv.:	189	228	201	215	203	208	200
(H/C) Atomic Ratio in HC :	2.25	2.20	2.20	2.23	2.26	2.22	2.24
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 MB # 6

(2) Not available

Table C-3 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
 (Run CT-256-2)

(Nitrogen-Free Basis)							
M.B. No.	2- 8	2- 12	2- 13	2- 14	2- 15	2- 16	2- 17
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, oC	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, oC	331	342	348	352	343	343	350
Outlet, oC	376	388	394	403	390	390	401
Pressure, MPa	1.136	1.136	1.480	1.480	1.480	1.825	1.825
GHSV, 1/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:	109.05	109.24	104.93	108.81	108.24	103.58	103.31
gHC/Nm ³ (H ₂ +CO) conv.:	230	218	216	212	212	193	201
(H/C) Atomic Ratio in HC :	2.24	2.30	2.25	2.28	2.28	2.26	2.27
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 C-4
Composition of Hydrocarbon Products from
Two-Stage Slurry F-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
I-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
I-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	4.98	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
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-METHYLPENTANE	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
UNKNOWNS (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 C-4 (cont'd)
Composition of Hydrocarbon Products from
Two-Stage Slurry F-T/ISM-5 Syngas Conversion
(Run CT-256-2)

M. B. No. Days On-stream	2-12 11.9	2-13 12.9	2-14 13.8	2-15 14.8	2-16 15.8	2-17 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
I-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
I-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	1.15
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	0.35	0.82	0.75
M-XYLENE	—	1.91	2.03	2.10	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-NAPHTHALENE	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 C-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, $iC_4^= + C_3^=$	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.

Table D-1
**First-Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances**
 (Second-Stage Not-operative)
 (Run CT-256-3)

(Nitrogen-Free Basis)

	3- 1 3.4	3- 2 4.4	3- 3 5.4	3- 4 6.4	3- 5 7.4	3- 46 48.5	3- 47 49.5	3- 48 50.5	3- 49 51.5	3- 50 52.5
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.701	0.676	0.677	0.689	0.677	0.675	0.680	0.678	0.681	0.693
Temperature, °C	257	259	259	259	259	261	261	261	262	262
Pressure, MPa	1.480	1.480	1.480	1.480	1.480	1.480	1.494	1.501	1.487	1.487
Feed Sup. Vel., cm/s	3.652	3.713	3.696	3.719	3.918	3.210	3.131	3.149	3.176	3.230
Space Vel., NL/gFe-hr	2.373	2.402	2.394	2.404	2.541	2.101	2.068	2.088	2.082	2.120
N ₂ in Feed, Mol %	6.5	6.7	6.6	6.7	6.4	6.5	6.4	6.4	6.5	6.4
Conversions, Mol % :										
H ₂	75.36	79.19	78.59	79.53	79.53	80.37	78.82	80.02	78.53	77.56
CO	90.29	91.75	90.68	90.98	91.59	89.85	88.74	90.42	90.13	88.92
H ₂ +CO	84.14	86.69	85.79	86.30	86.72	86.03	84.73	86.22	85.43	84.27
Yields, Wt % of Products :										
Hydrocarbons (1)	21.24	22.50	21.81	21.87	22.10	22.73	22.03	21.80	21.44	22.47
CO ₂	67.92	68.10	68.02	68.54	68.43	66.64	66.38	68.16	68.05	65.65
H ₂ O (1)	1.07	0.82	0.94	0.79	0.86	0.71	0.78	0.38	0.72	0.87
H ₂	1.11	0.94	0.93	0.89	0.92	0.85	0.91	0.89	0.95	1.01
CO	8.66	7.64	8.30	7.90	7.70	9.07	9.90	8.76	8.84	10.00
Total	100	100	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	106.71	102.87	107.10	108.70	104.12	106.68	108.39	104.16	106.33	105.52
gHC/Nm ₃ (H ₂ +CO) conv.:	207	208	212	213	207	220	219	205	208	218
(H/C) Atomic Ratio in HC :	2.19	2.20	2.20	2.12	2.20	2.24	2.25	2.28	2.25	2.24
Selectivities, Wt % of HC :										
Methane	5.69	5.85	5.85	5.86	6.15	7.59	7.86	7.88	8.20	7.97
Ethene	2.29	2.16	2.12	1.91	1.79	1.40	1.49	1.50	1.53	1.51
Ethane	2.75	2.61	2.60	2.61	2.74	2.85	2.95	3.17	3.33	3.11
Propene	7.64	7.54	7.56	7.32	7.54	7.84	8.18	8.05	8.41	8.17
Propane	1.38	1.39	1.50	1.51	1.59	1.88	1.88	2.20	2.27	1.93
Butenes	6.10	6.00	6.06	5.86	6.03	5.87	6.04	6.42	6.39	5.99
i-Butane	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
n-Butane	1.44	1.47	1.48	1.48	1.57	1.85	1.92	2.03	2.00	1.91
C ₅ - C ₁₁ (2)	14.79	15.71	15.34	14.49	14.52	8.64	9.12	7.00	9.19	8.79
Light Hydrocarbons (3)	21.15	20.42	19.90	20.63	20.60	33.34	31.02	30.12	28.96	31.90
Heavy Hydrocarbons (4)	23.82	24.17	25.54	25.85	25.69	22.23	23.29	20.62	23.62	22.75
Slurry Rx.-Wax	12.76	12.34	11.89	11.75	11.14	6.42	6.18	5.97	5.85	5.76
Total	100	100	100	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 D-2
First-Stage Fischer-Tropsch Slurry Reactor
Operating Conditions and Material Balances
(Based on Inter-Reactor Sample)
(Run CT-256-3)

(Nitrogen-Free Basis)									
M. B. No.	3- 8	3- 9	3- 11	3- 13	3- 19	3- 21	3- 22	3- 23	3- 24
Days On-stream	10.3	11.3	13.4	15.4	20.0	22.0	23.0	24.0	25.0
First-Stage Conditions:									
Charge H ₂ /CO (Molar)	0.680	0.678	0.680	0.683	0.688	0.683	0.685	0.687	0.685
Temperature, oC	259	260	260	260	259	260	260	259	260
Pressure, MPa	1.480	1.480	1.480	1.480	1.480	1.480	1.480	1.487	1.480
Feed Sup. Vel., cm/s	3.922	3.957	4.038	3.984	3.828	3.804	3.829	3.809	3.803
Space Vel., NL/gFe-hr	2.580	2.591	2.622	2.620	2.514	2.502	2.507	2.516	2.497
N ₂ in Feed, Mol %	6.3	6.7	7.4	6.3	6.4	6.2	6.6	6.3	6.2
Conversions, Mol % :									
H ₂	79.33	79.24	79.38	79.12	80.13	79.87	78.36	81.49	78.92
CO	91.78	91.33	91.94	90.89	91.57	91.37	89.37	91.12	90.78
H ₂ +CO	86.74	86.44	86.85	86.11	86.91	86.70	84.89	87.20	85.96
Yields, Wt % of Products :									
Hydrocarbons (1)	21.91	21.37	21.87	20.77	22.15	22.08	19.43	23.94	21.78
CO ₂	68.59	68.61	68.80	69.15	68.50	68.29	69.41	66.18	68.07
H ₂ O (1)	0.92	1.03	0.71	0.87	0.89	0.94	0.78	0.88	0.79
H ₂	0.94	0.94	0.96	0.93	0.89	0.90	0.95	0.84	0.95
CO	7.64	8.04	7.66	8.28	7.58	7.80	9.43	8.16	8.42
Total	100	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	102.54	102.75	100.33	104.91	105.94	105.38	107.36	103.66	104.29
gHC/Nm ³ (H ₂ +CO) conv.:	202	198	197	197	210	209	191	221	205
(H/C) Atomic Ratio in HC :	2.21	2.22	2.23	2.23	2.23	2.22	2.27	2.20	2.23
Selectivities, Wt % of HC :									
Methane	6.32	6.80	6.78	7.14	7.29	6.87	7.55	5.96	7.13
Ethene	1.64	1.64	1.58	1.39	1.45	1.45	1.64	1.30	1.54
Ethane	2.84	2.89	2.83	2.92	2.83	2.77	3.13	2.49	2.85
Propene	7.40	7.55	7.53	7.77	7.73	7.47	8.19	6.57	7.79
Propane	1.76	1.82	1.82	1.79	1.88	1.80	2.24	1.75	1.90
Butenes	5.99	5.96	6.16	6.28	6.32	5.93	6.98	5.45	6.19
i-Butane	0.00	0.07	0.07	0.07	0.06	0.06	0.07	0.06	0.07
n-Butane	1.66	1.73	1.78	1.83	1.94	1.83	2.12	1.67	1.92
C ₅ - C ₁₁ (2)	15.53	14.03	18.64	11.41	14.13	12.61	12.38	15.51	13.54
Light Hydrocarbons (3)	17.27	17.32	14.31	18.27	17.40	18.65	20.13	19.45	18.53
Heavy Hydrocarbons (4)	28.80	29.43	27.62	31.54	28.80	30.86	26.93	30.22	29.11
Slurry Rx.-Wax	10.43	10.26	9.88	9.60	9.26	9.00	8.91	8.68	8.62
Total	100	100	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 D-2 (cont'd)
**First-Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances**
 (Based on Inter-Reactor Sample)
 (Run CT-256-3)

(Nitrogen-Free Basis)											
M.B. No.	3- 25	3- 28	3- 29	3- 30	3- 31	3- 32	3- 33	3- 34	3- 35	3- 36	
Days On-stream	26.0	29.0	30.5	31.5	32.5	33.5	34.5	35.5	36.5	37.5	
First-Stage Conditions:											
Charge H ₂ /C ₀ (Molar)	0.689	0.694	0.665	0.686	0.679	0.702	0.696	0.695	0.685	0.674	
Temperature, °C	260	261	261	260	260	260	260	259	260	260	
Pressure, MPa	1.480	1.480	1.480	1.487	1.480	1.480	1.446	1.480	1.494	1.487	
Feed Sup. Vel., cm/s	3.734	3.658	3.599	3.617	3.496	3.496	3.544	3.481	3.444	3.462	
Space Vel., NL/gFe-hr	2.489	2.388	2.343	2.373	2.282	2.279	2.253	2.273	2.267	2.275	
N ₂ in Feed, Mol %	4.9	6.7	7.0	6.9	6.9	6.9	7.1	7.0	6.9	6.7	
Conversions, Mol % :											
H ₂	76.49	79.28	72.98	76.71	78.91	80.46	80.51	79.89	80.45	80.93	
C ₀	88.56	90.53	81.72	87.09	90.31	91.69	92.11	92.38	91.90	91.61	
H ₂ +C ₀	83.64	85.92	78.23	82.87	85.70	87.06	87.35	87.26	87.24	87.31	
Yields, Wt % of Products :											
Hydrocarbons (1)	21.84	22.27	20.75	22.00	22.29	23.25	22.72	23.91	23.36	22.88	
C ₀ 2	66.56	67.55	61.33	64.78	67.20	67.79	68.50	67.49	67.63	67.74	
H ₂ O (1)	0.51	0.77	0.35	0.58	0.79	0.54	0.83	0.84	0.86	0.72	
H ₂	1.03	0.93	1.16	1.03	0.94	0.90	0.88	0.91	0.87	0.86	
CO	10.06	8.48	16.41	11.60	8.78	7.52	7.07	6.85	7.28	7.80	
Total	100	100	100	100	100	100	100	100	100	100	
Bal Recovery, Wt % of Charge:	108.28	106.35	106.23	105.97	105.18	105.05	106.13	105.83	106.02	102.42	
gHC/Nm ³ (H ₂ +C ₀) conv.:	219	213	221	218	213	216	213	224	220	210	
(H/C) Atomic Ratio in HC :	2.23	2.23	2.25	2.24	2.24	2.24	2.24	2.23	2.23	2.23	
Selectivities, Wt % of HC :											
Methane	6.75	7.29	8.12	7.73	7.63	7.40	7.57	7.42	7.15	7.08	
Ethene	1.45	1.50	2.11	1.70	1.52	1.38	1.39	1.27	1.33	1.38	
Ethane	2.76	2.85	2.94	2.93	2.97	2.86	2.91	2.74	2.71	2.70	
Propene	7.32	7.86	8.43	8.05	8.01	7.70	7.92	7.77	7.47	7.53	
Propane	1.90	1.92	1.96	1.98	2.02	1.93	1.99	1.74	1.86	1.87	
Butenes	5.95	6.24	6.48	6.36	6.36	6.10	6.27	5.99	5.94	6.07	
i-Butane	0.06	0.07	0.08	0.07	0.07	0.06	0.07	0.06	0.06	0.06	
n-Butane	1.84	1.95	1.99	1.99	2.01	1.94	1.99	1.92	1.90	1.93	
C ₅ - C ₁₁ (2)	13.10	13.68	13.82	15.20	15.73	14.00	14.13	12.53	12.39	15.60	
Light Hydrocarbons (3)	18.30	18.67	21.67	19.07	18.12	18.25	18.05	19.78	18.70	18.32	
Heavy Hydrocarbons (4)	30.01	28.62	22.89	24.95	26.21	27.33	28.76	30.27	32.07	28.94	
Slurry Rx.-Wax	8.54	8.46	8.45	8.84	8.30	8.99	7.97	7.66	7.63	7.47	
Total	100	100	100	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 D-2 (cont'd)
 First-Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances
 (Based on Inter-Reactor Sample)
 (Run CT-256-3)

(Nitrogen-Free Basis)										
M.B. No.	3- 37	3- 38	3- 39	3- 40	3- 41	3- 42	3- 43	3- 44	3- 53	3- 56
Days On-stream	38.5	39.5	40.5	41.5	42.5	43.5	44.5	45.5	57.5	64.5
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.695	0.679	0.693	0.689	0.689	0.693	0.687	0.689	0.675	0.691
Temperature, °C	259	260	260	260	260	260	260	260	264	266
Pressure, MPa	1.480	1.494	1.480	1.480	1.480	1.508	1.494	1.494	1.480	1.577
Feed Sup. Vel., cm/s	3.474	3.429	3.464	3.439	3.457	3.323	3.355	3.331	3.251	2.855
Space Vel., NL/gFe-hr	2.273	2.282	2.288	2.269	2.277	2.228	2.232	2.217	2.095	2.036
N ₂ in Feed, Mol %	6.8	5.9	5.7	5.9	6.0	6.1	5.9	5.9	7.9	7.1
Conversions, Mol % :										
H ₂	80.97	81.55	80.92	79.55	78.93	77.40	77.56	75.57	79.73	72.17
CO	91.76	91.65	91.50	89.87	89.89	88.96	89.29	87.88	89.46	78.96
H ₂ +CO	87.34	87.57	87.17	85.66	85.42	84.23	84.51	82.86	85.54	76.19
Yields, Wt % of Products :										
Hydrocarbons (1)	24.28	22.99	21.92	20.55	22.10	19.77	22.89	21.61	22.15	20.15
CO ₂	66.61	67.81	68.46	66.87	66.63	67.14	65.29	65.40	66.71	60.42
H ₂ O (1)	0.88	0.74	0.76	2.34	0.75	2.08	0.91	0.75	0.55	0.16
H ₂	0.85	0.83	0.89	0.93	0.99	1.02	1.03	1.11	0.91	1.19
CO	7.38	7.63	7.96	9.31	9.53	9.99	9.88	11.12	9.69	18.08
Total	100	100	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	106.28	104.24	101.66	103.58	101.05	105.20	103.21	103.72	103.71	110.78
gHC/Nm ³ (H ₂ +CO) conv.:	228	213	198	193	203	191	217	210	210	227
(H/C) Atomic Ratio in HC :	2.22	2.22	2.24	2.24	2.23	2.25	2.22	2.24	2.25	2.32
Selectivities, Wt % of HC :										
Methane	6.64	6.87	7.57	7.83	7.36	8.10	6.94	7.67	8.21	10.77
Ethene	1.25	1.35	1.44	1.53	1.39	1.57	1.35	1.50	1.62	2.84
Ethane	2.50	2.61	2.81	2.92	2.76	3.10	2.64	2.85	3.43	4.85
Propene	7.02	7.21	7.95	8.23	7.62	8.40	7.17	7.87	8.69	11.40
Propane	1.74	1.86	1.93	2.04	1.87	2.15	1.82	1.96	2.28	2.90
Butenes	5.74	5.82	6.34	6.63	6.13	6.83	5.74	6.29	6.86	8.32
i-Butane	0.06	0.06	0.07	0.07	0.07	0.07	0.06	0.07	0.08	0.14
n-Butane	1.83	1.85	2.04	2.12	1.98	2.21	1.84	2.01	2.13	2.50
C ₅ - C ₁₁ (2)	16.09	14.58	15.83	17.37	16.73	17.64	14.26	15.52	15.36	22.38
Light Hydrocarbons (3)	19.20	21.31	18.13	22.96	17.81	18.87	21.48	17.21	17.46	14.23
Heavy Hydrocarbons (4)	29.37	28.29	27.87	20.27	28.36	23.13	29.10	29.39	28.03	14.07
Slurry Rx.-Wax	7.31	7.22	6.96	6.84	6.82	6.72	6.69	6.59	4.83	3.24
Total	100	100	100	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 D-2 (cont'd)
**First-Stage Fischer-Tropsch Slurry Reactor
 Operating Conditions and Material Balances**
 (Based on Inter-Reactor Sample)
 (Run CT-256-3)

(Nitrogen-Free Basis)							
M.B. No.	3- 57	3- 58	3- 59	3- 60	3- 61	3- 62	3- 63
Days On-stream	66.5	68.5	70.5	72.5	74.5	76.5	78.5
First-Stage Conditions:							
Charge H ₂ /CO (Molar)	0.693	0.601	0.601	0.607	0.596	0.600	0.634
Temperature, °C	265	265	266	265	266	266	264
Pressure, MPa	1.535	1.825	2.170	2.170	2.515	2.515	2.515
Feed Sup. Vel., cm/s	2.841	2.662	2.607	2.634	2.567	2.231	1.423
Space Vel., NL/gFe-hr	1.923	2.186	2.587	2.616	3.014	2.612	1.602
N ₂ in Feed, Mol %	9.5	7.6	6.0	6.0	4.0	4.3	8.3
Conversions, Mol % :							
H ₂	85.65	84.07	82.55	81.97	79.77	89.41	92.59
CO	82.58	83.47	81.64	81.01	78.68	88.58	93.55
H ₂ +CO	83.83	83.69	81.98	81.37	79.09	88.89	93.17
Yields, Wt % of Products :							
Hydrocarbons (1)	20.66	21.17	20.08	20.37	19.87	21.07	18.88
CO ₂	62.14	62.61	61.36	60.77	59.43	67.20	74.15
H ₂ O (1)	0.05	0.04	0.09	0.08	0.05	0.05	0.09
H ₂	0.68	0.65	0.73	0.75	0.81	0.45	0.34
CO	16.47	15.54	17.74	18.03	19.84	11.23	6.54
Total	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	100.68	101.90	99.14	100.88	102.95	97.39	94.35
gHC/Nm ³ (H ₂ +CO) conv.:	192	209	197	205	211	188	152
(H/C) Atomic Ratio in HC :	2.25	2.26	2.26	2.27	2.30	2.25	2.28
Selectivities, Wt % of HC :							
Methane	8.95	8.45	8.46	8.64	7.90	7.76	9.11
Ethene	2.51	2.25	2.56	2.37	2.36	2.05	2.37
Ethane	3.45	3.51	3.82	3.67	3.47	3.53	4.68
Propene	9.48	9.03	9.58	9.53	8.64	8.71	0.00
Propane	2.32	2.29	2.57	2.57	2.44	2.52	0.00
Butenes	8.59	6.69	7.17	7.21	6.63	6.67	9.13
i-Butane	0.07	0.09	0.13	0.12	0.13	0.12	0.16
n-Butane	0.51	2.07	2.25	2.31	2.29	2.29	2.67
C ₅ - C ₁₁ (2)	15.25	12.72	18.40	18.64	15.11	15.82	24.03
Light Hydrocarbons (3)	20.06	23.46	20.21	19.21	22.74	22.99	13.98
Heavy Hydrocarbons (4)	23.79	25.22	18.98	19.49	22.74	20.84	19.87
Slurry Rx.-Wax	4.13	3.76	4.04	4.59	4.59	5.62	12.23
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 D-3
Composition of Hydrocarbon Products from
First-Stage Slurry F-T Reactor
(Run CT-256-3)

M. B. No. Days On Stream	(1) 3-1 3.4	(1) 3-2 4.4	(1) 3-3 5.4	(1) 3-4 6.4	(1) 3-5 7.4	3-8 10.4	3-9 11.4	3-11 13.4	3-13 15.4	3-19 20.0
METHANE	5.69	5.85	5.85	5.86	6.15	6.32	6.80	6.78	7.14	7.29
ETHENE	2.29	2.16	2.12	1.91	1.79	1.64	1.64	1.58	1.39	1.45
ETHANE	2.75	2.61	2.60	2.61	2.74	2.84	2.89	2.83	2.92	2.83
PROPENE	7.64	7.54	7.56	7.32	7.54	7.40	7.55	7.53	7.77	7.73
PROPANE	1.38	1.39	1.50	1.51	1.59	1.76	1.82	1.82	1.79	1.88
I-BUTANE	0.08	0.07	0.07	0.07	0.07	0.00	0.07	0.07	0.07	0.06
1-BUTENE+2-METHYLPROPENE	5.68	5.58	5.66	5.46	5.61	5.56	5.70	5.74	5.90	5.94
N-BUTANE	1.44	1.47	1.48	1.48	1.57	1.66	1.73	1.78	1.83	1.94
TRANS-2-BUTENE	0.16	0.16	0.15	0.14	0.15	0.16	0.00	0.16	0.14	0.14
CIS-2-BUTENE	0.26	0.27	0.26	0.26	0.27	0.27	0.26	0.26	0.23	0.24
3-METHYL-1-BUTENE	0.39	0.34	0.45	0.31	0.30	0.34	0.26	0.26	0.25	0.24
I-PENTANE	0.24	0.36	0.22	0.18	0.17	0.18	0.16	4.47	0.17	0.15
1-PENTENE	4.21	4.30	4.32	4.11	4.19	4.10	4.21	1.49	0.04	4.51
2-METHYL-1-BUTENE	0.28	0.19	0.22	0.17	0.17	0.18	0.15	0.15	4.37	0.12
N-PENTANE	1.13	1.17	1.20	1.20	1.25	1.35	1.35	0.16	1.37	1.49
TRANS-2-PENTENE	0.11	0.12	0.12	0.12	0.13	0.13	0.13	0.01	0.06	0.12
CIS-2-PENTENE	0.15	0.15	0.14	0.14	0.15	0.15	0.15	0.00	0.12	0.13
2-METHYL-2-BUTENE	0.01	0.00	0.00	0.01	0.01	0.02	0.01	0.00	0.26	0.01
CYCLOPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00
HEXENES + ISO-HEXANES	0.62	0.67	0.74	0.68	0.66	0.62	0.57	0.79	0.11	0.06
2,3-DIMETHYLBUTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00
2-METHYL PENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.12	0.00
3-METHYL PENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.13	0.00
1-HEXENE	2.61	2.99	2.85	2.70	2.67	2.55	2.61	3.03	0.11	2.79
N-HEXANE	0.77	0.93	0.88	0.87	0.90	0.92	0.94	1.15	0.09	1.02
HEPTENES + ISO-HEPTANES	0.54	0.64	0.59	0.57	0.57	1.04	0.51	0.84	0.00	0.48
1-HEPTENE	1.38	1.60	1.58	1.46	1.38	1.16	1.17	1.80	0.00	1.26
1-TRANS-3-DIMETHYL-N5	0.00	0.00	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00
N-HEPTANE	0.49	0.56	0.54	0.55	0.54	0.50	0.51	0.85	0.00	0.54
C8-OLEFINS + ISO-P	0.45	0.33	0.35	0.31	0.31	0.68	0.22	0.65	0.00	0.23
1-OCTENE	0.60	0.63	0.55	0.53	0.52	0.39	0.35	0.97	0.00	0.40
N-OCTANE	0.28	0.29	0.24	0.27	0.25	0.21	0.19	0.53	0.00	0.24
C9-OLEFINS + ISO-P	0.26	0.16	0.15	0.11	0.16	0.83	0.26	0.76	0.00	0.14
C9-OLEFINS	0.19	0.17	0.13	0.12	0.11	0.09	0.07	0.35	0.00	0.11
N-NONANE	0.09	0.10	0.07	0.08	0.08	0.07	0.06	0.37	0.00	0.09
ACETONE	0.04	0.23	0.05	0.44	0.34	0.16	0.29	0.88	0.00	0.27
I-PROPANOL	0.06	0.04	0.04	0.23	0.24	0.20	0.22	0.15	0.00	0.31
N-BUTANONE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.34
UNKNOWN LITE HYDRO-CARB LIQ (2)	21.15	20.42	19.90	20.63	20.60	17.27	17.32	14.31	18.27	17.40
UNKNOWN HVY HYDRO-CARB LIQ (3)	23.82	24.17	25.54	25.85	25.69	28.80	29.43	27.62	31.54	28.80
SLURRY REACTOR-WAX	12.76	12.34	11.89	11.75	11.14	10.43	10.26	9.88	9.60	9.26

(1) Based on Inter-Reactor Sample

(2) Collected in Ambient and Chilled Condensers

(3) Collected in Hot Condenser

Table D-3 (cont'd)
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-3)

M. B. No. Days On Stream	(1) 3-21 22.0	(1) 3-22 23.0	(1) 3-23 24.0	(1) 3-24 26.0	(1) 3-25 27.0	(1) 3-28 29.0	(1) 3-29 30.5	(1) 3-30 31.5
METHANE	6.87	7.55	5.96	7.13	6.75	7.29	8.12	7.73
ETHENE	1.45	1.64	1.30	1.54	1.45	1.50	2.11	1.70
ETHANE	2.77	3.13	2.49	2.85	2.76	2.85	2.94	2.93
PROPENE	7.47	8.18	6.57	7.79	7.32	7.86	8.43	8.05
PROPANE	1.80	2.23	1.75	1.90	1.90	1.92	1.96	1.98
I-BUTANE	0.06	0.07	0.06	0.07	0.06	0.07	0.08	0.07
1-BUTENE+2-METHYLPROPENE	5.59	6.44	5.14	5.84	5.63	5.89	6.23	6.06
N-BUTANE	1.83	2.06	1.67	1.92	1.84	1.95	1.99	1.99
TRANS-2-BUTENE	0.13	0.14	0.12	0.13	0.12	0.13	0.09	0.11
CIS-2-BUTENE	0.21	0.23	0.19	0.22	0.20	0.21	0.16	0.19
3-METHYL-1-BUTENE	0.22	0.25	0.20	0.22	0.21	0.22	0.26	0.24
I-PENTANE	0.14	0.16	0.13	0.14	0.14	0.14	0.17	0.15
1-PENTENE	4.09	4.82	3.98	4.36	4.22	4.40	4.55	4.59
2-METHYL-1-BUTENE	0.11	0.13	0.11	0.11	0.11	0.11	0.12	0.13
N-PENTANE	1.36	1.59	1.32	1.46	1.38	1.47	1.43	1.52
TRANS-2-PENTENE	0.11	0.11	0.10	0.11	0.10	0.10	0.07	0.09
CIS-2-PENTENE	0.12	0.13	0.11	0.12	0.11	0.11	0.09	0.10
2,2-DIMETHYLBUTANE	0.00	0.00	0.04	0.00	0.05	0.00	0.00	0.00
CYCLOPENTANE	0.00	0.09	0.09	0.00	0.07	0.00	0.00	0.00
HEXENES + ISO-HEXANES	0.15	0.03	0.00	0.18	0.00	0.19	0.20	0.21
2,3-DIMETHYLBUTANE	0.00	0.11	0.06	0.00	0.06	0.00	0.00	0.00
1-HEXENE	2.35	3.27	2.62	2.61	2.55	2.66	2.81	2.91
N-HEXANE	0.87	1.18	0.98	0.95	0.91	0.96	0.93	1.01
HEPTENES + ISO-HEPTANES	0.33	0.09	0.69	0.40	0.38	0.40	0.35	0.43
1-HEPTENE	1.02	0.00	1.49	1.14	1.11	1.18	1.30	1.43
N-HEPTANE	0.39	0.00	0.64	0.48	0.47	0.48	0.47	0.56
C8-OLEFINS + ISO-P	0.56	0.00	0.48	0.17	0.18	0.20	0.17	0.27
1-OCTENE	0.24	0.00	0.73	0.37	0.36	0.39	0.42	0.54
N-OCTANE	0.14	0.00	0.43	0.22	0.20	0.22	0.20	0.27
C9-OLEFINS + ISO-P	0.28	0.00	0.77	0.37	0.29	0.23	0.10	0.39
1-NONENE	0.14	0.00	0.00	0.00	0.00	0.00	0.12	0.20
C9-OLEFINS	0.00	0.00	0.30	0.06	0.12	0.13	0.03	0.10
N-NONANE	0.00	0.00	0.25	0.06	0.09	0.09	0.04	0.08
ACETONE	0.20	0.08	0.29	0.22	0.28	0.26	0.33	0.36
I-PROPYANOL	0.25	0.05	0.24	0.28	0.25	0.34	0.38	0.38
N-BUTANONE	0.26	0.00	0.37	0.29	0.30	0.31	0.34	0.39
UNKNOWN LITE HYDRO-CARB LIQ (2)	18.65	20.13	19.45	18.53	18.30	18.67	21.67	19.07
UNKNOWN HVY HYDRO-CARB LIQ (3)	30.86	26.93	30.22	29.11	30.01	28.62	22.89	24.95
SLURRY REACTOR-WAX	9.00	8.91	8.68	8.62	8.54	8.46	8.45	8.84

(1) Based on Inter-Reactor Sample

(2) Collected in Ambient and Chilled Condensers

(3) Collected in Hot Condenser

Table D-3 (cont'd)
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-3)

M.B.No. Days On Stream	(1) 3-31 32.5	(1) 3-32 33.5	(1) 3-33 34.5	(1) 3-34 35.5	(1) 3-35 36.5	(1) 3-36 37.5	(1) 3-37 38.5	(1) 3-38 39.5	(1) 3-39 40.5	(1) 3-40 41.5
METHANE	7.63	7.40	7.57	7.42	7.15	7.08	6.64	6.87	7.57	7.83
ETHENE	1.52	1.38	1.39	1.27	1.33	1.38	1.25	1.35	1.44	1.53
ETHANE	2.97	2.86	2.91	2.74	2.71	2.70	2.50	2.61	2.81	2.92
PROPENE	8.01	7.70	7.92	7.77	7.47	7.53	7.02	7.21	7.95	8.23
PROPANE	2.02	1.93	1.99	1.74	1.86	1.87	1.74	1.86	1.93	2.04
I-BUTANE	0.07	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.07	0.07
1-BUTENE+2-METHYLPROPENE	6.04	5.78	5.92	5.64	5.62	5.75	5.42	5.54	6.02	6.29
N-BUTANE	2.01	1.94	1.99	1.92	1.90	1.93	1.83	1.85	2.04	2.12
TRANS-2-BUTENE	0.12	0.12	0.13	0.13	0.12	0.12	0.11	0.11	0.12	0.12
CIS-2-BUTENE	0.20	0.20	0.21	0.22	0.19	0.20	0.22	0.18	0.20	0.22
3-METHYL-1-BUTENE	0.23	0.21	0.22	0.20	0.20	0.21	0.20	0.20	0.21	0.22
I-PENTANE	0.15	0.14	0.14	0.14	0.13	0.14	0.13	0.13	0.14	0.15
1-PENTENE	4.58	4.31	4.48	4.19	4.18	4.48	4.37	4.29	4.70	4.88
2-METHYL-1-BUTENE	0.11	0.10	0.11	0.10	0.10	0.12	0.10	0.09	0.12	0.11
N-PENTANE	1.53	1.46	1.52	1.44	1.41	1.53	1.49	1.45	1.60	1.64
TRANS-2-PENTENE	0.10	0.10	0.10	0.10	0.10	0.10	0.09	0.09	0.10	0.10
CIS-2-PENTENE	0.11	0.11	0.12	0.11	0.11	0.11	0.11	0.10	0.11	0.11
2-METHYL-2-BUTENE	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
HEXENES + ISO-HEXANES	0.22	0.19	0.20	0.18	0.17	0.22	0.25	0.21	0.23	0.25
1-HEXENE	2.87	2.62	2.76	2.46	2.48	2.87	3.04	2.78	3.04	3.18
N-HEXANE	1.02	0.96	1.01	0.91	0.91	1.05	1.11	1.01	1.11	1.15
HEPTENES + ISO-HEPTANES	0.46	0.39	0.41	0.35	0.33	0.47	0.51	0.42	0.45	0.50
1-HEPTENE	1.44	1.19	1.22	1.03	1.05	1.44	1.57	1.35	1.41	1.68
N-HEPTANE	0.59	0.50	0.51	0.45	0.44	0.60	0.65	0.55	0.58	0.69
C8-OLEFINS + ISO-P	0.33	0.23	0.24	0.14	0.11	0.32	0.33	0.24	0.26	0.38
1-OCTENE	0.63	0.45	0.39	0.31	0.30	0.60	0.67	0.53	0.58	0.66
N-OCTANE	0.35	0.26	0.22	0.16	0.17	0.34	0.36	0.29	0.33	0.37
C9-OLEFINS + ISO-P	0.32	0.24	0.18	0.11	0.04	0.30	0.40	0.27	0.26	0.48
C9-OLEFINS	0.26	0.20	0.11	0.08	0.07	0.28	0.25	0.21	0.23	0.31
N-NONANE	0.19	0.16	0.09	0.06	0.05	0.21	0.19	0.16	0.17	0.23
N-DECANE	0.13	0.10	0.05	0.00	0.02	0.11	0.13	0.11	0.10	0.15
N-DECENES	0.11	0.10	0.04	0.00	0.02	0.11	0.13	0.10	0.10	0.14
ACETONE	0.31	0.30	0.29	0.24	0.21	0.32	0.42	0.31	0.33	0.37
I-PROPANOL	0.35	0.39	0.38	0.35	0.33	0.37	0.39	0.33	0.40	0.40
N-BUTANONE	0.38	0.29	0.32	0.25	0.25	0.35	0.42	0.33	0.34	0.41
UNKNOWN LITE HYDRO-CARB LIQ (2)	18.12	18.25	18.05	19.78	18.70	18.32	19.20	21.31	18.13	22.96
UNKNOWN HVY HYDRO-CARB LIQ (3)	26.21	27.33	28.76	30.27	32.07	28.94	29.37	28.29	27.87	20.27
SLURRY REACTOR-WAX	8.30	8.99	7.97	7.66	7.63	7.47	7.31	7.22	6.96	6.84

(1) Based on Inter-Reactor Sample

(2) Collected in Ambient and Chilled Condensers

(3) Collected in Hot Condenser

Table D-3 (cont'd)
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-3)

M.B.No. Days On Stream	(1) 3-41 42.5	(1) 3-42 43.5	(1) 3-43 44.5	(1) 3-44 45.5	(1) 3-46 48.5	(1) 3-47 49.5	(1) 3-48 50.5	(1) 3-49 51.5	(1) 3-50 52.5	(1) 3-53 57.5
METHANE	7.36	8.10	6.94	7.67	7.59	7.86	7.99	8.20	7.97	8.21
ETHENE	1.39	1.57	1.35	1.50	1.40	1.49	1.52	1.53	1.51	1.62
ETHANE	2.76	3.10	2.64	2.85	2.85	2.95	3.21	3.33	3.11	3.43
PROPENE	7.62	8.40	7.17	7.87	7.84	8.18	8.13	8.41	8.17	8.69
PROPANE	1.87	2.15	1.82	1.96	1.88	1.88	2.22	2.27	1.93	2.28
I-BUTANE	0.07	0.07	0.06	0.07	0.07	0.07	0.07	0.07	0.07	0.08
1-BUTENE+2-METHYLPROPENE	5.81	6.46	5.46	5.97	5.56	5.72	5.87	6.02	5.62	6.44
N-BUTANE	1.98	2.21	1.84	2.01	1.85	1.92	1.95	2.00	1.91	2.13
TRANS-2-BUTENE	0.12	0.13	0.11	0.11	0.12	0.12	0.13	0.14	0.14	0.16
CIS-2-BUTENE	0.20	0.24	0.17	0.21	0.19	0.20	0.21	0.23	0.23	0.26
3-METHYL-1-BUTENE	0.21	0.23	0.19	0.21	0.20	0.00	0.21	0.23	0.22	0.28
I-PENTANE	0.13	0.14	0.13	0.14	0.37	0.20	0.19	0.22	0.15	0.16
1-PENTENE	4.63	5.04	4.19	4.58	0.00	0.17	3.85	3.90	3.71	4.77
2-METHYL-1-BUTENE	0.10	0.11	0.09	0.11	0.00	0.26	0.09	0.09	0.10	0.13
N-PENTANE	1.59	1.75	1.43	1.57	3.58	3.80	1.25	1.29	1.28	1.61
TRANS-2-PENTENE	0.10	0.11	0.09	0.10	0.00	0.00	0.09	0.11	0.11	0.13
CIS-2-PENTENE	0.11	0.12	0.10	0.11	0.00	0.00	0.10	0.11	0.11	0.14
2-METHYL-2-BUTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	4.48	4.70	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.14	0.00
CYCLOPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.05	0.04	0.00
HEXENES + ISO-HEXANES	0.23	0.26	0.19	0.21	0.00	0.00	0.07	0.04	0.03	0.26
ISO-C6-P+0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.03	0.00
1-HEXENE	3.10	3.29	2.67	2.89	0.00	0.00	1.56	1.65	1.55	3.01
N-HEXANE	1.15	1.22	0.98	1.06	0.00	0.00	0.54	0.59	0.58	1.10
HEPTENES + ISO-HEPTANES	0.50	0.55	0.42	0.45	0.00	0.00	0.09	0.15	0.15	0.52
1-HEPTENE	1.57	1.66	1.29	1.41	0.00	0.00	0.32	0.37	0.33	1.39
N-HEPTANE	0.65	0.71	0.54	0.59	0.00	0.00	0.12	0.14	0.14	0.59
C8-OLEFINS + ISO-P	0.34	0.34	0.24	0.28	0.00	0.00	0.01	0.03	0.03	0.26
1-OCTENE	0.69	0.65	0.51	0.56	0.00	0.00	0.04	0.04	0.04	0.43
N-OCTANE	0.39	0.38	0.29	0.31	0.00	0.00	0.02	0.02	0.02	0.25
C9-OLEFINS + ISO-P	0.37	0.43	0.35	0.36	0.00	0.00	0.00	0.00	0.00	0.15
C9-OLEFINS	0.32	0.24	0.20	0.22	0.00	0.00	0.00	0.00	0.00	0.00
N-NONANE	0.24	0.19	0.15	0.17	0.00	0.00	0.00	0.00	0.00	0.00
N-DECANE	0.16	0.10	0.10	0.10	0.00	0.00	0.00	0.00	0.00	0.11
N-DECENES	0.16	0.11	0.10	0.11	0.00	0.00	0.00	0.00	0.00	0.08
ACETONE	0.35	0.42	0.30	0.34	0.03	0.00	0.16	0.17	0.13	0.28
I-PROPANOL	0.37	0.35	0.29	0.36	0.00	0.00	0.00	0.00	0.00	0.33
N-BUTANONE	0.38	0.43	0.33	0.36	0.00	0.00	0.00	0.00	0.00	0.40
UNKNOWN LITE HYDRO-CARB LIQ (2)	17.81	18.87	21.48	17.21	33.34	31.02	30.13	28.96	31.90	17.46
UNKNOWN HVY HYDRO-CARB LIQ (3)	28.36	23.13	29.10	29.39	22.23	23.29	23.73	23.62	22.75	28.03
SLURRY REACTOR-WAX	6.82	6.72	6.69	6.59	6.42	6.18	5.97	5.85	5.76	4.83

(1) Based on Inter-Reactor Sample

(2) Collected in Ambient and Chilled Condensers

(3) Collected in Hot Condenser

Table D-3 (cont'd)
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-3)

M. B. No. Days On Stream	(1) 3-56 64.5	(1) 3-57 66.5	(1) 3-58 68.5	(1) 3-59 70.5	(1) 3-60 72.5	(1) 3-61 74.5	(1) 3-62 76.5	(1) 3-63 78.5
METHANE	10.77	8.95	8.45	8.46	8.64	7.90	7.76	9.11
ETHENE	2.84	2.51	2.25	2.56	2.37	2.36	2.05	2.37
ETHANE	4.85	3.45	3.51	3.82	3.67	3.47	3.53	4.68
PROPENE	11.40	9.48	9.03	9.58	9.53	8.62	8.71	0.00
PROPANE	2.90	2.32	2.29	2.57	2.57	2.43	2.52	0.00
I-BUTANE	0.14	0.07	0.09	0.13	0.12	0.13	0.12	0.16
1-BUTENE+2-METHYLPROPENE	7.84	6.36	6.43	6.88	6.91	6.22	6.36	8.37
N-BUTANE	2.50	0.51	2.07	2.25	2.31	2.23	2.29	2.67
TRANS-2-BUTENE	0.16	2.11	0.09	0.09	0.10	0.08	0.11	0.29
CIS-2-BUTENE	0.32	0.11	0.16	0.19	0.20	0.18	0.20	0.47
3-METHYL-1-BUTENE	0.50	0.19	0.32	0.44	0.40	0.35	0.34	0.57
I-PENTANE	0.25	0.27	0.17	0.22	0.26	0.20	0.18	0.24
1-PENTENE	5.39	0.33	0.00	4.79	4.86	4.30	4.40	5.98
2-METHYL-1-BUTENE	0.20	4.88	0.00	0.16	0.16	0.14	0.14	0.25
N-PENTANE	1.85	0.13	0.00	1.66	1.71	1.58	1.64	2.09
TRANS-2-PENTENE	0.12	1.52	0.00	0.07	0.07	0.06	0.08	0.21
CIS-2-PENTENE	0.15	0.08	0.00	0.09	0.11	0.08	0.10	0.24
2-METHYL-2-BUTENE	0.00	0.10	0.00	0.00	0.12	0.02	0.02	0.00
HEXENES + ISO-HEXANES	0.46	0.28	0.00	0.38	0.37	0.29	0.33	0.58
1-HEXENE	3.51	2.96	4.36	3.17	3.23	2.68	2.67	3.98
N-HEXANE	1.29	0.96	1.43	1.16	1.19	1.04	1.08	1.55
HEPTENES + ISO-HEPTANES	1.01	0.41	0.83	0.71	0.65	0.52	0.50	1.20
1-HEPTENE	2.07	1.33	2.46	1.79	1.79	1.34	1.34	2.14
N-HEPTANE	0.87	0.48	0.85	0.73	0.74	0.57	0.64	1.02
C8-OLEFINS + ISO-P	0.78	0.21	0.32	0.50	0.47	0.29	0.35	0.70
1-OCTENE	1.08	0.42	0.98	0.80	0.83	0.56	0.59	1.00
N-OCTANE	0.58	0.19	0.37	0.39	0.42	0.28	0.33	0.60
C9-OLEFINS + ISO-P	0.85	0.50	0.11	0.45	0.44	0.29	0.38	0.61
C9-OLEFINS	0.54	0.00	0.28	0.35	0.32	0.21	0.26	0.40
N-NONANE	0.38	0.00	0.13	0.22	0.21	0.13	0.18	0.30
N-DECANE	0.26	0.00	0.07	0.18	0.16	0.10	0.14	0.19
N-DECENES	0.24	0.00	0.04	0.14	0.13	0.08	0.11	0.18
ACETONE	0.82	0.46	0.20	0.67	0.62	0.40	0.27	0.41
I-PROPANOL	0.50	0.00	0.26	0.38	0.44	0.30	0.29	0.52
N-BUTANONE	1.06	0.43	0.00	0.79	0.61	0.50	0.52	0.84
UNKNOWN LITE HYDRO-CARB LIQ (2)	14.23	20.06	23.46	20.21	19.21	22.74	22.99	13.98
UNKNOWN HVY HYDRO-CARB LIQ (3)	14.07	23.79	25.22	18.98	19.49	22.74	20.84	19.87
SLURRY REACTOR-WAX	3.24	4.13	3.76	4.04	4.59	4.59	5.62	12.23

(1) Based on Inter-Reactor Sample

(2) Collected in Ambient and Chilled Condensers

(3) Collected in Hot Condenser

Table D-4
 Composition of Fischer-Tropsch
 Hydrocarbon Phase Oxygenates
 (Run CT-256-3)

M.B.No. Days on Stream Component	3-4	3-48	3-61	3-64
	6.4	50.5	74.5	80.5
Weight % of Hydrocarbon Phase				
METHANOL	0.350	0.650	1.800	1.330
FORMIC ACID	0.033	0.090	0.040	0.120
ETHANOL	1.550	2.310	5.270	4.550
ACETIC ACID	0.140	0.290	0.340	0.510
ACETONE	0.170	0.420	0.540	0.370
PROPANOLS	1.520	2.250	3.940	3.410
PROPANOIC ACIDS	0.058	0.130	0.150	0.280
C4-ESTERS + KETONES	0.210	0.460	0.570	0.500
BUTANOLS	0.910	1.390	2.190	1.970
BUTANOIC ACIDS	0.037	0.081	0.070	0.140
C5-ESTERS + KETONES	0.190	0.360	0.410	0.380
PENTANOLS	0.843	0.842	1.132	0.940
C6-ESTERS + KETONES	0.000	0.000	0.000	0.204
HEXANOLS	0.151	0.334	0.638	0.000
C7-ESTERS + KETONES	0.001	0.001	0.039	0.568
HEPTANOLS	0.427	0.627	1.117	0.025
C8-ESTERS + KETONES	0.133	0.064	0.234	0.681
OCTANOLS	0.583	0.781	1.126	0.416
C9-ESTERS + KETONES	0.356	0.347	0.428	0.669
NONANOLS	0.532	0.667	0.941	1.501
C10-ESTERS + KETONES	0.432	0.447	0.533	0.621
DECANOLS	0.418	0.515	0.747	1.388
C11-ESTERS + KETONES	0.402	0.460	0.517	0.547
C11-ALKANOLS	0.283	0.380	0.558	1.105
C12 PLUS ESTERS + KETONES	1.376	1.781	2.249	2.111
C12 PLUS ALKANOLS	0.503	0.883	1.370	2.765
Total, Wt %	11.608	16.561	26.900	27.100
Yield per HC Produced, g/100g	4.793	8.922	12.293	--

Table D-5
 Composition of Fischer-Tropsch
Aqueous Phase Organic Oxygenates
 (Run CT-256-3)

M.B.No. Days On Stream	3-4 6.4	3-10 12.4	3-25 26.0	3-32 33.5	3-48 50.5
Component	Weight % of Aqueous Phase				
METHANOL	5.01	7.46	7.68	7.16	10.40
ETHANOL	11.49	15.45	14.85	14.26	17.45
ACETIC ACID	0.59	0.39	0.15	0.20	0.10
ACETONE	0.67	1.22	1.50	1.45	2.27
N-PROPANOL	3.07	4.80	5.45	5.27	5.10
I-PROPANOL	0.43	0.87	1.01	1.02	1.28
PROPANOIC ACIDS	0.16	0.15	0.14	0.17	0.10
C4-ESTERS + I-KETONE	0.23	0.21	0.73	0.68	1.09
N-BUTANOL	1.02	2.32	2.34	2.12	1.51
N-2-BUTANOL	0.11	0.09	0.36	0.36	0.31
OTHER BUTANOLS	0.03	0.03	0.02	0.02	0.03
BUTANOIC ACIDS	0.07	0.08	0.15	0.18	0.12
C5-N-METHYL KETONE	0.00	0.00	0.00	0.00	0.00
C5-ESTERS + I-PENTANONE	0.08	0.25	0.40	0.37	0.46
N-1-PENTANOL	0.35	0.72	1.11	0.95	0.45
N-2-PENTANOL	0.00	0.07	0.10	0.10	0.04
OTHER PENTANOLS	0.02	0.06	0.08	0.07	0.05
C6-N-METHYL KETONE	0.03	0.10	0.19	0.18	0.12
N-1-HEXANOL	0.08	0.22	0.41	0.33	0.12
N-1-HEPTANOL	0.00	0.06	0.13	0.11	0.02
N-1-OCTANOL	0.00	0.01	0.03	0.03	0.00
C9+ ALKANOLS	0.03	0.10	0.29	0.21	0.00
Total, Wt %	23.47	34.66	37.12	35.24	41.02
Yield per HC Produced, g/100g	0.84	---	1.34	1.20	1.22

Table D-6
Composition of Fischer-Tropsch Reactor Wax
(Run CT-256-3)

Days On-Stream	6	20.8	23.8	35	42.4	51.5	60.8	68.8	71.7	83.3
Press., MPa	1.48	1.48	1.48	1.48	1.48	1.48	1.82	1.48	2.17	2.51
Temp., oC	260	260	260	260	260	262	266	267	267	267
Carbon No.										
13-20	5.39	10.79	10.34	9.20	12.23	11.06	10.51	8.51	9.92	9.54
21-25	18.14	22.27	21.22	18.47	23.01	19.86	17.80	13.69	14.73	18.27
26-30	25.25	29.23	27.92	27.95	25.42	26.08	28.10	26.75	24.72	25.61
31-35	22.84	20.19	21.90	21.81	18.63	20.79	22.44	25.24	23.87	21.18
36-40	12.45	8.86	11.21	12.43	10.31	11.98	13.20	14.26	14.74	13.33
41-45	8.14	3.43	4.86	5.43	4.86	4.96	5.09	7.45	7.36	7.35
46-50	4.15	2.41	1.82	2.45	2.83	2.70	2.11	3.60	3.99	3.72
51-55	1.50	2.01	0.73	1.06	1.69	1.59	0.76	0.50	0.66	1.00
56-60	0.79	0.81	0.00	0.60	1.01	0.97	0.00	0.00	0.00	0.00
61-67	1.36	0.00	0.00	0.61	0.00	0.00	0.00	0.00	0.00	0.00
Mol Avg C-No.	30.0	27.4	27.6	28.3	27.3	27.8	27.8	29.1	28.7	28.4
Peak C-No.	35	27	28	28	26	28	28	30	31	30

Table D-7
Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
(Run CT-256-3)

(Nitrogen-Free Basis)										
M.B. No.	3- 7	3- 8	3- 9	3- 10	3- 11	3- 13	3- 19	3- 20	3- 21	
Days On-stream	9.3	10.3	11.3	12.4	13.4	15.4	20.0	21.0	22.0	
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.682	0.680	0.678	0.681	0.680	0.683	0.688	0.689	0.683	
Temperature, °C	260	259	260	260	260	260	259	259	260	
Pressure, MPa	1.480	1.480	1.480	1.480	1.480	1.480	1.480	1.480	1.480	
Feed Sup. Vel., cm/s	3.884	3.922	3.949	3.970	3.978	3.987	3.826	3.801	3.807	
Space Vel., NL/gFe-hr	2.535	2.580	2.591	2.632	2.622	2.620	2.514	2.498	2.502	
N ₂ in Feed, Mol %	5.7	6.3	6.5	5.5	6.0	6.3	6.4	6.4	6.3	
Second-Stage Conditions:										
Temp., Inlet, °C	332	316	302	329	329	388	347	332	315	
Outlet, °C	378	357	332	346	349	424	385	379	370	
Pressure, MPa	1.432	1.446	1.446	1.446	1.439	1.439	1.446	1.446	1.446	
GHSV, 1/hr	2882	3131	3151	2788	3187	3214	3091	3087	3069	
Days On-stream	1.3	2.4	3.4	4.4	5.4	7.4	2.2	3.2	4.1	
Conversions, Mol % :										
H ₂	80.89	78.86	79.34	81.42	78.62	79.67	80.83	79.92	80.19	
CO	92.61	91.62	91.29	92.68	91.65	90.53	91.71	91.02	91.42	
H ₂ +CO	87.86	86.46	86.46	88.12	86.38	86.12	87.27	86.49	86.86	
Yields, Wt % of Products :										
Hydrocarbons	21.83	20.53	20.40	23.20	20.22	23.05	22.60	20.42	21.21	
CO ₂	68.97	69.37	69.61	67.19	69.89	66.44	67.73	69.26	68.75	
H ₂ O	0.99	1.34	0.98	1.25	1.18	1.01	1.37	1.34	1.38	
H ₂	0.93	0.96	0.94	0.93	0.97	0.91	0.85	0.90	0.88	
CO	7.28	7.80	8.07	7.43	7.74	8.59	7.45	8.08	7.77	
Total	100	100	100	100	100	100	100	100	100	
Bal Recovery, Wt % of Charge:										
gHC/Nm ³ (H ₂ +CO) conv.:	187	189	189	193	188	219	213	194	200	
(H/C) Atomic Ratio in HC :	2.19	2.25	2.24	2.20	2.24	2.20	2.26	2.27	2.27	
Selectivities, Wt % of HC :										
Methane	6.57	6.98	7.17	5.63	7.39	6.28	7.41	7.83	7.46	
Ethene	0.75	0.82	1.06	2.12	1.45	1.14	0.55	0.53	0.55	
Ethane	3.07	3.18	3.16	2.62	3.29	2.86	3.07	3.34	3.11	
Propene	2.89	3.46	3.52	2.77	4.71	4.31	1.54	1.76	1.98	
Propane	5.78	4.60	3.78	1.92	3.68	7.36	9.03	8.55	7.04	
Butenes	4.63	7.24	8.79	7.49	10.63	5.82	1.96	2.47	3.13	
i-Butane	6.70	5.13	3.23	0.24	2.74	6.77	10.63	10.12	8.96	
n-Butane	5.60	5.29	4.17	2.03	3.74	5.79	8.20	7.83	7.37	
C ₅ - C ₁₁	52.65	49.81	48.32	51.55	49.40	48.35	45.64	45.94	49.28	
C ₁₂₊ (Excl. Rx.-Wax)	0.93	3.06	6.47	13.27	3.10	1.72	2.71	2.56	2.12	
Slurry Rx.-Wax	10.43	10.43	10.26	10.20	9.88	9.60	9.26	9.08	9.00	
Total	100	100	100	100	100	100	100	100	100	
i-C ₄ /(C ₃ = + C ₄ =) Molar :	0.76	0.42	0.23	0.02	0.16	0.57	2.56	2.03	1.50	
(C ₃ /C ₃ =) Molar Ratio :	1.91	1.27	1.02	0.66	0.75	1.63	5.60	4.64	3.39	
Alkylate, Wt % of HC :	12.70	10.09	6.34	0.48	5.38	13.13	7.66	9.22	11.09	
Cat-Poly, Wt % of HC :	1.51	5.74	9.19	10.02	12.70	3.76	0.00	0.00	0.00	
C ₅ - C ₁₁ PONA, Wt % :										
Paraffins	(1)	46.36	41.70	35.52	35.06	39.41	48.68	47.13	52.97	
Olefins	(1)	32.59	44.95	62.42	52.73	20.73	6.61	7.41	10.04	
Naphthenes	(1)	3.82	1.78	0.21	1.66	8.28	7.14	7.44	6.00	
Aromatics	(1)	17.23	11.58	1.85	10.54	31.58	37.57	38.02	31.00	

(1) Not Available

Table D-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
 Operating Conditions and Material Balances
 (Run CT-256-3)

(Nitrogen-Free Basis)										
M.B. No.	3- 22	3- 23	3- 24	3- 25	3- 26	3- 27	3- 28	3- 29	3- 30	
Days On-stream	23.0	24.0	25.0	26.0	27.0	28.0	29.0	30.5	31.5	
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.685	0.687	0.685	0.689	0.685	0.692	0.694	0.665	0.686	
Temperature, oC	260	259	260	260	260	261	261	261	260	
Pressure, MPa	1.480	1.487	1.480	1.480	1.480	1.480	1.480	1.480	1.487	
Feed Sup. Vel., cm/s	3.820	3.809	3.816	3.803	3.796	3.679	3.662	3.594	3.614	
Space Vel., NL/gFe-hr	2.507	2.516	2.497	2.489	2.497	2.409	2.388	2.343	2.373	
N ₂ in Feed, Mol %	6.4	6.3	6.6	6.6	6.2	6.4	6.8	6.9	6.8	
Second-Stage Conditions:										
Temp., Inlet, oC	306	308	312	314	321	329	334	347	352	
Outlet, oC	356	353	356	358	366	373	379	395	398	
Pressure, MPa	1.446	1.446	1.446	1.411	1.411	1.411	1.398	1.460	1.467	
GHSV, 1/hr	3101	3038	3084	3099	2956	2804	2970	3245	3102	
Days On-stream	5.1	6.2	7.2	8.2	9.2	10.2	11.2	12.6	13.6	
Conversions, Mol % :										
H ₂	79.59	79.91	78.79	79.13	79.42	80.76	79.86	72.85	76.76	
CO	90.06	90.89	90.37	89.57	89.77	91.37	90.66	80.89	87.01	
H ₂ +CO	85.80	86.42	85.66	85.31	85.56	87.04	86.24	77.68	82.85	
Yields, Wt % of Products :										
Hydrocarbons	20.95	21.59	19.98	20.29	19.79	22.26	22.65	21.78	21.71	
CO ₂	67.90	68.09	69.03	67.32	67.97	67.37	66.92	58.94	64.47	
H ₂ O	1.27	1.02	1.17	1.99	1.30	1.13	1.15	1.01	1.13	
H ₂	0.91	0.92	0.96	0.94	0.99	0.92	0.90	1.16	1.03	
CO	8.97	8.39	8.86	9.46	9.96	8.31	8.37	17.10	11.66	
Total	100	100	100	100	100	100	100	100	100	
Bal Recovery, Wt % of Charge:	105.58	103.43	103.52	104.97	97.77	98.77	106.20	106.56	106.09	
gHC/Nm ³ (H ₂ +CO) conv.:	200	200	187	193	176	195	216	235	216	
(H/C) Atomic Ratio in HC :	2.25	2.27	2.27	2.27	2.26	2.25	2.25	2.27	2.27	
Selectivities, Wt % of HC :										
Methane	6.77	7.27	8.19	7.37	8.00	7.33	7.21	7.73	7.93	
Ethene	0.95	0.60	0.74	0.71	0.86	0.81	0.81	0.94	0.93	
Ethane	2.99	2.97	3.27	3.17	3.29	3.01	3.00	3.05	3.30	
Propene	1.96	2.53	3.09	3.13	3.57	3.28	3.30	3.43	3.33	
Propane	5.60	4.92	4.93	5.01	5.29	5.27	5.72	6.64	7.62	
Butenes	4.43	5.55	6.09	6.94	6.66	5.60	5.40	4.98	4.51	
i-Butane	6.74	5.95	5.76	5.85	6.07	6.75	7.28	8.36	8.84	
n-Butane	6.28	5.81	5.54	5.65	5.43	5.79	6.07	6.59	6.94	
C ₅ - C ₁₁	52.88	53.46	51.26	50.92	49.56	51.03	50.33	48.37	45.93	
C ₁₂₊ (Excl. Rx.-Wax)	2.47	2.27	2.50	2.71	2.81	2.81	2.41	1.46	1.83	
Slurry Rx.-Wax	8.91	8.68	8.62	8.54	8.47	8.32	8.46	8.45	8.84	
Total	100	100	100	100	100	100	100	100	100	
i-C ₄ /(C ₃ = + C ₄ =) Molar :	0.92	0.64	0.54	0.51	0.51	0.65	0.72	0.84	0.95	
(C ₃ /C ₃ =) Molar Ratio :	2.73	1.85	1.52	1.53	1.42	1.53	1.66	1.84	2.18	
Alkylate, Wt % of HC :	12.72	11.64	11.33	11.50	11.94	13.05	13.90	15.65	16.37	
Cat-Poly, Wt % of HC :	0.41	2.39	3.62	4.42	4.36	2.59	2.08	1.12	0.31	
C ₅ - C ₁₁ PONA, Wt % :										
Paraffins	51.09	51.02	45.66	47.36	44.19	46.66	45.96	47.65	45.77	
Olefins	21.46	26.08	28.66	31.83	29.17	24.11	23.88	17.64	15.26	
Naphthenes	4.13	3.44	4.87	4.41	3.86	5.85	5.59	7.75	8.21	
Aromatics	23.32	19.46	20.81	16.39	22.78	23.38	24.57	26.97	30.76	

Table D-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
 Operating Conditions and Material Balances
 (Run CT-256-3)

(Nitrogen-Free Basis)									
M.B. No.	3- 31	3- 32	3- 33	3- 34	3- 35	3- 36	3- 37	3- 38	3- 39
Days On-stream	32.5	33.5	34.5	35.5	36.5	37.5	38.5	39.5	40.5
First-Stage Conditions:									
Charge H ₂ /CO (Molar)	0.679	0.702	0.696	0.695	0.685	0.674	0.695	0.679	0.693
Temperature, °C	260	260	260	259	260	260	259	260	260
Pressure, MPa	1.480	1.480	1.446	1.480	1.494	1.487	1.480	1.494	1.480
Feed Sup. Vel., cm/s	3.489	3.498	3.548	3.480	3.448	3.467	3.479	3.428	3.461
Space Vel., NL/gFe-hr	2.282	2.249	2.224	2.273	2.267	2.245	2.273	2.252	2.259
N ₂ in Feed, Mol %	6.7	7.0	7.2	6.9	7.0	6.8	6.9	5.9	5.6
Second-Stage Conditions:									
Temp., Inlet, °C	361	363	368	373	378	383	373	392	394
Outlet, °C	405	410	412	415	417	418	415	418	419
Pressure, MPa	1.446	1.411	0.101	1.411	1.411	1.377	1.411	1.398	1.377
GHSV, 1/hr	2883	2822	2805	2832	2810	2805	2833	2752	2720
Days On-stream	14.6	15.6	16.6	17.6	18.6	19.6	20.6	21.6	22.6
Conversions, Mol % :									
H ₂	79.45	80.88	81.16	80.74	81.98	80.92	81.33	81.69	81.48
CO	90.12	91.66	91.93	92.26	92.09	91.44	91.57	91.65	91.49
H ₂ +CO	85.81	87.22	87.51	87.54	87.98	87.20	87.37	87.62	87.39
Yields, Wt % of Products :									
Hydrocarbons	22.10	22.73	21.82	23.00	22.98	20.29	22.18	22.29	21.36
CO ₂	66.93	67.52	68.82	67.74	67.85	69.60	67.91	68.11	68.48
H ₂ O	1.14	1.31	1.25	1.43	1.25	1.24	1.48	1.15	1.33
H ₂	0.91	0.88	0.85	0.87	0.80	0.87	0.84	0.82	0.87
CO	8.92	7.56	7.25	6.96	7.12	8.00	7.58	7.63	7.96
Total	100	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:									
gHC/Nm ₃ (H ₂ +CO) conv.:	105.50	104.88	105.86	105.75	105.80	101.97	105.85	104.25	101.77
(H/C) Atomic Ratio in HC :	212	210	204	215	215	185	208	207	192
Selectivities, Wt % of HC :	2.27	2.27	2.27	2.27	2.26	2.28	2.25	2.25	2.28
Methane	7.91	7.68	8.08	7.69	7.43	8.44	7.54	7.30	7.87
Ethene	0.97	1.01	1.10	1.06	1.15	1.39	1.24	1.29	1.43
Ethane	3.34	3.31	3.45	3.25	3.21	3.62	3.21	3.15	3.35
Propene	3.32	3.35	3.59	3.90	3.91	4.62	4.31	4.46	5.10
Propane	8.39	8.89	9.46	9.03	9.08	10.23	9.08	9.02	9.40
Butenes	4.23	4.04	4.22	4.37	4.53	5.01	5.06	5.27	5.86
i-Butane	9.32	9.45	9.53	9.26	9.02	9.63	8.87	8.73	8.89
n-Butane	7.35	7.58	7.59	7.61	7.46	7.73	7.38	7.41	7.59
C ₅ - C ₁₁	44.89	45.11	44.25	44.46	44.79	39.91	44.15	45.23	42.99
C ₁₂₊ (Excl. Rx.-Wax)	1.99	0.59	0.75	1.70	1.77	1.94	1.84	0.94	0.57
Slurry Rx.-Wax	8.30	8.99	7.97	7.66	7.63	7.47	7.31	7.22	6.96
Total	100	100	100	100	100	100	100	100	100
i-C ₄ / (C ₃ = + C ₄ =) Molar :	1.04	1.07	1.02	0.93	0.89	0.83	0.79	0.75	0.68
(C ₃ =/C ₃ =) Molar Ratio :	2.41	2.53	2.52	2.21	2.21	2.11	2.01	1.93	1.76
Alkylate, Wt % of HC :	16.51	16.19	17.14	17.05	16.69	17.85	16.57	16.37	16.79
Cat-Poly, Wt % of HC :	0.00	0.00	0.00	0.48	0.78	1.41	1.68	2.09	3.06
C ₅ - C ₁₁ PONA, Wt % :									
Paraffins	44.82	44.13	42.46	44.93	43.90	40.50	42.46	42.89	43.15
Olefins	14.23	12.99	12.49	13.11	13.10	11.71	14.27	16.38	15.98
Naphthenes	8.55	8.76	9.27	9.15	8.86	8.68	8.35	7.63	8.60
Aromatics	32.40	34.12	35.79	32.80	34.14	39.12	34.92	33.10	32.28

Table D-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
 (Run CT-256-3)

(Nitrogen-Free Basis)										
M.B. No.	3- 51	3- 52	3- 53	3- 54	3- 55	3- 56	3- 57	3- 58	3- 59	
Days On-stream	53.5	55.5	57.5	59.5	62.5	64.5	66.5	68.5	70.5	
First-Stage Conditions:										
Charge H ₂ /CO (Molar)	0.687	0.686	0.675	0.687	0.675	0.691	0.693	0.601	0.601	
Temperature, °C	262	263	264	264	264	266	265	265	266	
Pressure, MPa	1.508	1.515	1.480	1.508	1.591	1.577	1.535	1.825	2.170	
Feed Sup. Vel., cm/s	3.163	3.186	3.247	3.171	2.917	2.919	2.773	2.605	2.564	
Space Vel., NL/gFe-hr	2.101	2.094	2.095	2.083	2.067	2.036	1.923	2.186	2.587	
N ₂ in feed, Mol %	6.6	7.8	7.8	7.8	8.7	9.1	7.3	5.6	4.4	
Second-Stage Conditions:										
Temp., Inlet, °C	317	303	304	313	327	337	344	354	361	
Outlet, °C	362	357	353	361	381	392	395	402	412	
Pressure, MPa	1.322	1.322	1.301	1.294	1.308	1.308	1.342	1.646	2.032	
GHSV, 1/hr	2636	2659	2646	2604	2907	2775	2387	2719	3068	
Days On-stream	0.6	2.6	4.6	6.6	9.7	11.7	13.7	15.7	17.7	
Conversions, Mol % :										
H ₂	79.29	79.62	79.95	80.04	72.38	76.09	84.21	82.97	81.86	
CO	88.86	89.44	89.58	89.87	76.28	81.49	81.00	82.43	80.49	
H ₂ +CO	84.96	85.45	85.70	85.87	74.70	79.29	82.31	82.63	81.01	
Yields, Wt % of Products :										
Hydrocarbons	22.58	20.57	21.88	20.29	19.75	22.02	20.02	19.55	20.70	
CO ₂	64.88	67.46	66.50	67.90	55.56	59.04	61.14	62.71	59.08	
H ₂ O	1.63	1.32	1.16	1.42	1.64	1.41	0.90	1.10	1.13	
H ₂	0.92	0.93	0.90	0.92	1.24	1.06	0.72	0.67	0.74	
CO	9.99	9.72	9.56	9.47	21.82	16.48	17.23	15.97	18.35	
Total	100	100	100	100	100	100	100	100	100	
Bal Recovery, Wt % of Charge:	106.25	103.42	103.87	101.81	103.61	106.94	104.97	105.42	101.85	
gHC/Nm ₃ (H ₂ +CO) conv.:	219	193	207	187	214	230	197	203	211	
(H/C) Atomic Ratio in HC :	2.28	2.30	2.29	2.25	2.33	2.29	2.29	2.28	2.26	
Selectivities, Wt % of HC :										
Methane	7.27	9.51	8.71	9.63	10.98	9.99	9.66	9.46	8.39	
Ethene	0.96	0.51	0.56	0.78	1.05	0.96	1.04	0.92	0.91	
Ethane	3.27	3.81	3.61	4.04	4.76	4.59	3.83	4.17	3.97	
Propene	0.87	2.08	2.28	3.07	3.78	3.29	3.58	2.99	3.24	
Propane	8.54	6.81	5.57	5.91	6.29	6.65	7.72	8.71	8.41	
Butenes	1.37	3.23	4.45	5.22	5.52	4.68	4.62	4.17	4.20	
i-Butane	10.64	8.51	6.86	7.22	7.54	7.81	8.95	9.01	8.61	
n-Butane	8.35	7.19	6.24	6.20	5.96	6.23	6.99	7.14	7.17	
C ₅ - C ₁₁	49.34	50.24	54.70	51.00	49.98	50.65	47.48	48.78	49.05	
C ₁₂₊ (Excl. Rx.-Wax)	3.83	2.94	2.19	2.41	1.73	1.91	2.00	0.88	2.01	
Slurry Rx.-Wax	5.56	5.17	4.83	4.52	2.41	3.24	4.13	3.76	4.04	
Total	100	100	100	100	100	100	100	100	100	
i-C ₄ /(C ₃ = + C ₄ =) Molar :	4.07	1.37	0.88	0.75	0.69	0.83	0.92	1.07	0.98	
(C ₃ /C ₃ =) Molar Ratio :	9.42	3.12	2.33	1.83	1.59	1.93	2.06	2.78	2.48	
Alkylate, Wt % of HC :	4.85	11.53	12.94	13.74	14.38	14.64	16.58	15.60	15.90	
Cat-Poly, Wt % of HC :	0.00	0.00	0.65	1.76	2.46	1.14	0.57	0.00	0.15	
C ₅ - C ₁₁ PONA, Wt % :										
Paraffins	49.96	49.38	50.78	39.93	44.67	43.11	43.71	42.84	40.40	
Olefins	8.70	12.78	20.57	17.26	22.21	18.02	16.36	13.34	17.85	
Naphthenes	8.13	6.44	5.55	6.79	6.70	7.86	7.97	7.97	7.50	
Aromatics	33.22	31.40	23.10	36.02	26.42	31.02	31.96	35.86	34.25	

Table D-7 (cont'd)
 Second-Stage Fixed-Bed ZSM-5 Reactor
Operating Conditions and Material Balances
 (Run CT-256-3)

(Nitrogen-Free Basis)					
M.B. No.	3- 60	3- 61	3- 62	3- 63	3- 64
Days On-stream	72.5	74.5	76.5	78.5	80.5
First-Stage Conditions:					
Charge H ₂ /CO (Molar)	0.607	0.596	0.600	0.634	0.603
Temperature, oC	265	266	266	264	265
Pressure, MPa	2.170	2.515	2.515	2.515	2.515
Feed Sup. Vel., cm/s	2.593	2.537	2.207	1.365	2.548
Space Vel., NL/gFe-hr	2.616	3.014	2.612	1.602	3.028
N ₂ in Feed, Mol %	4.5	2.9	3.3	4.4	2.9
Second-Stage Conditions:					
Temp., Inlet, oC	370	377	392	399	408
Outlet, oC	418	424	439	442	442
Pressure, MPa	2.032	2.390	2.384	2.370	2.515
GHSV, 1/hr	3218	3681	2760	1677	3666
Days On-stream	19.7	21.7	23.7	25.7	27.7
Conversions, Mol % :					
H ₂	80.31	78.81	88.78	91.32	75.46
CO	79.25	76.52	87.42	90.48	76.79
H ₂ +CO	79.65	77.37	87.93	90.81	76.29
Yields, Wt % of Products :					
Hydrocarbons	19.01	18.31	19.94	21.41	16.60
CO ₂	59.69	58.02	66.50	68.38	58.16
H ₂ O	1.28	1.08	0.92	0.90	1.51
H ₂	0.80	0.84	0.47	0.37	1.04
CO	19.22	21.74	12.17	8.94	22.68
Total	100	100	100	100	100
Bal Recovery, Wt % of Charge:					
gHC/Nm ³ (H ₂ +CO) conv.:	103.38	103.49	99.05	101.80	98.00
200	199	183	192	173	
(H/C) Atomic Ratio in HC :					
Selectivities, Wt % of HC :	2.27	2.26	2.26	2.27	2.22
Methane	9.14	8.81	8.51	7.70	7.71
Ethene	1.16	1.27	1.26	1.29	2.77
Ethane	4.31	4.10	4.29	4.08	3.25
Propene	3.92	4.45	4.01	4.17	9.46
Propane	9.11	8.86	10.22	9.60	7.44
Butenes	4.70	5.39	4.70	4.59	11.72
i-Butane	8.56	8.11	8.11	7.34	4.94
n-Butane	7.15	7.05	7.28	6.85	4.61
C ₅ - C ₁₁	45.30	45.12	43.36	32.48	40.36
C ₁₂₊ (Excl. Rx.-Wax)	2.05	2.26	2.64	9.37	1.41
Slurry Rx.-Wax	4.59	4.59	5.62	12.23	6.31
Total	100	100	100	100	100
i-C ₄ /(C ₃ = + C ₄ =) Molar :	0.83	0.69	0.78	0.70	0.20
(C ₃ /C ₃ =) Molar Ratio :	2.22	1.90	2.43	2.20	0.75
Alkylate, Wt % of HC :	15.94	15.33	15.15	13.81	9.71
Cat-Poly, Wt % of HC :	1.25	2.62	1.67	2.29	16.42
C ₅ - C ₁₁ PONA, Wt % :					
Paraffins	39.06	38.62	37.95	39.77	32.14
Olefins	14.31	16.53	15.10	12.19	32.04
Naphthenes	7.98	7.49	7.62	7.49	5.87
Aromatics	38.65	37.36	39.33	40.55	29.95

Table D-8

**Second-Stage ZSM-5 Reactor
Raw Gasoline (1) Properties**

(Run CT-256-3)

M. B. No.	7	8	9	11	19	20	21	22	26	32	53	54	57	58	59	60	64
DOS	9.3	10.3	11.3	13.4	20	21	22	23	27	33.5	57.5	59.5	66.5	68.5	70.5	72.5	80.5
Second-Stage Severity:																	
i-C ₄ /C ₃ ⁼ + C ₄ ⁼	0.76	0.42	0.23	0.16	2.56	2.03	1.5	0.92	0.51	1.07	0.88	0.75	0.92	1.07	0.98	0.83	0.20
C ₃ /C ₃ ⁼	1.91	1.27	1.02	0.75	5.61	4.64	3.39	2.72	1.42	2.53	2.33	1.83	2.06	2.77	2.48	2.32	0.75
Sp. Gr.	.768	.757	.744	.729	.726	.769	.771	.763	.759	.782	.767	.765	.784	.781	.770	.769	.702
Acid No. (Unwashed) mg KOH/mg	0.15	0.15	0.15	-	-	-	-	-	-	0.04	0.15	0.4	0.1	0.04	0.05	0.13	0.11
PONA, Wt %:																	
Paraffins	-	33.2	27.5	24.4	30.4	34.9	34.9	36.8	32.5	27.6	33.2	25.9	29.1	-	28.6	30.2	22.4
Olefins	-	32.3	43.8	50.2	4.6	7.8	10.3	21.5	28.0	11.9	21.2	16.8	14.1	-	18.1	13.9	32.0
Naphthenes	-	11.6	12.8	10.9	10.2	11.0	11.4	11.7	11.0	12.2	13.1	12.2	11.8	-	10.1	10.8	6.8
Aromatics	-	22.9	15.9	14.5	54.8	46.3	43.4	30.0	28.5	48.3	32.5	45.1	45.0	-	43.2	45.1	35.8
Octane Numbers:																	
R+0	90.5	89.3	85.4	85.1	89.6	92.0	89.3	86.9	87.4	93.9	87.6	87.9	94.0	92.3	92.7	92.0	91.1
M+0	80.8	80.1	75.6	83.4	83.4	82.8	80.4	78.4	79.0	83.5	79.7	79.5	81.8	82.5	82.7	82.8	80.7
ASTM Distillation, °C:																	
IBP	36	35	39	33	36	32	37	39	35	36	39	37	42	37	31	33	32
50 Vol %	128	122	126	120	130	125	128	127	128	130	130	128	133	128	124	123	123
90 Vol %	184	182	187	189	192	184	185	184	187	189	186	185	184	184	185	183	183
95 Vol %	218	214	231	232	245	238	224	212	232	236	218	219	222	220	237	236	238
EP	240	239	250	247	263	251	253	245	248	255	246	242	249	243	241	238	238
Residue, Vol %	3	3	1.1	1.1	0.9	0.7	1.2	1.1	1.0	1.3	1.4	1.3	0.9	1.0	0.9	1.0	1.0
Loss, Wt %	0	0	0	1.9	2.6	2.3	1.8	0.9	2.0	1.7	1.1	1.2	1.1	2.0	3.1	2.5	3.0

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

Table D-9
Composition of Hydrocarbon Products from
Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
(Run CT-256-3)

M.B.No. Days On Stream	3-7 9.3	3-8 10.3	3-9 11.3	3-10 12.4	3-11 13.4	3-13 15.4	3-19 20.0
METHANE	6.57	6.98	7.17	5.63	7.39	6.28	7.41
ETHENE	0.75	0.82	1.06	2.12	1.45	1.14	0.55
ETHANE	3.07	3.18	3.16	2.62	3.29	2.86	3.07
PROPENE	2.89	3.46	3.52	2.77	4.71	4.31	1.54
PROPANE	5.78	4.60	3.78	1.92	3.68	7.36	9.03
I-BUTANE	6.70	5.13	3.23	0.24	2.74	6.77	10.63
I-BUTENE+2-METHYLPROPENE	2.83	4.41	5.38	3.67	6.48	3.46	1.18
N-BUTANE	5.60	5.29	4.17	2.03	3.74	5.79	8.20
TRANS-2-BUTENE	1.07	1.68	2.04	2.32	2.48	1.38	0.46
CIS-2-BUTENE	0.73	1.15	1.37	1.49	1.67	0.97	0.32
3-METHYL-1-BUTENE	0.08	0.16	0.22	0.20	0.27	0.11	0.03
I-PENTANE	4.68	4.82	3.01	0.40	2.34	4.75	7.50
1-PENTENE	0.10	0.20	0.27	0.27	0.33	0.16	0.04
2-METHYL-1-BUTENE	0.00	1.18	1.74	1.83	2.10	0.78	0.22
N-PENTANE	3.20	4.12	3.36	1.88	2.88	3.47	4.42
TRANS-2-PENTENE	0.36	0.79	1.13	1.37	1.40	0.57	0.15
CIS-2-PENTENE	0.17	0.39	0.55	0.64	0.68	0.29	0.07
2-METHYL-2-BUTENE	1.32	3.05	4.75	5.72	5.67	1.86	0.54
C5-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2, 2-DIMETHYLBUTANE	0.04	0.04	0.03	0.00	0.03	0.06	0.02
CYCLOPENTANE	0.06	0.08	0.03	0.00	0.12	0.26	0.19
HEXENES + ISO-HEXANES	0.07	0.04	0.26	0.66	0.00	0.06	0.00
2, 3-DIMETHYLBUTANE	0.07	0.11	0.17	0.00	0.21	0.11	0.17
2-METHYLPENTANE	1.66	2.65	1.86	0.42	1.32	1.79	2.72
3-METHYLPENTANE	0.60	0.52	0.63	0.17	0.43	0.85	1.17
HEXENES	0.00	1.53	2.44	4.06	3.05	1.00	0.19
1-HEXENE	0.09	0.56	0.30	0.45	0.26	0.09	0.02
N-HEXANE	1.39	1.40	0.99	1.98	1.08	2.11	1.80
2, 4-DIMETHYLPENTANE	0.00	0.01	0.00	0.00	0.00	0.01	0.01
METHYLCYCLOPENTANE	0.33	0.22	0.07	0.03	0.07	1.17	0.89
3, 3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.00	0.02	0.00	0.00	0.00	0.03	0.02
HEPTENES + ISO-HEPTANES	0.68	0.00	0.00	4.84	0.00	0.68	0.20
2-METHYLHEXANE	0.46	0.79	0.55	0.25	0.43	0.60	0.85
2, 3-DIMETHYLPENTANE	0.03	0.08	0.04	0.01	0.04	0.19	0.18
3-METHYLHEXANE	0.38	0.70	0.46	0.23	0.37	0.58	0.83
1-CIS-3-DIMETHYL-N5	0.10	0.14	0.05	0.00	0.05	0.37	0.29
1-TRANS-3-DIMETHYL-N5	0.00	0.19	0.05	0.01	0.05	0.26	0.20
1-TRANS-2-DIMETHYL-N5	0.10	0.00	0.03	0.00	0.03	0.30	0.25
3-ETHYL-PENTANE	0.55	0.00	0.00	0.00	0.00	0.00	0.00
N-HEPTANE	0.59	1.35	1.27	1.87	1.29	1.33	0.68
C7-OLEFINS	0.00	2.21	3.07	5.11	3.92	1.14	0.24
METHYLCYCLOHEXANE	0.07	0.15	0.07	0.01	0.06	0.19	0.15
C8-OLEFINS + ISO-P	0.75	0.00	0.00	0.95	0.00	0.51	0.49
MONOMETHYL-ISO-C8-P	0.00	1.22	0.96	0.35	0.72	0.48	0.67
OTHER ISO-C8-P	0.00	0.10	0.05	0.01	0.04	0.15	0.12
C8-OLEFINS	0.00	4.20	4.68	4.60	5.46	1.65	0.33
C8-NAPHTHENES (N5+N6)	0.00	0.74	0.30	0.03	0.28	1.11	1.00
N-OCTANE	0.13	1.10	1.24	1.36	1.29	0.71	0.22
C9-OLEFINS + ISO-P	0.70	0.00	0.00	0.11	0.00	0.55	0.36
MONOMETHYL-ISO-C9-P	0.00	0.76	0.68	0.32	0.48	0.27	0.30
OTHER ISO-C9-P	0.00	0.15	0.03	0.02	0.08	0.12	0.13
C9-OLEFINS	0.00	1.97	2.56	2.01	2.92	0.63	0.12
C9-NAPHTHENES (N5+N6)	0.00	0.39	0.25	0.02	0.15	0.31	0.26
N-NONANE	0.00	0.64	0.96	1.08	1.04	0.30	0.05
ISO-C10-P + O + N5 + N6	0.00	2.49	3.60	7.30	3.23	1.11	0.37
BENZENE	0.25	0.31	0.27	0.21	0.33	0.80	0.68
TOLUENE	0.38	0.99	0.42	0.12	0.42	2.89	3.73
ETHYLBENZENE	0.44	0.30	0.11	0.07	0.09	1.10	1.52
P-XYLENE	0.00	0.37	0.13	0.02	0.10	0.85	0.00
M-XYLENE	0.00	1.03	0.51	0.07	0.37	2.10	3.25
O-XYLENE	0.00	0.40	0.46	0.07	0.72	1.02	1.01
ISOPROPYLBENZENE	0.00	0.00	0.00	0.00	0.15	0.00	0.00
N-PROPYLBENZENE	0.00	0.18	0.12	0.04	0.10	0.16	0.11
1-METHYL-3-ETHYL-BENZENE	0.00	1.59	0.87	0.02	0.62	2.20	2.30
1, 3, 5-TRIMETHYL-BENZENE	0.00	0.07	0.16	0.00	0.14	0.08	0.08
1-METHYL-2-ETHYLBENZENE	0.00	0.05	0.00	0.00	0.00	0.13	0.00
ISO-C4-BENZENE	0.00	0.00	0.05	0.00	0.04	0.00	0.20
SEC-C4-BENZENE	0.00	0.00	0.17	0.00	0.20	0.00	0.00
1, 2, 4-TRIMETHYLBENZENE	0.00	0.86	0.47	0.07	0.71	1.52	1.51
1-METHYL-2-ISO-C3-BENZENE	0.00	0.13	0.10	0.00	0.03	0.03	0.07
1, 3-DIETHYLBENZENE	0.00	0.00	0.00	0.00	0.10	0.42	0.07
1-METHYL-3-N-C3-BENZENE	0.00	0.52	0.33	0.00	0.00	0.11	0.41
N-C4-BENZENE	0.00	0.19	0.15	0.00	0.00	0.11	0.00
1, 2, 3-TRIMETHYLBENZENE	0.00	0.02	0.04	0.00	0.01	0.08	0.13
1, 2-DIETHYLBENZENE	0.00	0.00	0.00	0.00	0.06	0.00	0.11
1-METHYL-2-N-C3-BENZENE	0.00	0.02	0.02	0.00	0.03	0.00	0.00
C10-ALKYLBENZENES	0.00	0.70	0.09	0.04	0.29	0.64	0.67
1, 2, 4, 5-TETRAMETHYLBENZENE	0.00	0.05	0.01	0.01	0.03	0.07	0.09
1, 2, 3, 4-TETRAMETHYLBENZENE	0.00	0.00	0.00	0.00	0.00	0.04	0.07
C11-ALKYLBENZENES	0.00	0.80	1.08	0.19	0.65	0.88	1.07
NAPHTHALENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
METHYL-NAPHTHALENES	0.00	0.00	0.00	0.00	0.01	0.00	0.00
METHANOL	0.00	0.00	0.00	0.04	0.00	0.00	0.00
DIMETHYL ETHER	0.00	0.00	0.08	0.00	0.00	0.00	0.00
I-PROPANOL	0.00	0.00	0.00	0.12	0.00	0.00	0.00
UNKNOWN (HC AROMATICS)	0.00	0.00	0.00	0.02	0.00	0.00	0.05
UNKNOWN LITE HYDRO-CARB LIQ (1)	32.81	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN C12+	0.93	3.06	6.47	13.27	3.10	1.72	2.71
SLURRY REACTOR-WAX	10.43	10.43	10.26	10.20	9.88	9.60	9.26

(1) Collected in Chilled and Ambient Condensers

Table D-9 (cont'd)
 Composition of Hydrocarbon Products from
 Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
 (Run CT-256-3)

M.B.No. Days On Stream	3-20	3-21	3-22	3-23	3-24	3-25	3-26	3-27	3-28
	21	22	23	24	25	26	27	28	29
METHANE	7.83	7.46	6.77	7.27	8.20	7.37	8.00	7.33	7.21
ETHENE	0.53	0.55	0.95	0.60	0.74	0.71	0.86	0.81	0.81
ETHANE	3.34	3.11	2.99	2.97	3.27	3.17	3.29	3.01	3.00
PROPENE	1.76	1.98	1.96	2.53	3.09	3.13	3.57	3.28	3.30
PROPANE	8.55	7.04	5.60	4.92	4.93	5.01	5.29	5.27	5.72
I-BUTANE	10.12	8.96	6.74	5.95	5.76	5.85	6.07	6.75	7.28
1-BUTENE+2-METHYLPROPENE	1.50	1.90	2.70	3.37	3.76	4.25	4.09	3.40	3.26
N-BUTANE	7.83	7.37	6.28	5.81	5.54	5.65	5.43	5.79	6.07
TRANS-2-BUTENE	0.58	0.73	1.03	1.29	1.40	1.61	1.53	1.31	1.27
CIS-2-BUTENE	0.39	0.50	0.70	0.88	0.93	1.08	1.03	0.89	0.87
3-METHYL-1-BUTENE	0.03	0.05	0.09	0.12	0.12	0.15	0.13	0.11	0.11
I-PENTANE	6.64	7.00	5.87	5.27	4.34	4.82	4.37	5.39	5.66
1-PENTENE	0.04	0.06	0.11	0.16	0.15	0.18	0.15	0.14	0.14
2-METHYL-1-BUTENE	0.26	0.44	0.71	0.97	0.92	1.13	0.89	0.81	0.78
N-PENTANE	4.12	5.10	4.86	4.71	3.71	4.20	3.45	4.11	4.21
TRANS-2-PENTENE	0.19	0.29	0.47	0.65	0.59	0.74	0.58	0.55	0.53
CIS-2-PENTENE	0.09	0.14	0.23	0.32	0.28	0.37	0.28	0.27	0.26
2-METHYL-2-BUTENE	0.67	1.13	1.87	2.65	2.34	2.95	2.21	2.07	2.00
2, 2-DIMETHYLBUTANE	0.01	0.03	0.03	0.03	0.02	0.03	0.05	0.04	0.04
CYCLOPENTANE	0.14	0.11	0.09	0.08	0.04	0.05	0.04	0.08	0.09
HEXENES + ISO-HEXANES	0.00	0.03	0.08	0.13	0.04	0.04	0.08	0.08	0.03
2, 3-DIMETHYLBUTANE	0.13	0.15	0.09	0.11	0.08	0.10	0.08	0.09	0.15
2-METHYLPENTANE	2.48	3.31	3.18	3.04	2.08	2.54	1.95	2.56	2.55
3-METHYLPENTANE	1.01	1.27	1.11	1.02	0.70	0.88	0.69	0.93	0.95
HEXENES	0.35	0.42	0.89	1.18	1.42	2.07	1.20	0.90	0.80
1-HEXENE	0.02	0.05	0.08	0.15	0.07	0.08	0.06	0.10	0.10
N-HEXANE	1.86	2.76	3.10	3.26	2.27	2.79	2.05	2.59	2.56
2, 4-DIMETHYLPENTANE	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
METHYLCYCLOPENTANE	0.58	0.41	0.26	0.20	0.27	0.27	0.19	0.56	0.62
3, 3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02
HEPTENES + ISO-HEPTANES	0.02	0.00	0.11	0.24	0.37	0.24	0.74	0.66	0.70
2-METHYLHEXANE	0.84	0.82	0.92	0.87	0.99	0.98	0.82	1.00	0.96
2, 3-DIMETHYLPENTANE	0.17	0.13	0.09	0.08	0.08	0.09	0.09	0.12	0.13
3-METHYLHEXANE	0.81	0.76	0.78	0.72	0.80	0.80	0.73	0.85	0.84
1-CIS-3-DIMETHYL-N5	0.27	0.22	0.15	0.12	0.13	0.14	0.17	0.23	0.25
1-TRANS-3-DIMETHYL-N5	0.27	0.21	0.15	0.09	0.13	0.20	0.11	0.18	0.17
1-TRANS-2-DIMETHYL-N5	0.20	0.15	0.10	0.00	0.09	0.00	0.01	0.07	0.21
N-HEPTANE	0.82	0.94	1.31	1.38	1.61	1.55	1.44	1.64	1.58
C7-OLEFINS	0.42	0.58	1.29	1.85	2.01	2.41	1.97	1.34	1.12
METHYLCYCLOHEXANE	0.21	0.19	0.19	0.16	0.16	0.16	0.17	0.22	0.22
C8-OLEFINS + ISO-P	0.00	0.00	0.51	0.00	0.04	0.00	0.12	0.85	0.69
MONOMETHYL-ISO-C8-P	1.01	1.09	1.33	1.29	0.79	1.14	1.11	0.52	0.83
OTHER ISO-C8-P	0.16	0.14	0.11	0.09	0.07	0.10	0.11	0.09	0.12
C8-OLEFINS	1.00	1.07	2.88	3.56	4.18	4.01	3.73	2.63	3.02
C8-NAPHTHENES (N5+N6)	1.32	1.19	0.85	0.84	1.27	0.66	0.83	1.24	0.85
N-OCTANE	0.00	0.52	0.93	1.08	1.17	1.02	1.00	0.92	0.17
C9-OLEFINS + ISO-P	0.00	0.00	0.00	0.00	0.02	0.00	0.37	0.36	0.49
MONOMETHYL-ISO-C9-P	0.48	0.58	0.81	0.81	0.81	0.19	0.66	0.51	0.46
OTHER ISO-C9-P	0.17	0.17	0.16	0.08	0.15	0.12	0.20	0.14	0.16
C9-OLEFINS	0.33	0.73	2.11	2.09	2.18	1.87	2.03	1.51	1.29
C9-NAPHTHENES (N5+N6)	0.41	0.44	0.37	0.34	0.39	0.74	0.37	0.38	0.37
N-NONANE	0.10	0.17	0.07	0.60	0.67	0.55	0.55	0.39	0.36
ISO-C10-P + O + N5 + N6	0.83	1.11	2.17	2.69	3.00	2.18	2.47	1.84	1.37
BENZENE	0.44	0.31	0.41	0.26	0.39	0.40	0.40	0.52	0.51
TOLUENE	2.91	2.24	1.30	0.99	0.97	0.95	1.26	1.61	1.77
ETHYLBENZENE	1.04	0.82	0.51	0.37	0.38	0.30	0.59	0.93	0.92
P-XYLENE	1.05	0.85	0.57	0.44	0.42	0.36	0.55	0.56	0.62
M-XYLENE	2.62	2.15	1.59	1.30	1.33	1.04	1.38	1.47	1.53
o-XYLENE	1.10	0.89	0.66	0.60	0.66	0.50	0.54	0.66	0.69
ISOPROPYLBENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.00
N-PROPYLBENZENE	0.17	0.22	0.26	0.26	0.24	0.18	0.25	0.24	0.22
1-METHYL-3-ETHYL-BENZENE	3.00	2.91	2.53	2.02	2.02	1.53	2.18	2.10	2.22
1, 3, 5-TRIMETHYL-BENZENE	0.07	0.07	0.09	0.13	0.14	0.10	0.11	0.08	0.08
1-METHYL-2-ETHYL-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
ISO-C4-BENZENE	0.04	0.05	0.00	0.06	0.06	0.04	0.04	0.05	0.05
SEC-C4-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00
1, 2, 4-TRIMETHYL-BENZENE	1.72	1.51	1.21	1.02	1.05	0.77	1.05	1.10	1.15
1-METHYL-2-ISO-C3-BENZENE	0.06	0.04	0.05	0.05	0.05	0.02	0.15	0.19	0.17
1, 3-DIETHYL-BENZENE	0.00	0.00	0.00	0.69	0.70	0.50	0.00	0.00	0.00
1-METHYL-3-N-C3-BENZENE	0.57	0.67	0.76	0.24	0.25	0.19	0.66	0.59	0.57
N-C4-BENZENE	0.16	0.18	0.20	0.18	0.18	0.12	0.21	0.18	0.17
1, 2, 3-TRIMETHYL-BENZENE	0.00	0.05	0.04	0.03	0.03	0.01	0.02	0.00	0.00
1, 2-DIETHYL-BENZENE	0.10	0.14	0.23	0.00	0.00	0.00	0.00	0.00	0.00
1-METHYL-2-N-C3-BENZENE	0.12	0.04	0.04	0.03	0.03	0.02	0.03	0.07	0.06
C10-ALKYLBENZENES	0.21	0.17	0.12	0.77	0.80	0.59	0.79	0.10	0.13
1, 2, 4, 5-TETRAMETHYL-BENZENE	0.10	0.09	0.08	0.07	0.07	0.05	0.10	0.07	0.06
1, 2, 3, 5-TETRAMETHYL-BENZENE	0.00	0.00	0.00	0.02	0.02	0.00	0.05	0.00	0.00
1, 2, 3, 4-TETRAMETHYL-BENZENE	0.13	0.10	0.08	0.01	0.00	0.06	0.15	0.06	0.07
C11-ALKYLBENZENES	1.82	1.76	1.58	0.85	0.83	0.60	0.57	1.32	1.38
NAPHTHALENE	0.00	0.00	0.03	0.00	0.02	0.02	0.00	0.01	0.00
METHYL-NAPHTHALENE	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00
UNKNOWN (HC AROMATICS)	0.06	0.01	0.00	0.00	0.00	0.00	0.04	0.00	0.00
UNKNOWN (C12+)	2.56	2.12	2.47	2.27	2.50	2.71	2.81	2.81	2.41
SLURRY REACTOR-WAX	9.08	9.00	8.91	8.68	8.62	8.54	8.47	8.32	8.46

Table D-9 (cont'd)
 Composition of Hydrocarbon Products from
 Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
 (Run CT-256-3)

M.B.No. Days On Stream	3-29 30.5	3-30 31.5	3-31 32.5	3-32 33.5	3-33 34.5	3-34 35.5	3-35 36.5	3-36 37.5	3-37 38.5
METHANE	7.73	7.93	7.91	7.68	8.08	7.69	7.43	8.44	7.54
ETHENE	0.94	0.93	0.97	1.01	1.10	1.06	1.15	1.39	1.24
ETHANE	3.05	3.30	3.34	3.31	3.45	3.25	3.21	3.62	3.21
PROPENE	3.43	3.33	3.32	3.35	3.59	3.90	3.91	4.62	4.31
PROPANE	6.64	7.62	8.39	8.89	9.46	9.03	9.08	10.23	9.08
I-BUTANE	8.36	8.84	9.32	9.45	9.53	9.26	9.02	9.63	8.87
1-BUTENE+2-METHYLPROPENE	2.96	2.71	2.54	2.42	2.54	2.62	2.71	3.03	3.04
N-BUTANE	6.59	6.94	7.35	7.58	7.59	7.61	7.46	7.73	7.38
TRANS-2-BUTENE	1.18	1.06	1.00	0.95	1.00	1.03	1.07	1.17	1.19
CIS-2-BUTENE	0.83	0.73	0.69	0.66	0.69	0.72	0.75	0.81	0.83
3-METHYL-1-BUTENE	0.09	0.08	0.07	0.07	0.07	0.07	0.08	0.08	0.08
I-PENTANE	6.76	6.16	6.29	6.28	5.92	6.12	6.02	5.28	5.61
1-PENTENE	0.13	0.10	0.10	0.09	0.09	0.10	0.11	0.10	0.11
2-METHYL-1-BUTENE	0.69	0.55	0.50	0.46	0.46	0.50	0.52	0.47	0.56
N-PENTANE	4.40	3.95	4.03	3.99	3.77	4.02	4.01	3.30	3.74
TRANS-2-PENTENE	0.49	0.38	0.35	0.32	0.33	0.36	0.38	0.33	0.40
CIS-2-PENTENE	0.24	0.18	0.17	0.16	0.16	0.18	0.19	0.16	0.19
2-METHYL-2-BUTENE	1.76	1.33	1.21	1.09	1.07	1.18	1.24	1.06	1.29
C5-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,2-DIMETHYLBUTANE	0.06	0.04	0.04	0.04	0.03	0.04	0.04	0.03	0.04
CYCLOPENTANE	0.20	0.19	0.22	0.24	0.25	0.28	0.29	0.15	0.17
HEXENES + ISO-HEXANES	0.07	0.02	0.02	0.02	0.00	0.05	0.02	0.00	0.05
2,3-DIMETHYLBUTANE	0.16	0.16	0.15	0.14	0.13	0.13	0.16	0.11	0.12
2-METHYLPENTANE	2.69	2.23	2.14	2.09	1.91	2.04	2.06	1.40	1.81
3-METHYLPENTANE	1.14	0.96	0.94	0.96	0.90	0.94	0.96	0.66	0.84
HEXENES	0.45	0.48	0.46	0.42	0.67	0.43	0.44	0.58	0.58
1-HEXENE	0.11	0.06	0.05	0.05	0.02	0.05	0.07	0.03	0.06
N-HEXANE	2.31	2.01	1.93	1.96	1.79	1.97	2.05	1.37	1.87
2,4-DIMETHYLPENTANE	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00
METHYLCYCLOPENTANE	1.02	0.95	1.00	1.12	1.08	1.20	1.23	0.88	1.11
3,3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.00
CYCLOHEXANE	0.02	0.02	0.03	0.03	0.04	0.02	0.02	0.03	0.00
HEPTENES + ISO-HEPTANES	0.59	0.36	0.30	0.30	0.07	0.35	0.40	0.14	0.38
2-METHYLHEXANE	0.77	0.75	0.70	0.69	0.61	0.67	0.62	0.43	0.57
2,3-DIMETHYLPENTANE	0.17	0.18	0.18	0.19	0.20	0.20	0.19	0.15	0.18
3-METHYLHEXANE	0.73	0.72	0.68	0.67	0.62	0.67	0.61	0.44	0.57
1-CIS-3-DIMETHYL-N5	0.32	0.33	0.33	0.35	0.34	0.38	0.34	0.28	0.34
1-TRANS-3-DIMETHYL-N5	0.32	0.33	0.33	0.35	0.34	0.38	0.35	0.28	0.34
1-TRANS-2-DIMETHYL-N5	0.25	0.26	0.27	0.28	0.27	0.30	0.28	0.22	0.27
N-HEPTANE	1.08	1.10	1.01	0.98	0.89	1.09	0.97	0.76	1.02
C7-OLEFINS	0.61	0.64	0.57	0.52	0.67	0.50	0.54	0.61	0.63
METHYLCYCLOHEXANE	0.24	0.25	0.23	0.24	0.19	0.25	0.19	0.16	0.20
C8-OLEFINS + ISO-P	0.69	0.52	0.41	0.40	0.01	0.50	0.40	0.01	0.42
MONOMETHYL-ISO-C8-P	0.57	0.61	0.56	0.51	0.57	0.44	0.43	0.46	0.43
OTHER ISO-C8-P	0.12	0.13	0.13	0.13	0.16	0.12	0.12	0.15	0.19
C8-OLEFINS	1.11	1.10	1.30	1.17	1.37	0.83	0.58	0.81	0.84
C8-NAPHTHENES (N5+N6)	1.03	1.10	1.11	1.05	1.26	0.99	0.97	1.10	0.87
N-OCTANE	0.52	0.51	0.06	0.06	0.00	0.42	0.42	0.42	0.49
C9-OLEFINS + ISO-P	0.88	0.56	0.35	0.41	0.08	0.37	0.38	0.04	0.42
MONOMETHYL-ISO-C9-P	0.29	0.32	0.28	0.25	0.27	0.23	0.22	0.26	0.29
OTHER ISO-C9-P	0.13	0.14	0.13	0.12	0.13	0.11	0.02	0.09	0.14
C9-OLEFINS	0.68	0.67	0.54	0.41	0.45	0.40	0.54	0.26	0.33
C9-NAPHTHENES (N5+N6)	0.34	0.35	0.32	0.29	0.32	0.27	0.29	0.37	0.39
N-NONANE	0.17	0.17	0.14	0.14	0.15	0.14	0.19	0.22	0.23
ISO-C10-P + O + N5 + N6	0.88	0.85	0.71	0.70	0.72	0.52	0.53	0.61	0.55
BENZENE	0.64	0.64	0.68	0.76	0.75	0.81	0.82	0.61	0.74
TOLUENE	2.49	2.87	3.10	3.33	3.24	3.02	3.52	3.37	3.44
ETHYLBENZENE	1.31	1.24	1.16	1.32	0.91	1.25	1.27	0.85	1.38
P-XYLENE	0.62	0.73	0.71	0.88	0.99	2.90	2.91	0.84	0.79
M-XYLENE	1.61	1.81	2.06	2.11	2.43	0.00	0.00	2.43	2.12
O-XYLENE	0.70	0.79	0.88	0.93	1.07	0.92	0.90	1.01	0.91
N-PROPYLBENZENE	0.15	0.15	0.14	0.12	0.13	0.12	0.13	0.13	0.13
1-METHYL-3-ETHYL-BENZENE	1.98	2.14	2.13	2.14	2.31	1.98	2.00	2.23	2.05
1,3,5-TRIMETHYL-BENZENE	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.06
1-METHYL-2-ETHYL-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05
ISO-C4-BENZENE	0.04	0.03	0.03	0.00	0.03	0.03	0.03	0.03	0.03
1,2,4-TRIMETHYL-BENZENE	1.21	1.32	1.37	1.46	1.60	1.40	1.43	1.61	1.46
1-METHYL-2-ISO-C3-BENZENE	0.11	0.11	0.10	0.04	0.04	0.12	0.03	0.04	0.03
1,3-DIETHYL-BENZENE	0.00	0.00	0.00	0.00	0.40	0.00	0.36	0.39	0.37
1-METHYL-3-N-C3-BENZENE	0.42	0.43	0.40	0.38	0.08	0.34	0.07	0.08	0.08
N-C4-BENZENE	0.09	0.09	0.00	0.09	0.10	0.00	0.09	0.10	0.09
1,2,3-TRIMETHYL-BENZENE	0.04	0.03	0.03	0.00	0.06	0.00	0.08	0.09	0.05
1,2-DIETHYL-BENZENE	0.00	0.00	0.08	0.08	0.00	0.07	0.00	0.00	0.00
1-METHYL-2-N-C3-BENZENE	0.07	0.07	0.08	0.08	0.03	0.08	0.00	0.00	0.03
C10-ALKYLBENZENES	0.61	0.64	0.61	0.61	0.64	0.15	0.57	0.64	0.59
1,2,4,5-TETRAMETHYL-BENZENE	0.06	0.07	0.07	0.07	0.08	0.07	0.07	0.08	0.07
1,2,3,5-TETRAMETHYL-BENZENE	0.00	0.00	0.00	0.05	0.05	0.00	0.04	0.05	0.04
1,2,3,4-TETRAMETHYL-BENZENE	0.09	0.09	0.09	0.01	0.11	0.10	0.10	0.11	0.10
C11-ALKYLBENZENES	0.69	0.76	0.75	0.77	0.67	1.11	0.75	0.76	0.72
NAPHTHALENE	0.06	0.07	0.00	0.07	0.08	0.07	0.00	0.09	0.00
METHYL-NAPHTHALENES	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN (HC AROMATICS)	0.00	0.00	0.01	0.02	0.00	0.00	0.06	0.01	0.07
UNKNOWN C12+	1.46	1.83	1.99	0.59	0.75	1.70	1.77	1.94	1.84
SLURRY REACTOR-WAX	8.45	8.84	8.30	8.99	7.97	7.66	7.63	7.47	7.31

Table D-9 (cont'd)
Composition of Hydrocarbon Products from
Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
(Run CT-256-3)

M.B.No. Days On Stream	3-38 39.5	3-39 40.5	3-51 53.5	3-52 55.5	3-53 57.5	3-54 59.5	3-55 62.5	3-56 64.5	3-57 66.5
METHANE	7.30	7.87	7.27	9.51	8.71	9.63	10.98	9.99	9.66
ETHENE	1.29	1.43	0.96	0.51	0.56	0.78	1.05	0.96	1.04
ETHANE	3.15	3.35	3.27	3.81	3.61	4.04	4.76	4.59	3.83
PROPENE	4.46	5.10	0.87	2.08	2.28	3.07	3.78	3.29	3.58
PROPANE	9.02	9.40	8.54	6.81	5.57	5.91	6.29	6.65	7.72
I-BUTANE	8.73	8.89	10.64	8.51	6.86	7.22	7.54	7.81	8.95
1-BUTENE+2-METHYLPROPENE	3.15	3.52	0.85	1.99	2.73	3.21	3.35	2.80	2.79
N-BUTANE	7.41	7.59	8.35	7.19	6.24	6.20	5.96	6.23	6.99
TRANS-2-BUTENE	1.24	1.37	0.31	0.74	1.03	1.20	1.30	1.11	1.08
CIS-2-BUTENE	0.88	0.96	0.21	0.50	0.69	0.81	0.88	0.77	0.76
3-METHYL-1-BUTENE	0.09	0.10	0.03	0.05	0.09	0.09	0.10	0.08	0.08
I-PENTANE	5.89	5.62	7.74	6.14	5.86	5.18	5.90	5.96	6.21
1-PENTENE	0.13	0.14	0.33	0.08	0.11	0.11	0.13	0.12	0.11
2-METHYL-1-BUTENE	0.63	0.65	0.16	0.40	0.68	0.66	0.74	0.63	0.55
N-PENTANE	4.07	3.87	4.76	4.40	4.71	3.69	3.88	3.85	3.88
TRANS-2-PENTENE	0.46	0.46	0.11	0.27	0.45	0.42	0.50	0.27	0.39
CIS-2-PENTENE	0.23	0.23	0.06	0.13	0.21	0.20	0.24	0.25	0.18
2-METHYL-2-BUTENE	1.50	1.49	0.41	1.04	1.83	1.63	1.96	1.60	1.39
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00
2,2-DIMETHYLBUTANE	0.05	0.05	0.04	0.02	0.03	0.03	0.05	0.04	0.04
CYCLOCAPTANE	0.22	0.20	0.04	0.02	0.05	0.06	0.12	0.12	0.14
HEXENES + ISO-HEXANES	0.06	0.05	0.11	0.03	0.07	0.04	0.09	0.05	0.02
2,3-DIMETHYLBUTANE	0.13	0.12	0.16	0.10	0.09	0.08	0.12	0.12	0.13
2-METHYLPENTANE	1.96	1.75	2.88	2.58	3.10	1.94	2.65	2.45	2.28
3-METHYLPENTANE	0.89	0.81	1.19	0.93	1.04	0.75	1.05	1.06	0.94
HEXENES	0.58	0.64	0.38	0.59	0.79	0.81	0.58	0.82	0.60
1-HEXENE	0.07	0.07	0.65	0.03	0.08	0.05	0.13	0.07	0.06
N-HEXANE	2.00	1.87	2.20	2.25	2.99	1.76	2.33	2.23	2.01
2,4-DIMETHYLPENTANE	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.01
METHYLCYCLOCAPTANE	1.15	1.10	0.69	0.48	0.46	0.58	0.79	0.97	0.99
3,3-DIMETHYLPENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.00	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.03
HEPTENES + ISO-HEPTANES	0.42	0.39	0.18	0.14	0.53	0.23	0.80	0.38	0.35
2-METHYLHEXANE	0.55	0.49	0.97	1.12	1.34	0.74	0.99	0.90	0.79
2,3-DIMETHYLPENTANE	0.18	0.17	0.15	0.12	0.11	0.15	0.17	0.21	0.18
3-METHYLHEXANE	0.55	0.50	0.91	0.97	1.09	0.70	0.86	0.85	0.73
1-CIS-3-DIMETHYL-N5	0.34	0.32	0.26	0.23	0.21	0.27	0.29	0.36	0.36
1-TRANS-3-DIMETHYL-N5	0.34	0.32	0.75	0.24	0.17	0.26	0.30	0.35	0.32
1-TRANS-2-DIMETHYL-N5	0.28	0.26	0.51	0.23	0.06	0.19	0.25	0.28	0.28
N-HEPTANE	1.06	1.01	0.66	1.23	1.82	1.03	1.32	1.26	0.99
C7-OLEFINS	0.64	0.67	0.48	0.81	1.37	1.14	0.85	0.95	0.72
METHYLCYCLOHEXANE	0.23	0.23	0.25	0.20	0.22	0.32	0.34	0.33	0.36
C8-OLEFINS + ISO-P	0.52	0.43	0.55	0.01	0.25	0.01	0.87	0.70	0.56
MONOMETHYL-ISO-C8-P	0.25	0.38	0.89	1.41	0.76	0.94	0.69	0.72	0.63
OTHER ISO-C8-P	0.19	0.12	0.13	0.14	0.08	0.16	0.11	0.15	0.13
C8-OLEFINS	1.34	0.97	0.55	1.88	2.96	2.24	1.95	1.36	1.13
C8-NAPHTHENES (N5+N6)	0.61	0.91	1.10	1.25	1.48	1.24	0.84	1.12	0.98
N-OCTANE	0.51	0.49	0.46	0.75	1.02	0.60	0.54	0.55	0.44
C9-OLEFINS + ISO-P	0.33	0.32	0.20	0.00	0.55	0.00	1.36	0.86	0.99
MONOMETHYL-ISO-C9-P	0.22	0.26	0.42	0.79	0.77	0.51	0.39	0.13	0.33
OTHER ISO-C9-P	0.03	0.13	0.16	0.20	0.16	0.18	0.14	0.28	0.13
C9-OLEFINS	0.47	0.30	0.21	0.99	1.37	1.22	0.87	0.90	0.67
C9-NAPHTHENES (N5+N6)	0.29	0.34	0.39	0.56	0.36	0.51	0.42	0.41	0.32
N-NONANE	0.23	0.24	0.08	0.25	0.45	0.26	0.18	0.18	0.15
ISO-C10-P + O + N5 + N6	0.59	0.62	0.74	1.39	2.28	1.63	0.85	0.82	0.73
BENZENE	0.75	0.71	0.48	0.36	0.45	0.48	0.61	0.69	0.69
TOLUENE	3.46	3.22	3.15	2.09	1.56	2.65	2.27	3.06	3.43
ETHYLBENZENE	1.30	1.17	1.12	0.74	0.72	0.88	1.19	1.55	1.65
P-XYLENE	0.76	0.73	0.81	0.76	0.54	1.00	0.57	0.79	0.79
M-XYLENE	2.05	1.94	2.20	2.07	1.51	2.34	1.52	1.91	2.27
O-XYLENE	0.87	0.82	0.87	0.78	0.55	0.98	0.60	0.80	0.93
N-PROPYLBENZENE	0.13	0.12	0.16	0.30	0.29	0.29	0.19	0.19	0.19
1-METHYL-3-ETHYL-BENZENE	1.96	1.83	2.71	3.13	2.37	3.26	2.14	2.41	2.57
1,3,5-TRIMETHYL-BENZENE	0.06	0.05	0.10	0.09	0.10	0.11	0.06	0.06	0.07
1-METHYL-2-ETHYLBENZENE	0.04	0.00	0.00	0.03	0.03	0.08	0.10	0.10	0.13
ISO-C4-BENZENE	0.03	0.02	0.04	0.06	0.06	0.00	0.01	0.02	0.00
1,2,4-TRIMETHYLBENZENE	1.40	1.30	1.52	1.53	1.17	1.93	1.23	1.41	1.29
1-METHYL-2-ISO-C3-BENZENE	0.03	0.03	0.07	0.06	0.05	0.09	0.08	0.03	0.03
1,3-DIETHYLBENZENE	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.43
1-METHYL-3-N-C3-BINZENE	0.07	0.33	0.54	0.84	0.76	0.80	0.53	0.51	0.09
N-C4-BENZENE	0.09	0.08	0.15	0.22	0.19	0.23	0.14	0.13	0.12
1,2,3-TRIMETHYLBENZENE	0.08	0.07	0.12	0.11	0.04	0.17	0.04	0.05	0.06
1,2-DIETHYLBENZENE	0.00	0.07	0.09	0.19	0.24	0.18	0.12	0.11	0.00
1-METHYL-2-N-C3-BENZENE	0.05	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
C10-ALKYLBENZENES	0.51	0.53	0.83	1.04	0.89	1.23	0.77	0.77	0.19
1,2,4,5-TETRAMETHYLBENZENE	0.07	0.07	0.11	0.11	0.08	0.17	0.09	0.09	0.02
1,2,3,5-TETRAMETHYLBENZENE	0.04	0.04	0.10	0.06	0.03	0.08	0.03	0.05	0.01
1,2,3,4-TETRAMETHYLBENZENE	0.09	0.08	0.11	0.10	0.08	0.12	0.08	0.10	0.02
C11-ALKYLBENZENES	0.71	0.63	1.04	1.08	0.89	1.29	0.80	0.87	0.20
NAPHTHALENE	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN (HC AROMATICS)	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
UNKNOWN C12+	0.94	0.57	3.83	2.94	2.19	2.41	1.73	1.91	2.00
SLURRY REACTOR-WAX	7.22	6.96	5.56	5.17	4.83	4.52	2.41	3.24	4.13

Table D-9 (cont'd)
Composition of Hydrocarbon Products from
Two-Stage Slurry F-T/ZSM-5 Syngas Conversion
(Run CT-256-3)

M.B.No.	3-58	3-59	3-60	3-61	3-62	3-63	6-64
Days On Stream	68.5	70.5	72.5	74.5	76.5	78.5	80.5
METHANE	9.46	8.39	9.14	8.81	8.51	7.70	7.72
ETHENE	0.92	0.91	1.16	1.27	1.26	1.29	2.77
ETHANE	4.17	3.97	4.31	4.10	4.29	4.08	3.25
PROPENE	2.99	3.24	3.92	4.45	4.01	4.17	9.46
PROPANE	8.71	8.41	9.11	8.86	10.22	9.60	7.44
I-BUTANE	9.01	8.61	8.56	8.11	8.11	7.34	4.94
1-BUTENE+2-METHYLPROPENE	2.51	2.51	2.82	3.22	2.79	2.76	6.77
N-BUTANE	7.14	7.17	7.15	7.05	7.28	6.85	4.61
TRANS-2-BUTENE	0.98	0.99	1.10	1.27	1.12	1.06	2.86
CIS-2-BUTENE	0.68	0.70	0.77	0.90	0.80	0.76	2.10
3-METHYL-1-BUTENE	0.07	0.08	0.08	0.10	0.09	0.07	0.21
1-PENTANE	6.06	6.29	5.39	5.13	4.85	4.28	3.04
1-PENTENE	0.10	0.10	0.11	0.13	0.13	0.11	0.28
2-METHYL-1-BUTENE	0.50	0.53	0.53	0.61	0.57	0.46	1.23
N-PENTANE	3.89	4.01	3.46	3.38	3.38	3.01	2.44
TRANS-2-PENTENE	0.36	0.38	0.38	0.44	0.41	0.33	0.87
CIS-2-PENTENE	0.17	0.19	0.19	0.22	0.21	0.17	0.45
2-METHYL-2-BUTENE	1.25	1.26	1.23	1.35	1.24	0.95	2.55
2, 2-DIMETHYLBUTANE	0.04	0.03	0.03	0.03	0.03	0.02	0.05
CYCLOPENTANE	0.19	0.13	0.10	0.12	0.13	0.11	0.15
HEXENES + ISO-HEXANES	0.03	0.03	0.00	0.01	0.01	0.00	0.07
2, 3-DIMETHYLBUTANE	0.10	0.13	0.12	0.11	0.11	0.08	0.06
2-METHYLPENTANE	2.17	2.18	1.70	1.62	1.52	1.18	0.93
3-METHYLPENTANE	0.96	0.42	0.81	0.79	0.77	0.60	0.47
HEXENES	0.54	2.98	0.87	0.94	0.95	0.67	1.61
1-HEXENE	0.06	0.05	0.03	0.04	0.04	0.03	0.08
N-HEXANE	1.98	1.93	1.61	1.62	1.65	1.22	1.36
2, 4-DIMETHYL-PENTANE	0.01	0.01	0.01	0.01	0.01	0.00	0.01
METHYLCYCLOPENTANE	1.00	1.03	0.91	0.86	0.96	0.79	0.63
3, 3-DIMETHYL-PENTANE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CYCLOHEXANE	0.03	0.03	0.03	0.00	0.03	0.02	0.02
HEPTENES + ISO-HEPTANES	0.32	0.27	0.14	0.14	0.14	0.06	0.32
2-METHYLHEXANE	0.75	0.69	0.56	0.55	0.48	0.30	0.28
2, 3-DIMETHYL-PENTANE	0.19	0.19	0.17	0.16	0.17	0.12	0.11
3-METHYLHEXANE	0.73	0.68	0.58	0.57	0.50	0.34	0.31
1-CIS-3-DIMETHYL-N5	0.35	0.33	0.30	0.28	0.28	0.20	0.20
1-TRANS-3-DIMETHYL-N5	0.35	0.32	0.30	0.28	0.29	0.20	0.19
1-TRANS-2-DIMETHYL-N5	0.27	0.26	0.25	0.22	0.24	0.17	0.14
N-HEPTANE	1.01	0.91	0.83	0.89	0.89	0.51	0.91
C7-OLEFINS	0.65	0.65	0.80	0.95	0.77	0.44	1.74
METHYLCYCLOHEXANE	0.27	0.21	0.21	0.18	0.17	0.09	0.10
C8-OLEFINS + ISO-P	0.41	0.31	0.04	0.06	0.16	0.05	0.00
MONOMETHYL-ISO-C8-P	0.64	0.57	0.57	0.57	0.42	0.28	0.34
OTHER ISO-C8-P	0.14	0.14	0.15	0.15	0.13	0.10	0.11
C8-OLEFINS	1.05	1.00	1.26	1.23	0.88	0.40	2.61
C8-NAPHTHENES (N5+N6)	1.11	1.06	1.11	1.12	0.98	0.71	0.77
N-OCTANE	0.43	0.38	0.42	0.47	0.42	0.23	0.63
C9-OLEFINS + ISO-P	0.36	0.56	0.30	0.55	0.77	0.06	0.03
MONOMETHYL-ISO-C9-P	0.30	0.28	0.28	0.29	0.21	0.13	0.21
OTHER ISO-C9-P	0.13	0.12	0.04	0.12	0.10	0.02	0.11
C9-OLEFINS	0.67	0.42	0.53	0.70	0.21	0.18	0.97
C9-NAPHTHENES (N5+N6)	0.32	0.30	0.40	0.31	0.21	0.13	0.17
N-NONANE	0.15	0.14	0.18	0.22	0.16	0.09	0.46
ISO-C10-P + O + N5 + N6	1.15	0.69	0.79	0.75	0.66	0.41	1.08
BENZENE	0.71	0.72	0.69	0.65	0.78	0.71	0.59
TOLUENE	3.59	3.44	3.36	3.10	3.80	3.38	1.86
ETHYLBENZENE	1.35	1.38	1.15	1.25	1.48	0.72	0.59
P-XYLENE	0.87	0.97	1.02	0.99	0.99	0.82	0.73
M-XYLENE	2.37	2.30	2.57	2.43	2.51	2.20	1.66
O-XYLENE	1.01	0.97	1.10	1.07	1.09	0.93	0.75
N-PROPYLBENZENE	0.18	0.15	0.18	0.19	0.14	0.08	0.17
1-METHYL-3-ETHYL-BENZENE	2.59	2.49	2.66	2.58	2.19	1.47	1.93
1, 3, 5-TRIMETHYL-BENZENE	0.07	0.06	0.07	0.07	0.07	0.06	0.08
1-METHYL-2-ETHYL-BENZENE	0.14	0.00	0.02	0.02	0.01	0.01	0.03
ISO-C4-BENZENE	0.02	0.03	0.04	0.04	0.03	0.02	0.10
1, 2, 4-TRIMETHYL-BENZENE	1.67	1.63	1.81	1.74	1.64	1.19	1.27
1-METHYL-2-ISO-C3-BENZENE	0.03	0.03	0.04	0.03	0.04	0.03	0.02
1, 3-DIETHYL-BENZENE	0.62	0.00	0.49	0.00	0.39	0.00	0.09
1-METHYL-3-N-C3-BENZENE	0.00	0.46	0.11	0.48	0.08	0.22	0.39
N-C4-BENZENE	0.02	0.12	0.13	0.12	0.09	0.05	0.09
1, 2, 3-TRIMETHYL-BENZENE	0.07	0.09	0.10	0.09	0.09	0.07	0.06
1, 2-DIETHYL-BENZENE	0.14	0.09	0.00	0.11	0.00	0.04	0.11
1-METHYL-2-N-C3-BENZENE	0.00	0.00	0.00	0.00	0.00	0.00	0.03
C10-ALKYL-BENZENES	0.74	0.76	0.81	0.80	0.67	0.43	0.62
1, 2, 4, 5-TETRAMETHYL-BENZENE	0.13	0.10	0.10	0.10	0.09	0.04	0.08
1, 2, 3, 5-TETRAMETHYL-BENZENE	0.01	0.05	0.06	0.05	0.05	0.01	0.04
1, 2, 3, 4-TETRAMETHYL-BENZENE	0.02	0.11	0.12	0.10	0.10	0.06	0.08
C11-ALKYL-BENZENES	1.14	0.76	0.90	0.79	0.69	0.55	0.68
NAPHTHALENE	0.02	0.06	0.00	0.00	0.00	0.01	0.01
METHYL-NAPHTHALENE	0.00	0.00	0.00	0.00	0.02	0.02	0.00
UNKNOWN (HC AROMATICS)	0.00	0.00	0.00	0.03	0.00	0.06	0.00
DIMETHYL ETHER	0.00	0.00	0.00	0.00	0.00	0.30	0.00
UNKNOWN C12+	0.88	2.01	2.05	2.26	2.64	9.37	1.41
SLURRY REACTOR-WAX	3.76	4.04	4.59	4.59	5.62	12.23	6.31

Table E-1
First-Stage Fischer-Tropsch Slurry-Reactor
Operating Conditions and Material Balances
(Second-Stage Not-operative)
(Run CT-256-4)

(Nitrogen-Free Basis)	4- 18	4- 19	4- 20	4- 21	4- 22	4- 23	4- 24	4- 25	4- 26
M.B. No.	4- 18	4- 19	4- 20	4- 21	4- 22	4- 23	4- 24	4- 25	4- 26
Days On-stream	19.3	20.3	21.3	22.3	23.3	24.3	25.3	26.3	27.3
First-Stage Conditions:									
Charge H ₂ /CO (Molar)	0.693	0.693	0.692	0.694	0.696	0.688	0.688	0.686	0.688
Temperature, oC	256	256	256	256	256	256	256	256	256
Pressure, MPa	2.508	2.508	2.508	2.515	2.508	2.515	2.515	2.515	2.521
Feed Sup. Vel., cm/s	2.172	2.152	2.182	2.177	2.165	2.183	2.206	2.192	2.186
Space Vel., NL/gFe-hr	2.835	2.817	2.907	2.903	2.888	2.919	2.936	2.922	2.920
N ₂ in Feed, Mol %	8.3	8.1	8.3	8.6	8.2	8.5	9.3	9.3	9.3
Conversions, Mol % :									
H ₂	39.65	36.67	40.26	39.10	37.59	39.44	38.19	37.52	37.67
CO	45.72	41.86	46.13	44.15	40.39	40.18	42.18	42.73	41.97
H ₂ +CO	43.24	39.74	43.73	42.08	39.24	39.88	40.55	40.61	40.22
Yields, Wt % of Products :									
Hydrocarbons (1)	12.77	12.90	13.11	12.31	11.28	11.29	11.97	11.68	11.75
CO ₂	32.29	29.73	32.76	31.72	29.73	29.10	29.06	29.05	28.50
H ₂ O (1)	1.55	1.41	1.46	1.46	1.49	1.51	1.51	1.48	1.39
H ₂	2.81	2.89	2.76	2.82	2.87	2.78	2.89	2.96	2.95
CO	50.58	53.06	49.90	51.69	54.62	55.31	54.56	54.83	55.41
Total	100	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	102.14	104.30	102.76	102.84	103.86	102.98	100.90	99.47	99.73
gHC/Nm ³ (H ₂ +CO) conv.:	233	261	238	232	230	226	230	222	225
(H/C) Atomic Ratio in HC :	2.13	2.13	2.14	2.14	2.14	2.14	2.13	2.13	2.13
Selectivities, Wt % of HC :									
Methane	2.50	2.72	2.91	2.90	2.78	2.76	2.58	2.67	2.56
Ethene	1.95	2.01	2.10	2.09	2.05	2.02	1.89	1.95	1.88
Ethane	0.58	0.58	0.63	0.61	0.61	0.59	0.56	0.57	0.56
Propene	3.20	3.23	3.32	3.24	3.11	3.04	2.81	2.88	2.76
Propane	0.71	0.75	0.79	0.80	0.77	0.76	0.71	0.74	0.72
Butenes	2.40	2.44	2.49	2.43	2.32	2.27	2.08	2.15	2.04
i-Butane	0.13	0.14	0.12	0.14	0.18	0.19	0.13	0.17	0.16
n-Butane	0.78	0.84	0.88	0.89	0.85	0.86	0.80	0.83	0.80
C ₅ - C ₁₁ (2)	5.72	6.14	6.22	6.23	6.13	6.00	5.59	5.84	5.52
Light Hydrocarbons (3)	18.47	16.79	15.95	15.98	15.77	15.56	17.75	16.70	17.38
Heavy Hydrocarbons (4)	17.48	18.26	18.50	18.56	19.34	19.74	19.04	19.44	19.47
Slurry Rx.-Wax	46.00	46.00	46.00	46.00	46.00	46.00	46.00	46.00	46.00
Total	100	100	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 E-1 (cont'd)
First-Stage Fischer-Tropsch Slurry-Reactor
Operating Conditions and Material Balances
(Second-Stage Not-operative)
(Run CT-256-4)

(Nitrogen-Free Basis)								
M.B. No.	4- 27	4- 28	4- 29	4- 30	4- 31	4- 32	4- 33	4- 35
Days On-stream	28.3	29.3	30.3	31.3	32.3	33.3	34.3	36.3
First-Stage Conditions:								
Charge H ₂ /CO (Molar)	0.695	0.691	0.688	0.702	0.695	0.695	0.702	0.689
Temperature, °C	256	255	256	255	256	256	256	259
Pressure, MPa	2.521	2.515	2.515	2.521	2.521	2.521	2.521	1.473
Feed Sup. Vel., cm/s	2.163	2.162	2.168	2.179	2.138	2.147	2.166	2.473
Space Vel., NL/gFe-hr	2.919	2.916	1.948	1.971	1.951	1.963	1.980	1.166
N ₂ in Feed, Mol %	8.3	8.3	8.3	9.4	8.5	8.3	8.4	18.5
Conversions, Mol % :								
H ₂	36.38	35.23	36.19	37.00	35.81	36.74	36.19	47.73
CO	40.16	39.09	44.76	43.40	40.75	41.96	40.74	53.82
H ₂ +CO	38.61	37.51	41.27	40.76	38.72	39.82	38.86	51.34
Yields, Wt % of Products :								
Hydrocarbons (1)	11.20	10.88	13.17	12.67	12.62	13.03	12.46	16.41
CO ₂	28.27	27.78	31.81	29.73	29.00	28.29	28.79	37.19
H ₂ O (1)	1.44	1.50	1.11	1.12	1.10	1.10	1.09	0.90
H ₂	2.99	3.01	2.92	3.01	2.95	2.98	2.98	2.42
CO	56.09	56.84	50.99	53.47	54.33	54.60	54.67	43.07
Total	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:	101.52	102.02	103.15	100.69	103.78	101.16	103.10	102.07
gHC/Nm ³ (H ₂ +CO) conv.:	227	228	255	240	261	255	254	253
(H/C) Atomic Ratio in HC :	2.14	2.14	2.13	2.13	2.13	2.13	2.13	2.13
Selectivities, Wt % of HC :								
Methane	2.71	2.72	2.34	2.16	2.23	2.16	2.36	2.59
Ethene	1.97	2.00	1.43	1.30	1.44	1.49	1.67	1.89
Ethane	0.58	0.59	0.44	0.40	0.43	0.43	0.49	0.48
Propene	2.90	2.90	2.01	1.92	2.11	2.18	2.42	2.84
Propane	0.77	0.77	0.67	0.64	0.68	0.68	0.76	0.67
Butenes	2.15	2.17	1.51	1.47	1.59	1.63	1.79	2.12
i-Butane	0.15	0.15	0.29	0.38	0.37	0.35	0.34	0.23
n-Butane	0.85	0.87	0.80	0.81	0.83	0.82	0.89	0.80
C ₅ - C ₁₁ (2)	5.98	6.05	5.00	5.07	5.21	5.22	5.54	5.85
Light Hydrocarbons (3)	16.50	16.22	16.69	18.63	17.93	17.89	18.89	16.87
Heavy Hydrocarbons (4)	19.37	19.52	20.77	19.22	19.18	19.16	18.85	19.37
Slurry Rx.-Wax	46.00	46.00	48.00	48.00	48.00	48.00	46.00	46.00
Total	100	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 E-2
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-4)

M. B. No. Days On Stream	4-18 19.3	4-19 20.3	4-20 21.3	4-21 22.3	4-22 23.3	4-23 24.3	4-24 25.3	4-25 26.3	4-26 27.3
METHANE	2.50	2.72	2.91	2.90	2.78	2.76	2.58	2.67	2.56
ETHENE	1.95	2.01	2.10	2.09	2.05	2.02	1.89	1.95	1.88
ETHANE	0.58	0.58	0.63	0.61	0.61	0.59	0.56	0.57	0.56
PROPENE	3.20	3.23	3.32	3.24	3.11	3.04	2.81	2.88	2.76
PROPANE	0.71	0.75	0.79	0.80	0.77	0.76	0.71	0.74	0.72
I-BUTANE	0.13	0.14	0.12	0.14	0.18	0.19	0.13	0.17	0.16
1-BUTENE+2-METHYLPROPENE	2.34	2.38	2.43	2.37	2.26	2.23	2.05	2.12	2.01
N-BUTANE	0.78	0.84	0.88	0.89	0.85	0.86	0.80	0.83	0.80
TRANS-2-BUTENE	0.02	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.00
CIS-2-BUTENE	0.04	0.04	0.04	0.04	0.04	0.04	0.03	0.03	0.03
3-METHYL-1-BUTENE	0.13	0.13	0.14	0.13	0.13	0.13	0.11	0.11	0.11
I-PENTANE	0.22	0.25	0.25	0.27	0.27	0.21	0.25	0.25	0.17
1-PENTENE	1.70	1.76	1.79	1.75	1.68	1.66	1.55	1.58	1.52
2-METHYL-1-BUTENE	0.08	0.08	0.08	0.08	0.07	0.06	0.06	0.07	0.05
N-PENTANE	0.59	0.64	0.67	0.67	0.66	0.65	0.62	0.64	0.63
CIS-2-PENTENE	0.02	0.02	0.02	0.02	0.00	0.00	0.00	0.02	0.02
HEXENES + ISO-HEXANES	0.27	0.30	0.29	0.29	0.28	0.28	0.26	0.27	0.24
1-HEXENE	1.16	1.24	1.25	1.22	1.20	1.20	1.11	1.14	1.09
N-HEXANE	0.41	0.46	0.47	0.48	0.48	0.47	0.45	0.47	0.44
HEPTENES + ISO-HEPTANES	0.11	0.08	0.09	0.10	0.09	0.07	0.05	0.06	0.05
1-HEPTENE	0.56	0.62	0.62	0.63	0.65	0.65	0.58	0.62	0.59
N-HEPTANE	0.21	0.23	0.24	0.25	0.26	0.26	0.23	0.25	0.25
1-OCTENE	0.17	0.21	0.21	0.22	0.23	0.23	0.21	0.22	0.22
N-OCTANE	0.06	0.07	0.07	0.08	0.08	0.08	0.08	0.09	0.08
C9-OLEFINS + ISO-P	0.03	0.04	0.03	0.04	0.04	0.04	0.04	0.05	0.05
ACETONE	0.08	0.11	0.09	0.13	0.09	0.15	0.07	0.06	0.05
I-PROPANOL	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.08
UNKNOWN LITE HYDRO-CARB LIQ (1)	18.47	16.79	15.95	15.98	15.77	15.56	17.75	16.70	17.38
UNKNOWN HVY HYDRO-CARB LIQ (2)	17.48	18.26	18.50	18.56	19.34	19.74	19.04	19.44	19.47
SLURRY REACTOR-WAX	46.00	46.00	46.00	46.00	46.00	46.00	46.00	46.00	46.00

(1) Collected in Chilled and Ambient Condensers

(2) Collected in Hot Condenser

Table E-2 (cont'd)
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-4)

M.B. No. Days On Stream	4-27 28.3	4-28 29.3	4-29 30.3	4-30 31.3	4-31 32.3	4-32 33.3	4-33 34.3	4-35 36.3
METHANE	2.71	2.72	2.34	2.16	2.23	2.16	2.36	2.59
ETHENE	1.97	2.00	1.43	1.30	1.44	1.49	1.67	1.89
ETHANE	0.58	0.59	0.44	0.40	0.43	0.43	0.49	0.48
PROPENE	2.90	2.90	2.01	1.92	2.11	2.18	2.42	2.84
PROPANE	0.77	0.77	0.67	0.64	0.68	0.68	0.76	0.67
I-BUTANE	0.15	0.15	0.29	0.38	0.37	0.35	0.34	0.23
1-BUTENE+2-METHYLPROPENE	2.12	2.13	1.49	1.45	1.57	1.61	1.77	2.12
N-BUTANE	0.85	0.87	0.80	0.81	0.83	0.82	0.89	0.80
TRANS-2-BUTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CIS-2-BUTENE	0.03	0.03	0.02	0.02	0.02	0.02	0.02	0.00
3-METHYL-1-BUTENE	0.12	0.11	0.07	0.08	0.09	0.10	0.11	0.15
I-PENTANE	0.27	0.29	0.33	0.35	0.36	0.37	0.38	0.10
1-PENTENE	1.61	1.62	1.20	1.18	1.21	1.23	1.32	1.66
2-METHYL-1-BUTENE	0.06	0.06	0.04	0.04	0.04	0.05	0.05	0.03
N-PENTANE	0.66	0.67	0.66	0.68	0.69	0.68	0.72	0.66
CIS-2-PENTENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEXENES + ISO-HEXANES	0.27	0.26	0.24	0.25	0.29	0.29	0.30	0.30
1-HEXENE	1.16	1.17	0.88	0.87	0.88	0.89	0.96	1.21
N-HEXANE	0.49	0.50	0.48	0.51	0.52	0.51	0.54	0.50
HEPTENES + ISO-HEPTANES	0.05	0.06	0.08	0.09	0.09	0.09	0.09	0.00
1-HEPTENE	0.63	0.65	0.48	0.46	0.46	0.46	0.49	0.65
N-HEPTANE	0.27	0.28	0.25	0.28	0.28	0.27	0.29	0.27
1-OCTENE	0.24	0.24	0.18	0.16	0.16	0.16	0.17	0.22
N-OCTANE	0.09	0.09	0.08	0.09	0.09	0.09	0.09	0.09
C9-OLEFINS + ISO-P	0.05	0.05	0.03	0.03	0.03	0.03	0.03	0.03
ACETONE	0.07	0.06	0.05	0.00	0.00	0.00	0.00	0.00
I-PROPANOL	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29
UNKNOWN LITE HYDRO-CARB LIQ (1)	16.50	16.22	16.69	18.63	17.93	17.89	18.89	16.87
UNKNOWN HVY HYDRO-CARB LIQ (2)	19.37	19.52	20.77	19.22	19.18	19.16	18.85	19.37
SLURRY REACTOR-WAX	46.00	46.00	48.00	48.00	48.00	48.00	46.00	46.00

(1) Collected in Chilled and Ambient Condensers

(2) Collected in Hot Condenser

Table E-3
Fischer-Tropsch Hydrocarbon Selectivities
(Run CT-256-4; DOS = 26.3)

<u>Components</u>	<u>wt %</u>
Methane	2.7
Ethene	2.0
Ethane	0.6
Propene	2.9
Propane	0.7
Butenes	2.2
i-Butane	0.2
n-Butane	0.8
C5 - C11	21.7
C12+ (Excl. Rx.-Wax)	20.2
<u>Slurry Rx.-Wax</u>	<u>46.0</u>
Total	100.0

Table E-4
Composition of Fischer-Tropsch Reactor Wax
(Run CT-256-4)

Days On Stream	1.70	6.80	17.30	29.50
Press., MPa	1.48	2.52	2.52	2.52
Temp., °C	257	257	257	257
Carbon No.		Weight %		
13-20	6.70	3.77	10.00	9.30
21-25	10.62	13.16	17.57	18.65
26-30	21.82	21.98	20.92	22.47
31-35	28.06	22.67	17.74	18.26
36-40	13.66	16.85	13.57	13.50
41-45	10.72	12.47	8.46	8.99
46-50	4.71	5.41	5.24	5.34
51-55	1.52	1.88	2.84	2.15
56-60	0.95	1.02	1.82	0.87
61-65	0.79	0.69	1.25	0.47
66-70	0.44	0.10	0.59	0.00
Mole Avg C-No.	30.9	31.6	29.5	29.3
Peak C-No.	35	35	27	27
Viscosity, cSt				
at 194 °C	4.6	9.9	8.6	7.7
at 204 °C	2.6	4.9	4.6	4.3

Table F-1
First-Stage Fischer-Tropsch Slurry Reactor
Operating Conditions and Material Balances
(Second-Stage Not-operative)
(Run CT-256-5)

(Nitrogen-Free Basis)								
M.B. No.	5- 3	5- 4	5- 5	5- 8	5- 9	5- 10	5- 11	5- 12
Days On-stream	3.8	4.8	5.8	8.8	9.8	10.8	11.8	12.8
First-Stage Conditions:								
Charge H ₂ /CO (Molar)	0.696	0.710	0.693	0.700	0.699	0.709	0.699	0.711
Temperature, oC	240	245	244	249	250	250	249	249
Pressure, MPa	1.473	1.473	1.473	1.487	1.487	1.487	1.487	1.487
Feed Sup. Vel., cm/s	3.466	3.538	3.484	3.335	3.326	3.050	3.019	3.000
Space Vel., NL/gFe-hr	2.168	2.258	2.268	2.324	2.343	2.382	2.373	2.378
N ₂ in Feed, Mol %	8.4	9.2	9.0	9.6	9.5	1.0	0.9	0.9
Conversions, Mol % :								
H ₂	46.62	53.11	52.34	63.14	63.93	63.81	62.69	61.82
CO	50.60	59.51	57.21	72.93	73.17	73.55	71.14	74.23
H ₂ +CO	48.96	56.85	55.22	68.90	69.37	69.51	67.67	69.07
Yields, Wt % of Products :								
Hydrocarbons (1)	12.78	14.83	16.06	15.54	14.92	15.52	14.31	15.46
CO ₂	35.52	42.10	39.10	55.25	55.45	55.86	54.47	56.31
H ₂ O (1)	1.24	1.20	1.14	1.19	1.21	1.27	1.33	1.28
H ₂	2.60	2.34	2.31	1.80	1.80	1.79	1.83	1.90
CO	47.87	39.52	41.40	26.22	26.62	25.56	28.07	25.05
Total	100	100	100	100	100	100	100	100
Bal Recovery, Wt % of Charge:								
gHC/Nm ₃ (H ₂ +CO) conv.:	98.21	97.40	98.37	98.22	95.89	98.38	97.82	97.78
(H/C) Atomic Ratio in HC :	1.97	1.94	2.21	1.70	1.59	1.68	1.59	1.67
Selectivities, Wt % of HC :								
Methane	1.12	1.12	1.14	2.09	2.23	2.25	2.46	2.80
Ethene	0.98	1.03	1.05	1.66	1.77	1.76	1.89	1.70
Ethane	0.17	0.18	0.20	0.42	0.44	0.47	0.51	0.50
Propene	1.47	1.55	1.60	2.76	2.94	2.95	3.16	2.87
Propane	0.27	0.27	0.28	0.44	0.48	0.49	0.54	0.49
Butenes	1.05	1.09	1.16	2.02	2.14	2.17	2.33	2.10
i-Butane	0.13	0.18	0.14	0.08	0.10	0.09	0.06	0.08
n-Butane	0.30	0.30	0.30	0.48	0.51	0.53	0.58	0.53
C ₅ - C ₁₁ (2)	3.39	3.44	3.53	5.21	5.58	5.32	5.56	5.04
Light Hydrocarbons (3)	5.99	6.46	11.00	8.09	7.43	7.43	9.38	11.91
Heavy Hydrocarbons (4)	7.13	7.39	8.53	14.68	15.37	16.53	14.40	14.84
Slurry Rx.-Wax	78.00	77.00	71.00	62.00	61.00	60.00	59.00	57.00
Total	100	100	100	100	100	100	100	100

(1) Including Oxygenates

(2) In Gas Phase Only

(3) Collected in Chilled and Ambient Condenser

(4) Collected in Hot Condenser

Table F-2
 Composition of Hydrocarbon Products from
 First-Stage Slurry F-T Reactor
 (Run CT-256-5)

M.B. No. Days On Stream	5-3 3.8	5-4 4.8	5-5 5.8	5-8 8.8	5-9 9.8	5-10 10.8	5-11 11.8	5-12 12.8
METHANE	1.12	1.12	1.14	2.09	2.23	2.25	2.46	2.80
ETHENE	0.98	1.03	1.05	1.66	1.77	1.76	1.89	1.70
ETHANE	0.17	0.18	0.20	0.42	0.44	0.47	0.51	0.50
PROPENE	1.47	1.55	1.60	2.76	2.94	2.95	3.16	2.87
PROPANE	0.27	0.27	0.28	0.44	0.48	0.49	0.54	0.49
I-BUTANE	0.13	0.18	0.14	0.08	0.10	0.09	0.06	0.08
1-BUTENE+2-METHYLPROPENE	1.05	1.09	1.14	1.97	2.09	2.12	2.27	2.05
N-BUTANE	0.30	0.30	0.30	0.48	0.51	0.53	0.58	0.53
TRANS-2-BUTENE	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.02
CIS-2-BUTENE	0.00	0.00	0.02	0.04	0.03	0.03	0.04	0.04
3-METHYL-1-BUTENE	0.06	0.08	0.08	0.27	0.27	0.26	0.14	0.12
I-PENTANE	0.16	0.18	0.15	0.11	0.17	0.17	0.18	0.14
1-PENTENE	0.78	0.82	0.85	1.46	1.55	1.56	1.66	1.51
2-METHYL-1-BUTENE	0.03	0.04	0.04	0.07	0.07	0.07	0.07	0.07
N-PENTANE	0.25	0.24	0.25	0.37	0.40	0.41	0.44	0.41
TRANS-2-PENTENE	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01
HEXENES + ISO-HEXANES	0.22	0.22	0.20	0.26	0.29	0.26	0.28	0.25
1-HEXENE	0.63	0.64	0.67	1.08	1.17	1.13	1.18	1.11
N-HEXANE	0.14	0.21	0.20	0.29	0.30	0.30	0.32	0.31
HEPTENES + ISO-HEPTANES	0.10	0.12	0.13	0.12	0.13	0.11	0.12	0.12
1-HEPTENE	0.45	0.42	0.45	0.63	0.68	0.59	0.62	0.59
N-HEPTANE	0.16	0.14	0.14	0.17	0.18	0.16	0.17	0.16
C8-OLEFINS + ISO-P	0.00	0.00	0.02	0.02	0.02	0.00	0.02	0.00
1-OCTENE	0.24	0.20	0.22	0.24	0.25	0.18	0.23	0.18
N-OCTANE	0.08	0.06	0.06	0.06	0.06	0.05	0.06	0.05
C9-OLEFINS + ISO-P	0.07	0.07	0.06	0.04	0.05	0.04	0.04	0.03
ACETONE	0.00	0.00	0.06	0.00	0.00	0.00	0.13	0.12
I-PROPANOL	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.03
UNKNOWN LITE HYDRO-CARB LIQ (1)	5.99	6.46	11.00	8.09	7.43	7.43	9.38	11.91
UNKNOWN HVY HYDRO-CARB LIQ (2)	7.13	7.39	8.53	14.68	15.37	16.53	14.40	14.84
SLURRY REACTOR-WAX	78.00	77.00	71.00	62.00	61.00	60.00	59.00	57.00

(1) Collected in Chilled and Ambient Condensers

(2) Collected in Hot Condenser

Table F-3
Composition of Fischer-Tropsch Reactor Wax
(Run CT-256-5)

Days On Stream	12.30
Press., MPa	1.48
Temp., °C	250

Carbon No.	Weight %
------------	----------

13-20	11.20
21-25	18.59
26-30	17.68
31-35	15.40
36-40	12.51
41-45	9.11
46-50	6.38
51-55	3.76
56-60	2.54
61-65	1.80
66-70	1.02

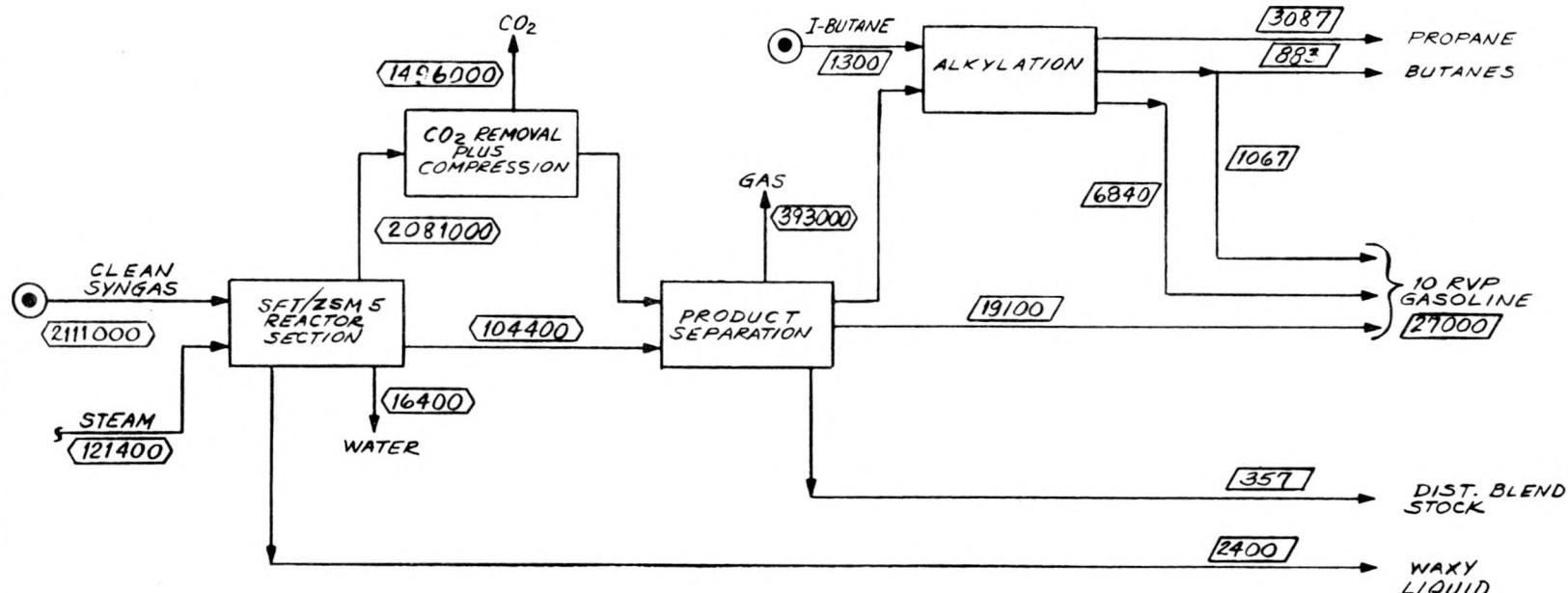
Mole Avg C-No.	29.6
Peak C-No.	28
Viscosity, cSt	
at 149 °C	20.6
at 204 °C	10.1

Table F-4

Fischer-Tropsch Hydrocarbon Selectivities
 (Run CT-256-5)

DOS	3.8	8.8
<u>Components</u>	<u>wt %</u>	<u>wt %</u>
Methane	1.1	2.1
Ethene	1.0	1.7
Ethane	0.2	0.4
Propene	1.5	2.8
Propane	0.3	0.4
Butenes	1.1	2.0
i-Butane	0.1	0.1
n-Butane	0.3	0.5
C5 - C11	8.0	13.9
C12+ (Excl. Rx.-Wax)	8.4	15.1
<u>Slurry Rx.-Wax</u>	<u>78.0</u>	<u>62.0</u>
Total	100.0	100.0

T-5



LEGEND
1496000 APPROVED
121400
393000
1300
3087
882
27000
357
2400
16400
10 RVP GASOLINE
WAXY LIQUID
DIST. BLEND STOCK
WATER
CO₂
104400
19100
6840
1067
3087
1300
393000
104400
16400
10 RVP GASOLINE
WAXY LIQUID
DIST. BLEND STOCK
WATER
CO₂

FIGURE G-1

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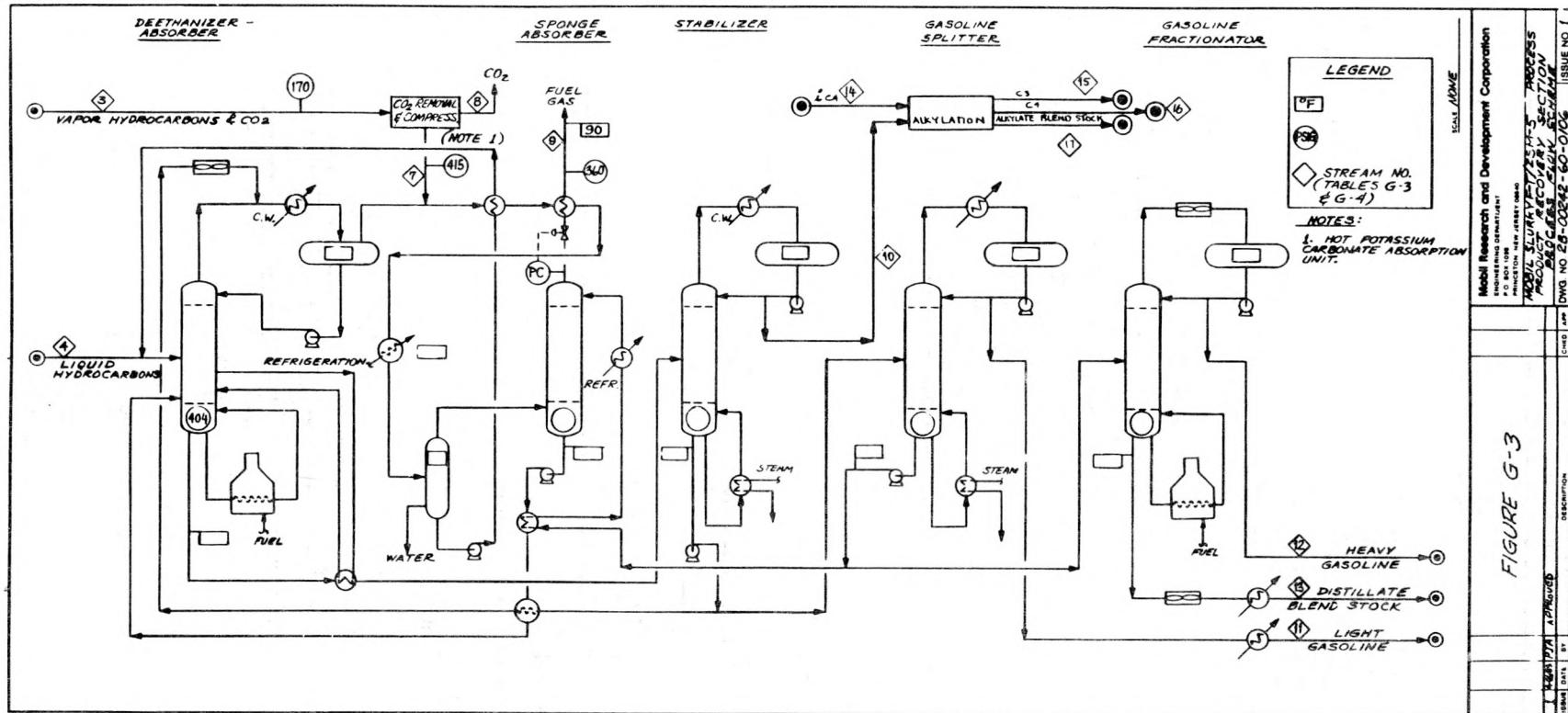
ENGINEERING DEPARTMENT

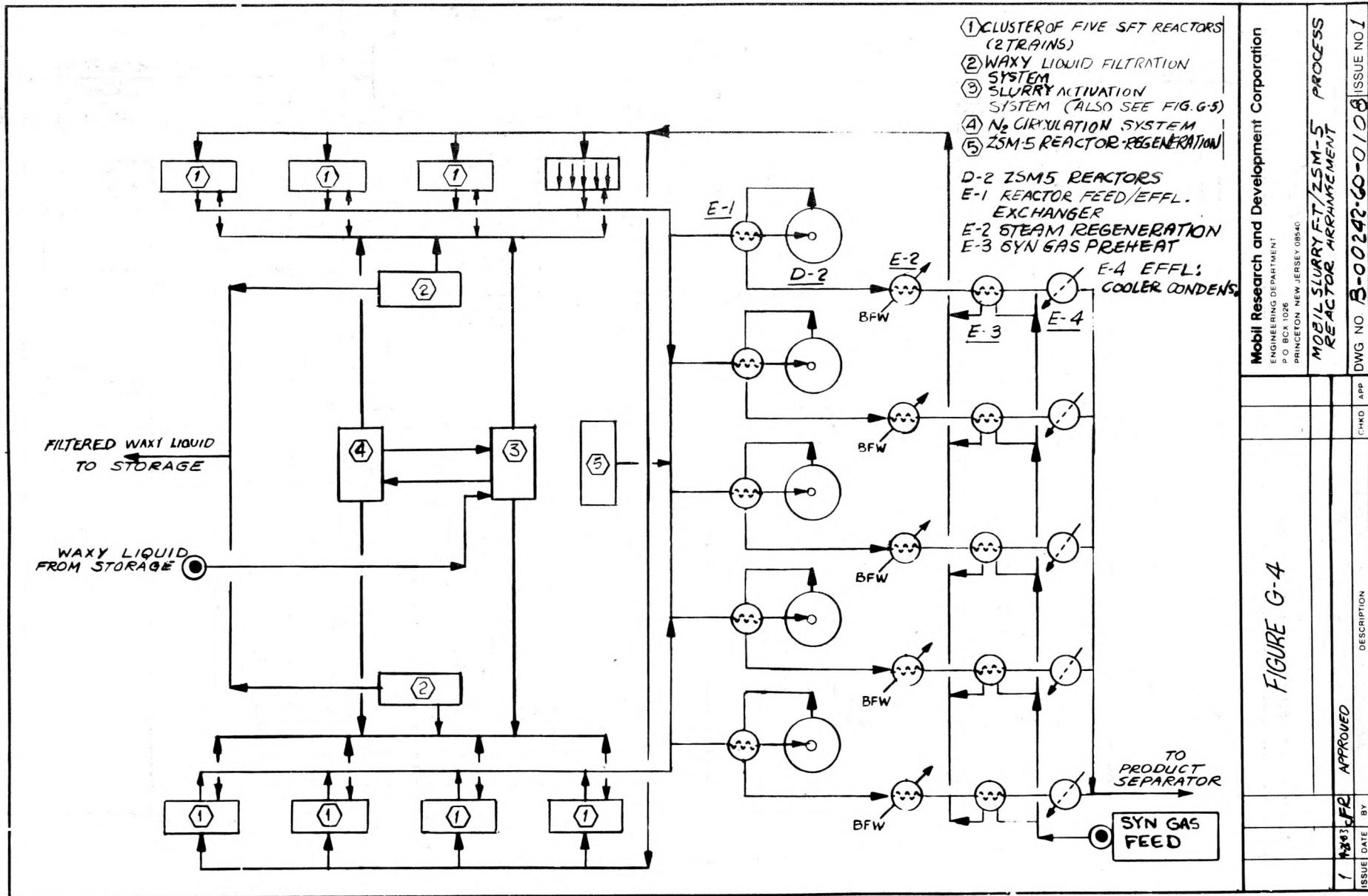
PRINCETON, NEW JERSEY 08544

MOBIL SLURRY F/T/ZSM-5 PROCESS

BLOCK DIAGRAM

DWG NO B-00242-60-0107 ISSUE NO 1





Mobil Research and Development Corporation

ENGINEERING DEPARTMENT
PO BOX 1026
PRINCETON, NEW JERSEY 08540

MOBIL S₂ SLURRY F-T/ZSM-5 PROCESS
REACTOR SLURRY PROCESSING SCHEME
DWG NO E-00242-60-0109 ISSUE NO 1

FIGURE G-5

