

## 2.0 MOBIL TWO STAGE SFT/ZSM-5 PROCESS DEVELOPMENT AND STATUS

### 2.1 Conceptual Basis

This section is intended to highlight those features of the Mobil ZSM-5 hydrocarbon upgrading process which would allow its coupling with a slurry Fischer-Tropsch reactor operating with a CO-rich feed. Two chemical features of special concern herein are the flexibility of the zeolite base catalyst to accept raw Fischer-Tropsch liquids, and the minimum reaction temperature required to achieve high conversion to high quality (i.e., high octane number) gasoline.

As originally developed, the Mobil methanol-to-gasoline (MTG) process utilizing ZSM-5 was intended to convert methanol or methanol-dimethyl ether mixtures in high selectivity to  $C_5$  to  $C_{11}$  hydrocarbons having a much higher octane number than traditional F-T "gasoline" because of the production of aromatic and branched aliphatic hydrocarbons. The key to the process is a shape-selective, high silica zeolite catalyst, identified as ZSM-5. Detailed chemical studies<sup>(1)</sup> have revealed that the process occurs by conversion of methanol to dimethyl ether which is rapidly transformed to light olefins which are dimerized to form  $C_5+$  olefins that are subsequently converted to paraffins and aromatics. Extensive studies by Anderson and coworkers<sup>(2)</sup> support the key role of olefins as an intermediate on the route to aromatics and indicated that ethylene is generally less reactive than propylene.

Anderson's results also indicate that under vigorous enough conditions (e.g., temperatures above 400°C) even C<sub>6</sub> paraffins would probably be converted (i.e., isomerized and/or aromatized) to improve its octane number. Specific data for individual compounds are not available concerning whether the zeolite catalyst would degrade the C<sub>11</sub><sup>+</sup> component of F-T product. However, to the extent that acidic zeolite serves as a carbonium ion catalyst, and to the extent that the temperatures for the Mobil ZSM-5 process are approximately those where olefins oligomerization and catalytic cracking of olefins and paraffins are thermodynamically balanced, breakdown of large molecules into gasoline range may be feasible.

Moreover, the predominantly straight chain character of an F-T product should be advantageous since it could still penetrate the shape selective zeolite catalyst.<sup>(2)</sup> In fact, the Mobil Distillate Dewaxing Process<sup>(3)</sup> appears to operate on just this principle by selectively cracking the least bulky components of fuel oils.

It has also been shown<sup>(4)</sup> that much of the Mobil ZSM-5 process heat is released in the hydrocarbon condensation step of this process. Hence, in a two stage process there would be less heat load on the zeolite catalyzed stage with crude F-T feed than with the methanol feed typically used in a Mobil ZSM-5 process.

In addition, it has been indicated<sup>(5)</sup> that aromatization of olefins over ZSM-5 catalyst requires a temperature of at least 370°C which is approximately 100°C higher than typical for the

SFT reactor. As a result, a single step conversion of syngas to gasoline with mixed F-T and zeolite catalysts would appear to be currently difficult. The temperature optima of presently known F-T and zeolite catalyst are not as well matched as would be desirable. Deactivation of the synthesis function could also be a serious problem in a single reactor, as well as a single set of regeneration conditions would need to be found.

The above considerations suggest that typical F-T products could feasibly be upgraded by ZSM-5 catalyst in a two-stage, rather than one-stage process. The optimum feed for the zeolite upgrading stage of such a two stage process would be derived from an F-T catalyst and process which emphasize formation of high olefinic or oxygenated products of as low an average molecular weight as possible without excessive methane formation.<sup>(4)</sup> Such feed is possible from a slurry Fischer-Tropsch process.

More specific data are still needed on the ability of the ZSM-5 catalyst to transform typical F-T product mixture as a function of temperature and on its aging characteristics as a function of the feed. To this end, a patent disclosure<sup>(6)</sup> by Mobil Oil Corporation indicated that a gasoline range F-T product ( $C_5$  to  $204^{\circ}C$ , RON = 66) was processed over HZSM-5 at about  $265^{\circ}C$ , 48 atm. pressure and LHSV 0.6 to give an octane improved gasoline fraction and a high boiling ( $204-343^{\circ}C$ ) fuel oil fraction with minimal gas formation. The yield loss to fuel oil associated with an improvement in RON to 81 was 12 percent. Increasing severity

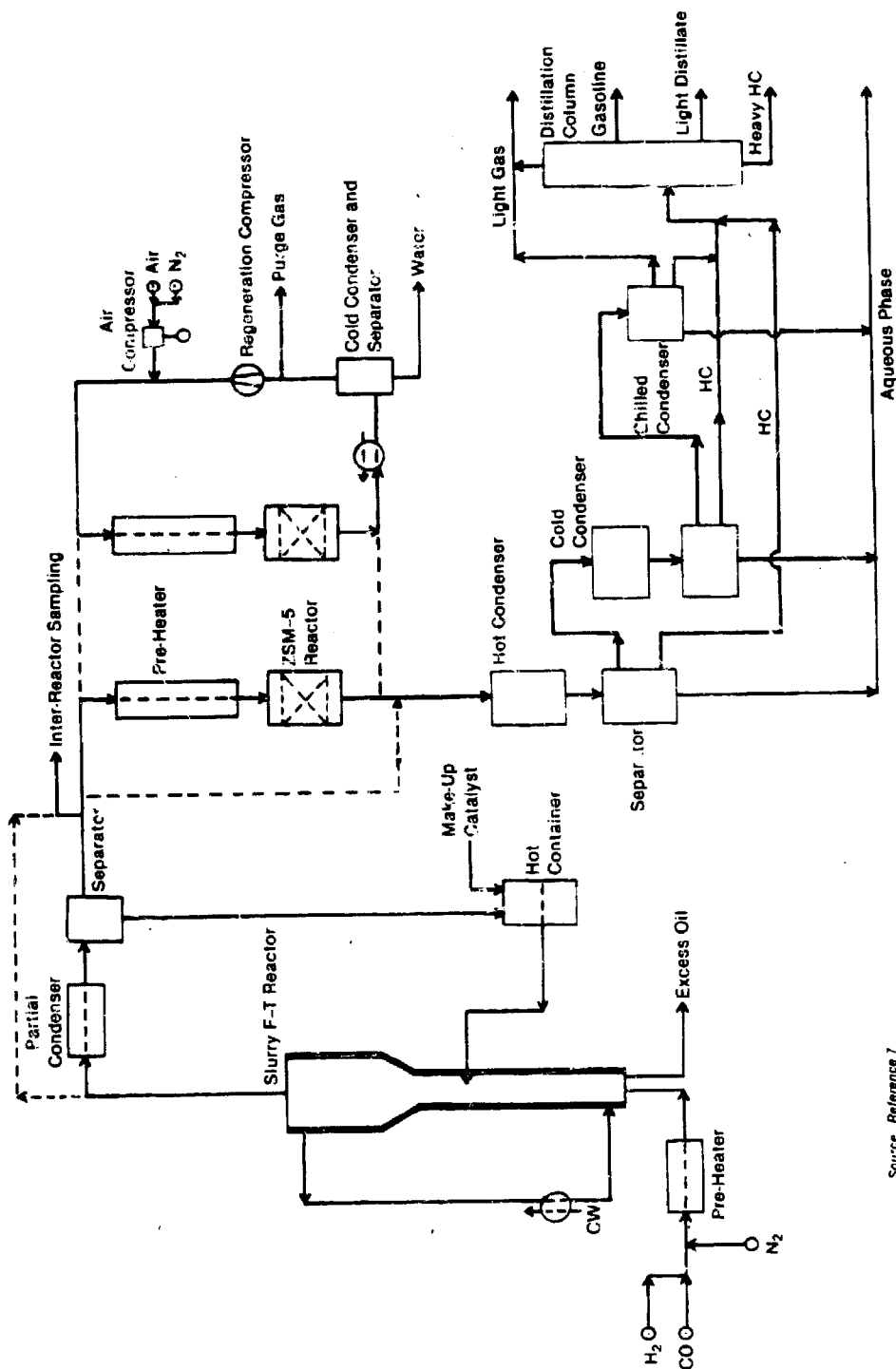
gave only modest further octane improvement but at the expense of further yield loss. The upgraded gasoline had a relatively high olefin to aromatic ratio.

More detailed studies have been undertaken by MRDC since 1980 to demonstrate the viability of their two stage SFT/ZSM-5 process on a bench-scale unit. A description of this unit, as well as a discussion of its test run results are elaborated below.

## 2.2 Bench-scale Unit Description

A flow diagram of the bench-scale unit, BSU, is shown in Figure 2-1, and Table 2-1 lists the design bases. The unit consists of four sections--gas feed, SFT reactor, fixed bed ZSM-5 reactor, and product recovery and liquid hydrocarbon product distillation.<sup>(7)</sup>

In the gas feed section, carbonyl free hydrogen and carbon monoxide gases are mixed to give a simulated synthesis gas with a desired  $H_2:CO$  ratio (typically 0.67). The mixed gaseous stream is preheated before entering the bottom zone of a bubble column slurry Fischer-Tropsch reactor through a sintered metal distributor at a typical rate of  $1.87 \text{ Nm}^3/\text{hr}$ .<sup>(7)</sup> The catalyst slurry is prepared in a  $26,000 \text{ Cm}^3$  slurry tank and is transferred to the reactor above the distributor by applying nitrogen gas pressure in the slurry tank. The temperature of this reactor is controlled by circulating hydrocarbon oil (e.g., Mobil therm 600) in a jacket which surrounds the entire column. At the top, the SFT reactor is connected to a disengager. This disengager serves to prevent carryover of entrained slurry with the outgoing product vapors.



Source Reference 7

**FIGURE 2-1**  
**SIMPLIFIED FLOW DIAGRAM OF TWO-STAGE PILOT PLANT FOR SYNTHESIS GAS CONVERSION**

TABLE 2-1

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) x 305(L)	5.08(ID) x 305 762(L)
ZSM-5 Catalyst Bed, cm	5.08(ID) x 20.3(L)	5.08(ID) x 10.2-45.7(L)
<u>II. Material Balance Basis</u>		
<u>Normal Operation</u>		
Syngas Feed Rate, Nm <sup>3</sup> /hr	1.87	0.94 - 3.75
H <sub>2</sub> /CO Mole Ratio	0.67	0.5 - 2
H <sub>2</sub> +CO Conversion, Mol %	90	50 - 97
<u>ZSM-5 Reactor Regeneration</u>		
Air + Recycle Gas Flow Rate, Nm <sup>3</sup> /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), 1/hr	128	64 - 2.56
Catalyst Load, g	1544	1544 - 3859
Reaction Heat Removal Rate, MJ/hr	4.8	1.4 - 16
<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, 1/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 2-1  
(Continued)

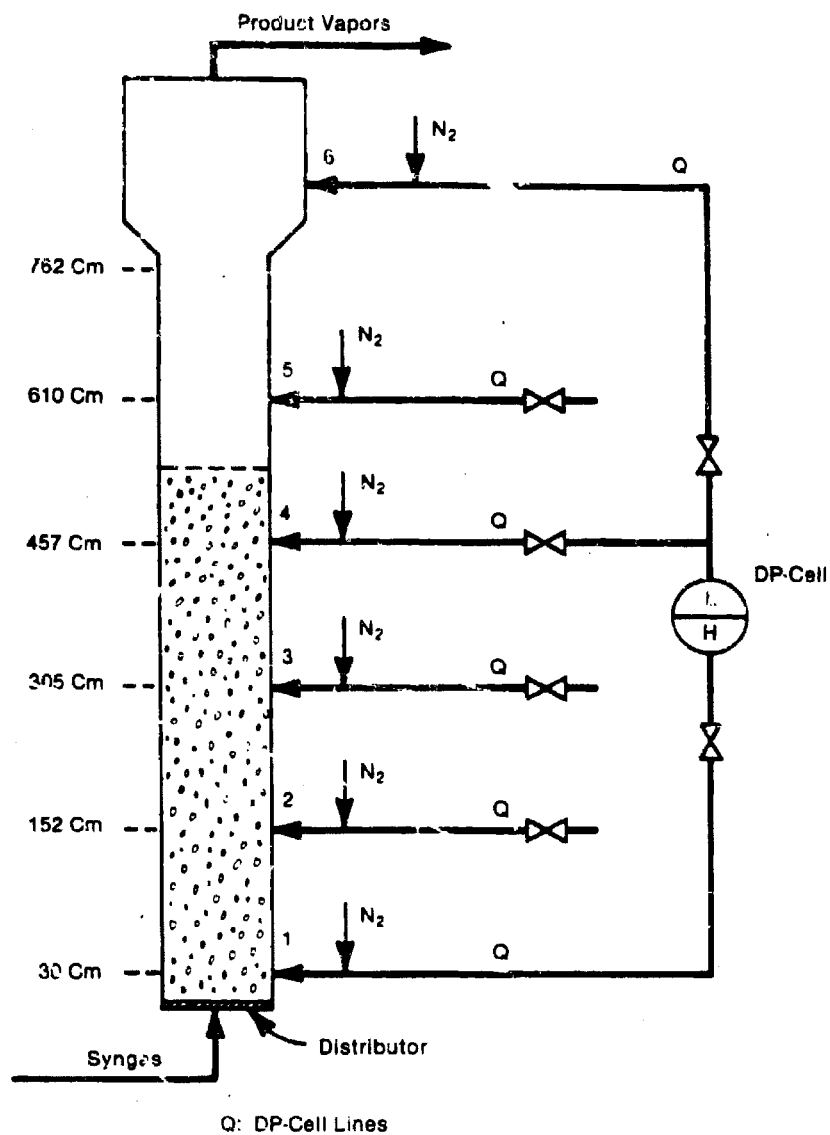
IV. <u>ZSM-5 Reactor Preheater</u>	<u>Normal</u>	<u>Design Range</u>
<u>Normal Operation</u>		
Inlet Temperature, °C	260	177 - 343
Exit Temperature, °C	316 - 399	316 - 427
Pressure, MPa	1.31	0.69 - 4.14
<u>Regeneration Operation</u>		
Inlet Temperature, °C	Room	-
Exit Temperature, °C	343 - 482	316 - 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 <sub>4+</sub>	-
Bottom Product	C <sub>12+</sub>	-

The slim SFT reactor has an internal diameter of 5.1 cm, and is 762 cm high. The liquid level and gas holdup in the SFT reactor are particularly important process variables. Figure 2-2 shows the schematic arrangement of six differential-pressure (DP) cells with six nitrogen-purge lines installed along the reactor height to measure the pressure gradient, as a surrogate measure by which the gas holdup and liquid level could be calculated with a maximum error of 3 percent for the average gas holdup when the liquid level is above 305 cm. The maximum error in the liquid level is estimated to be 6 percent. (7)

A partial condenser (liquid drop-out pot) is provided on the vapor product line to recover some of the heavier hydrocarbons from the SFT reactor effluents before the vapor products are sent to the second stage or ZSM-5 upgrading reactor. Reactor wax, which consists of accumulated heavy ( $C_{20}^{+}$ ) F-T products is removed regularly by on-line catalyst settling vessels as shown in Figure 2-3. Reactor wax is never processed over the second stage zeolite reactor.

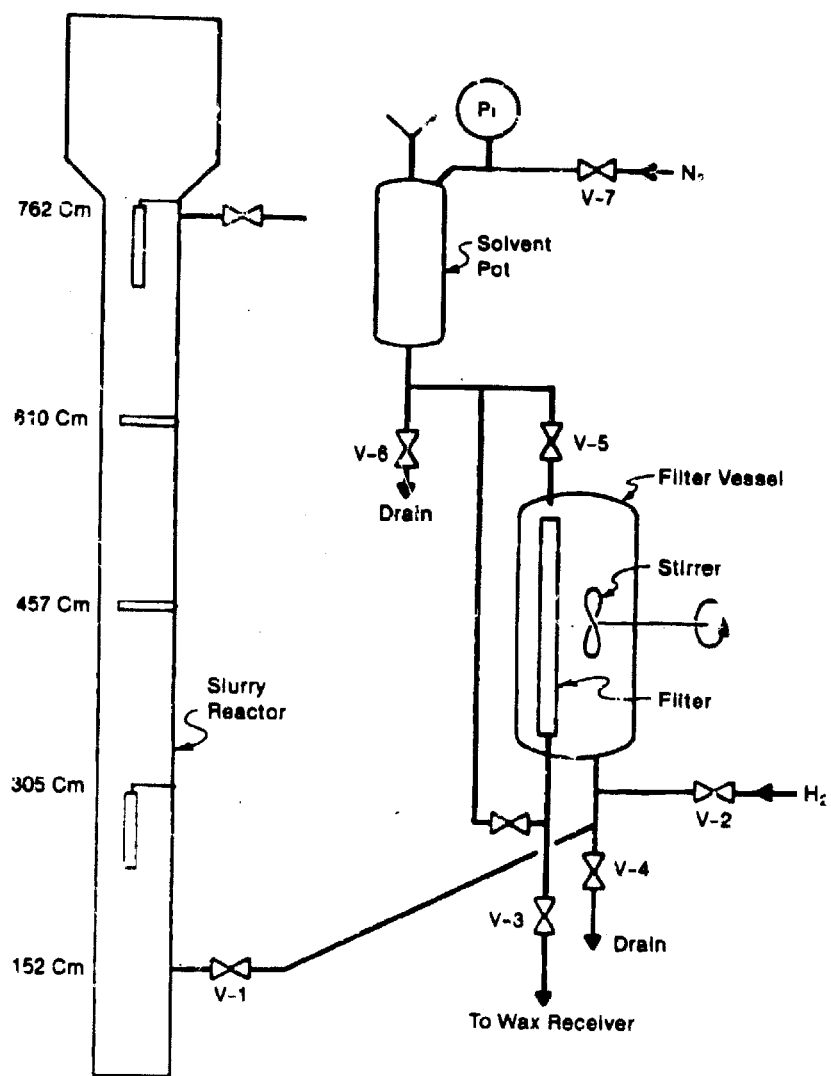
The second stage consists of two fixed-bed adiabatic zeolite ZSM-5 catalyst-filled reactors which are arranged in parallel to allow for alternating operation and regeneration of catalyst. Each ZSM-5 reactor is 5.08 cm in internal diameter and is 101.6 cm high with the top 38 cm section acting as a preheater. In each reactor, the maximum catalyst bed height is 58 cm and the capacity is 1100  $cm^3$ . The ZSM-5 reactor containing the caked catalyst is





Source: Reference 7.

**FIGURE 2-2**  
**SCHEMATIC ARRANGEMENT OF DP-CELL FOR**  
**LIQUID LEVEL MEASUREMENT**



Source: Reference 7.

**FIGURE 2-3**  
**SCHEMATIC OF THE EXTERNAL**  
**WAX FILTER ASSEMBLY**

regenerated under pressure with a controlled supply of oxygen (0.7 to 21 mol percent.)<sup>(7)</sup>

The product stream from the ZSM-5 reactor passes through hot (100°C), cold (about 18°C), and chilled (0°C) condensers. Each condenser is followed by a separator where the liquid hydrocarbons, aqueous phases, are separated into a gasoline range product and a heavier fraction liquid product (if any), respectively. The uncondensed light gases containing mostly carbon dioxide are metered, analyzed, and finally vented off. The liquid hydrocarbon products collected from the hot, cold, and chilled separators are sent to a distillation column for further separation.

### 2.3 Overview of Mobil BSU Experimental Test Runs

In all, to date, five BSU test runs were conducted by MRDC. These runs ranged in duration from 13 to 86 days on-stream (DOS). During these runs, three SFT precipitated iron-base catalysts developed by MRDC were evaluated. Syngas conversion as low as 26 percent and as high as 91 percent were attained. Methane and ethane yield (i.e., gas make) as low as 1.7 weight percent of SFT reactor hydrocarbon output were observed. However, such low gas make was always associated with a dramatic increase in the SFT reactor wax yield to 80 weight percent of the SFT reactor output.

In those experiments where a second stage ZSM-5 reactor was included, it performed well in converting the SFT reactor output into high octane gasoline.<sup>(7)</sup> The actual yield and octane number of the raw gasoline was dependent on the second stage (i.e., zeolite

reactor) severity which is defined as the ratio of iso-butane to the combined sum of propene and butenes [i.e.,  $(i-C_4)/(C_3+C_4)$ ].

A high-severity operation indicates high conversion of propenes and butenes and large formation of iso-butaness. On the other hand, a severity of 1.0 indicates theoretically the best alkylate yield and therefore usually coincides with a high total gasoline yield of high octane number.

It should also be noted that during these experiments the zeolite catalyst (i.e., ZSM-5) was regenerated twice without any noticeable loss in initial catalyst activity.<sup>(7)</sup> Each regeneration took about 14 hours and the activity of ZSM-5 was successfully restored. Of the above-mentioned five test runs, the first two runs, designated as Runs CT-256-1 and CT-256-2, respectively, were short duration runs of exploratory nature to test the operational conditions and limits of the BSU. In general, these two runs were fairly successful but suffered from occasional operational upsets, low SFT catalyst loading due primarily to a high gas holdup of up to 66 volume percent, and a rather high zeolite reactor severity ranging from 1.39 to 3. Details of these experiments are given in MRDC report (Reference 7), but the ranges of process variables studied and the results obtained are summarized in Table 2-2.

The last two test runs (i.e., CT-256-4 and 5) were also short duration runs in which only the first stage (SFT reactor) was operated to explore different ways of minimizing the gas make, to evaluate methods for on-line separation of reactor wax, and to test the

TABLE 2-2

RANGES OF PROCESS VARIABLES STUDIED AND OPERATION RESULTS  
(RUN CT-256-1 AND CT-256-2)

	Run CT-256-1	Run CT-256-2
<u>Process Variables</u>		
<u>First Stage</u>		
DOS	61 days	20 days
Temperature (°C)	260-282	258-260
Pressure (MPa)	1.14-1.83	1.14-1.82
Superficial Feed		
Gas Vel. (cm/s)	1.0-3.2	3.2-4.1
SV (NL/gFe/hr)	5-18	1.4-2.7
Feed H <sub>2</sub> /CO (Molar Ratio)	0.6-1.2	0.67
Catalyst & Initial Catalyst Loading (Wt. %)	I-A ( )	I-B (19.5)
<u>Second Stage</u>		
DOS	49 days	17 days
Inlet Temperature (°C)	288-371	284-350
GHSV (STP) (1/hr)	716-2600	1435-3255
Catalytic Severity (1-C <sub>4</sub> /C <sub>3</sub> +C <sub>4</sub> )	3.35-8.49	0.61-1.63
Catalyst Used	II-A	II-B (215 g)
<u>Operation Results</u>		
<u>First Stage</u>		
H <sub>2</sub> + CO Conv. (Mol. %)	26-91	45-86
Methane + Ethane Yield (Wt. % HC)	6-20	9-15
Reactor-Wax Yield (Wt. % HC)	5-33	1-14
<u>Second Stage Hydrocarbon Yield   (Before Alkylation) (Wt. %)</u>		
C <sub>1</sub> + C <sub>2</sub>	10-14	9-14
C <sub>3</sub> + C <sub>4</sub>	27-44	18-33
C <sub>5</sub> + C <sub>11</sub>	36-51	49-52
C <sub>12</sub> + (excl. reactor-wax)	1-4	1-4

TABLE 2-2  
(CONCLUDED)

	Run CT-256-1	Run CT-256-2
<u>Properties of Raw</u>		
<u>Liquid Hydrocarbons</u> <sup>(1)</sup>		
Aromatics (Wt. %)	17-81	27-47
Acid No. (mgKOH/gHC)	0.09-1.8	0.02-0.5
Octane Number		
R+O	90-98	86-94
M+O	79-85	76-82

(1) Collected in ambient and chilled condensers

performance of a novel SFT catalyst developed by MRDC for in-situ activation. Details of such runs are discussed in Reference 7 and are summarized in Table 2-3.

The longest and most important BSU test run carried out by MRDC to date is the third run, designated as CT-256-3. This run, which extended for 86 days, demonstrated a very stable operation with high catalyst loading (20.7 weight percent initially), high syngas throughput, and high syngas conversion, as shown in Table 2-4. Indeed, it has been selected by MRDC as the basis for the Mobil conceptual process design and scoping cost estimate for a battery limit commercial plant to produce 27,000 BPSD high octane gasoline from clean synthesis gas.<sup>(7)</sup> Therefore, Run CT-256-3 is also selected in this study as being representative of expected performance of the Mobil two-stage SFT/ZSM-5 process for low wax make conditions.

The SFT catalyst used in the first stage of Run CT-256-3 is a proprietary precipitated iron base catalyst developed by MRDC for this purpose and is designated as I-B. The second stage catalyst used in this run is another proprietary catalyst, II-B, of the ZSM-5 class. The major events of this run are summarized in Table 2-5 and the ranges of process variables studied are shown in Table 2-6. Examination of Table 2-5 indicates that there were two minor and one major interruptions in the F-T synthesis operation (i.e., in the first stage). The minor interruptions resulted in a slight loss in F-T catalyst activity and a slight increase in the methane yield. However, the major interruption, which occurred on the 61st day

TABLE 2-

RANGES OF PROCESS VARIABLES STUDIED AND OPERATING RESULTS  
(RUNS CT-256-4 AND CT-256-5)

	Range	
	Run CT-256-4	Run CT-256-5
<u>First Stage Process Variable</u>		
DOS	37 days	17 days
Temperature (°C)	257 - 280	240 - 250
Pressure (MPa)	1.14 - 2.52	1.48
Superficial Feed Gas Velocity (cm/s)	2 - 5	3.0 - 6.0
SV (NL/gFe/hr)	1.2 - 6.5	2.1 - 2.7
Catalyst Loading, Nominal (Wt. %)	4.4 - 22.2	10 - 20
Catalyst	1-B	1-C
<u>Operation Results</u>		
H <sub>2</sub> + CO Conversion (Mol %)	17 - 75	50 - 70
Methane + Ethane Yield (Wt. % HC)	3.5 - 5	1.6 - 3.5
Reactor-Wax Yield (Wt. % HC)	46 - 51	57 - 85

Source: Reference (7)



TABLE 2-4  
RANGES OF OPERATION RESULTS  
(RUN CT-256-3)

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First Stage

H <sub>2</sub> + CO Conversion (Mol %)	54 - 93
Methane + Ethane	
Yield (Wt. % HC)	6 - 18
Reactor-Wax Yield (Wt. % HC)	3 - 13

Second Stage Hydrocarbon

Yield, Before Alkylation (Wt. %)

C <sub>1</sub> + C <sub>2</sub>	9 - 20
C <sub>3</sub> - C <sub>4</sub>	14 - 38
C <sub>5</sub> - C <sub>11</sub>	32 - 55
C <sub>12</sub> + (excl. reactor-wax)	1 - 9

Properties of Raw Liquid Hydrocarbons<sup>(1)</sup>

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

(1) Collected in ambient and chilled condensers

TABLE 2-5

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	Synthesis Started: 1st Stage: 282°C; 1.48 MPa; 4.2-3.7 cm/s
8.0-16.0	2nd Stage on: 329-385°C
18.0-29.4	1st Stage: 260-261°C; 3.7-3.5 cm/s 2nd Stage: 340-346°C
29.7	Upset: Leak at 305 cm level flange; unit under nitrogen purge 36.5 hours
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 50 hours
60.9-67.9	1st Stage: 267°C; 1.48 MPa; 3.1-2.5 cm/s H <sub>2</sub> /CO in Feed: 0.7-0.6 2nd Stage: 323-349°C
67.9-80.0	1st Stage: 1.48-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 2-6  
RANGE OF OPERATING VARIABLES STUDIED  
(RUN CT-256-3)

First Stage

DOS	86 Days
H <sub>2</sub> + CO Flow Rate (Nm <sup>3</sup> /hr)	1.0 - 2.6
Temperature (°C)	259 - 267
Pressure (MPa)	1.13 - 2.51
H <sub>2</sub> /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	I - B

Second Stage

DOS	67 Days
Pressure (MPa)	1.3 - 1.47
Inlet Temperature (°C)	288 - 466
GHSV (S <sup>-1</sup> P) (1/hr)	1350 - 4580
Catalyst Severity (1-C <sub>4</sub> /C <sub>3</sub> +C <sub>4</sub> )	0.15 - 4.07
Catalyst	II-B (215g)

on-stream, did result in a substantial deterioration in the catalyst activity and a substantial increase in gas make (from 13 to 19 weight percent) with significant reduction in syngas conversion from 87 to 70 percent.

Run CT-256-3 can be roughly divided into two parts. In the first part, a long-term aging study on the Catalyst I-B was conducted. During this study, a carbon monoxide-rich syngas feed of  $H_2:CO$  ratio of 0.6 was used for 26 days with no significant effect on the SFT catalyst stability. Lower gas make was observed during this period.

After the long term stability of the synthesis operation was established for 61 days, a period of process variable studies was started. These studies examined the effect of changes in reactor pressure, syngas feed  $H_2:CO$  ratio, superficial feed gas velocity, and the addition of a potassium salt.

Increasing the operating pressure in the SFT reactor at a constant superficial gas velocity resulted in a slight drop (about 2 percent) in syngas conversion. This drop in conversion may be due to experimental data scattering. As shown in Table 2-7, however, the space velocities were greatly increased at high pressure operations. This increase in space velocity is more than sufficient to compensate for the slightly lower conversion observed.

Table 2-7 also indicates a significant reduction in gas make at high pressure operation probably due to an increased likelihood of chain growth at higher pressures. Also, as the pressure is increased, so is the oxygenate yield (Table 2-3).

TABLE 2-7  
EFFECT OF PRESSURE ON SLURRY FISCHER-TROPSCH  
REACTOR PERFORMANCE<sup>(1)</sup>

	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 <sub>2</sub> + 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

<sup>(1)</sup> 0.6 H<sub>2</sub>/CO, 267°C, 2.6 cm/s superficial feed gas velocity

TABLE 2-8  
EFFECT OF PRESSURE ON OXYGENATES YIELD FROM  
FIRST STAGE FISCHER-TROPSCH REACTOR

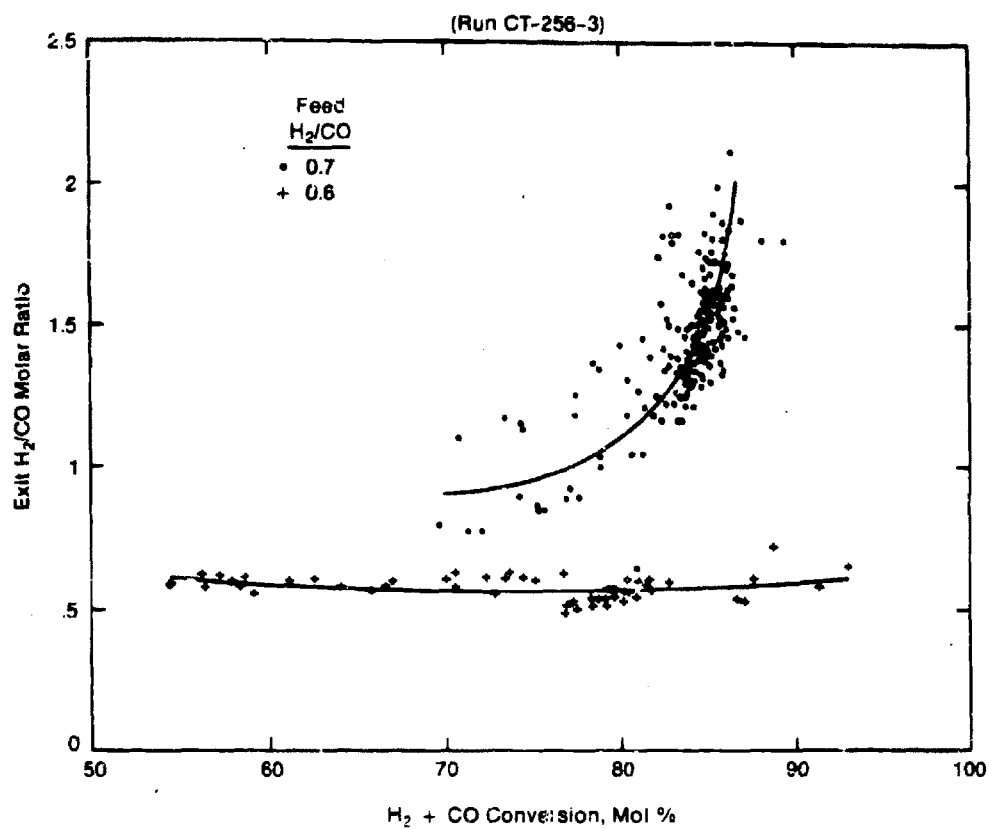
	Run CT-256-3	
DOS	50.6	74.5
Pressure (MPa)	1.48	2.51
Temperature ( $^{\circ}\text{C}$ )	263	267
Feed $\text{H}_2/\text{CO}$ (Molar)	0.7	0.6
Superficial Feed Gas Velocity (cm/s)	3.1	2.6
SV (NL/gFe/hr)	2.18	3.15
$\text{H}_2 + \text{CO}$ Conversion (Mol %)	85.2	77.5
Oxygenates (Wt. % HC)	8.6	12.0

The effect of changing the syngas feed  $H_2:CO$  ratio is shown in Figure 2-4. From this figure, it appears that there are distinct advantages in operating at syngas feed  $H_2:CO$  ratios as close to the usage ratio as possible. This leads to a lower gas make and a better usage of syngas. However, the long-term effects of such carbon monoxide-rich syngas on catalyst aging has yet to be determined. In general, the exit  $H_2:CO$  ratio increases with increasing syngas conversion because the water/gas shift reaction favors the formation of hydrogen.

As expected, a reduction in the superficial gas velocity increases the syngas residence time and therefore increases the syngas conversion, as shown in Table 2-9. In addition, the methane yield is slightly reduced. A "hydrodynamic upset" of the slurry F-T reactor occurred on the 82'nd day on-stream following the sensitivity study of the superficial gas velocity and resulted in a low syngas conversion. This upset appears to be due to catalyst settling when the superficial gas velocity was reduced to 1.1 Cm/S.

Addition of potassium salt in the SFT reactor drastically decreased the gas make from 13 weight percent of total reactor hydrocarbon output to 8 weight percent. Unfortunately, no conclusion could be drawn as to the effect of potassium salt on syngas conversion or rate of catalyst deactivation.

In the second stage (i.e., ZSM-5 reactor) a catalytic operating severity of 0.5 to 1.0 resulted in maximum gasoline yields of 85 to 90 weight percent. Higher pressure operation had no significant effect



Source: Reference 7.

**FIGURE 2-4**  
**EXIT H<sub>2</sub>/CO RATIO OF FIRST-STAGE**  
**SLURRY FISCHER-TROPSCH REACTOR**



TABLE 2-9

EFFECT OF SUPERFICIAL FEED GAS VELOCITY  
ON SLURRY FISCHER-TROPSCH REACTOR PERFORMANCE<sup>(1)</sup>

DOS	75.4	76.5	77.4
Gas Superficial Velocity (cm/s)	2.5	2.1	1.6
$\dot{V}$ (NL/gFE/hr)	3.12	2.53	1.95
H <sub>2</sub> + 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

<sup>(1)</sup> 0.6 H<sub>2</sub>/CO, 267°C, 2.51 MPa

on the second stage operation and yield. Peak research octane numbers of 90 to 94 were obtained for the raw gasoline at a catalytic severity of 0.3 to 2.0 in the second stage.

Run CT-256-4 was designed to test different reactor wax withdrawal systems and was thus operated in such a manner as to produce a relatively high wax make (46-51 weight percent of hydrocarbon product). The wax was regularly withdrawn from the slurry reactor during the run, but all the catalyst removed with the wax was not successfully returned to the reactor. Therefore, loss of catalyst was experienced due to the wax withdrawal system so that addition of fresh catalyst was attempted after 29 days on stream. However, this catalyst apparently failed to activate under synthesis conditions.

Approximately 1.7 kg of wax per day was removed with the settling and withdrawal system. This wax contained approximately .05-0.2 weight percent of unrecovered catalyst particles.

The run was voluntarily terminated after 37 days, since the  $H_2$  and CO molar conversion had dropped from an initial value of 80 percent to a value of 40 percent. The addition of the fresh catalyst did not significantly increase the conversion of syngas. This run formed the basis for the conceptual high-wax case in the MITRE conceptual plant design. However, the low value of 40 percent syngas conversion was not used. Instead, data provided by Mobil and currently substantiated in an ongoing BSU run was used as the basis for the high-wax design.

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