

## UPGRADING FISCHER-TROPSCH NAPHTHA

### ABSTRACT

Reforming of Fischer-Tropsch (F-T) naphtha was studied at UOP in a program sponsored by the Pittsburgh Energy Technology Center of the U.S. Department of Energy. This topical report documents a pilot plant study, and its translation into economic evaluations of various alternatives for upgrading F-T naphtha into a high-octane gasoline blending stock.

There is a significant economic advantage to reform naphtha at low pressure (50 psig) as opposed to high pressure (125 psig). This is particularly true for the extremely lean naphtha produced by F-T synthesis. For the case of a 40,000 BPD unit processing a full-boiling range (FBR) Arge naphtha, an additional 5.4 vol-% yield is obtained at low pressure. This translates into 767,000 bbl of additional reformate over the course of a year. Process economics are closely related to liquid product yield, and the additional reformate yield of the 50 psig operation adds over \$29,000/day to the gross margin. Although the low pressure unit has a larger catalyst regenerator (more capital) and has a higher utility consumption, the after-tax IRR increases by a factor of 1.3 as pressure is reduced from 125 to 50 psig because of the yield advantage.

Two naphtha upgrading process flow schemes are evaluated in this report. Low pressure reforming of the FBR naphtha is compared to a split-naphtha scheme where light and heavy naphtha is processed separately, so as to maximize yield. For gasoline production, we show that the additional complexity and capital required for the split-naphtha case are not economically justified.

Finally, two sources of F-T naphtha were evaluated. Arge synthesis produces a straight-chain naphtha without aromatics. Synthol F-T synthesis produces a naphtha that is highly branched, and has some aromatic content (15 wt-%). Although branched paraffins are more difficult to reform than normal paraffins, Synthol naphtha produces more attractive reforming economics than Arge naphtha. The economic advantage results from a lower capital cost design (higher LHSV) that is made possible by the presence of aromatics in the feed.

reactors. Tubular fixed-bed reactors, on the other hand, operate under conditions that favor the production of diesel range products. Less light ends are made because operations favor high chain growth. In this mode, a large fraction of waxy material is produced (C<sub>19</sub>+). In either case, production of transportation fuels generates a relatively large amount of by-products (Table 1.1).

Recent indirect coal liquefaction work has focused on highly active Fischer-Tropsch catalysts and advanced reactor designs that minimize the production of light hydrocarbons and waxes. Significant advances continue to be made in these areas. Nevertheless, given the fundamental constraints in controlling Fischer-Tropsch product distributions, it appears likely that upgrading of Fischer-Tropsch light hydrocarbons and wax by-products will remain an important consideration for the production of transportation fuels.

## 1.2 NEW TECHNOLOGIES APPLIED TO F-T PRODUCTS UPGRADING

Upgrading F-T wax was covered in another DOE sponsored program, completed in 1988 (4). The current program is specifically concerned with light F-T products, from C<sub>3</sub> through C<sub>11</sub>. The light hydrocarbons are treated as two separate species: LPG (C<sub>3</sub>-C<sub>4</sub> liquefied gases) and naphtha (C<sub>5</sub>-C<sub>11</sub> liquid product). New processes developed for the petroleum refining industry are evaluated as upgrading routes for LPG and naphtha.

### 1.2.1 LPG to Aromatics via the Cyclar Process

The UOP\* Cyclar\* process is a one-step conversion of LPG to aromatics (5). The aromatic Cyclar product can be used to shift the gasoline-pool octane upwards to a more valuable grade of gasoline or to blend with low octane materials, further increasing the size of the gasoline pool. The hydrogen co-product may be used in hydroprocessing units within the upgrading complex or in the upstream synthesis of

## 1.0 INTRODUCTION

UOP is studying the upgrading of light Fischer-Tropsch (F-T) products in a program sponsored by the Pittsburgh Energy Technology Center of the U.S. Department of Energy. The goal of the program is to increase the overall yield of marketable transportation fuels from a F-T complex, with a focus on LPG and naphtha upgrading. Naphtha upgrading is the specific topic of this report.

### 1.1 PRODUCT DISTRIBUTION FROM FISCHER-TROPSCH REACTORS

The Fischer-Tropsch reaction is a fundamental component of indirect coal liquefaction. As the first step, coal or another carbon-containing material is converted to a synthesis gas composed primarily of hydrogen and carbon monoxide. In the Fischer-Tropsch reaction, these synthesis gas components are rebuilt into a wide range of hydrocarbons, from methane to paraffinic wax (1).

The distribution of Fischer-Tropsch products can be described by the Anderson-Schulz-Flory polymerization law by which the probability of step-wise chain growth of hydrocarbons is independent of carbon number. The chain-growth probability is a fundamental property of any known F-T catalyst, and determines the overall product distribution (2).

Selectivity to specific product distributions is adjusted through the careful choice of F-T catalysts and process operating conditions (3). It is generally desired to maximize the production of transportation fuels. One consequence of the Anderson-Schulz-Flory law is that a wide range of products will be produced. Accordingly, the theoretical maximum yield of transportation fuel is relatively low.

If maximum gasoline yield is desired, a penalty must be paid through the associated production of light ends (C<sub>1</sub>-C<sub>4</sub>). This type of operation is typical of Fischer-Tropsch synthesis in fluidized-bed

hydrocarbons from coal. A separate topical report covers the Cyclar process work done within this contract (6).

### 1.2.2 Naphtha Upgrading via New Reforming Technologies

Two new reforming technologies were used to upgrade F-T naphtha into high octane gasoline. The low-pressure CCR Platforming\* process is an extension of existing commercial technology (7). This second generation CCR Platforming process operates at half the pressure of a typical first generation unit, achieving higher liquid product yield for a given product octane. A new light naphtha Platforming process was also used to improve the liquid product yield from the C<sub>6</sub>-C<sub>8</sub> cut of F-T naphtha. The light naphtha process has not yet been commercialized.

TABLE 1.1  
Fischer-Tropsch Product Distribution

F-T Technology* <u>Reactor Type</u>	<u>Arge Fixed-Bed</u>	<u>Synthol Fluidized Bed</u>
Product Distribution, wt-%		
C <sub>4</sub> - (Light Ends)	13.3	43.0
C <sub>5</sub> -C <sub>11</sub> (Naphtha)	17.9	40.0
C <sub>12</sub> -C <sub>18</sub> (Kerosine)	13.9	7.0
C <sub>19</sub> + (Wax)	51.7	4.0
Water Soluble Chemicals	<u>3.2</u>	<u>6.0</u>
	100.0	100.0

\*M. E. Dry, "The Sasol Route to Fuels," Chem. Tech., pp. 744-50, December, 1982

## 2.0 PROCESS DESCRIPTIONS

Commercial process descriptions for naphtha hydrotreating and reforming units are included in this section. Although upgrading from low octane naphtha to high octane gasoline occurs in the reforming step, hydrotreating is essential upstream of all commercial reforming processes.

### 2.1 NAPHTHA HYDROTREATING

Hydrotreating removes contaminant materials from naphtha by selectively reacting sulfur, nitrogen and oxygen containing compounds with hydrogen. Hydrotreating also saturates olefinic hydrocarbons. Hydrotreating removes compounds that would otherwise damage the performance of the downstream reforming unit. Design of naphtha hydrotreaters focuses on the feedstock composition and the requirements of the downstream process units.

A Fischer-Tropsch naphtha bears little resemblance to straight-run petroleum naphtha. Removal of sulfur and nitrogen compounds is of primary importance with petroleum naphthas, whereas sulfur and nitrogen are almost entirely eliminated upstream of the Fischer-Tropsch reactor. Despite the near absence of sulfur and nitrogen, hydrotreating F-T naphtha is still challenging. F-T naphtha has high levels of oxygenates and olefins which must be removed prior to reforming. Oxygenate removal requires temperatures and pressures that would polymerize di-olefins and rapidly coke-up the hydrotreating catalyst. Therefore, the hydrotreater design must first accommodate the saturation of olefins at low temperature and then the conversion of oxygenates at higher temperature, after the olefin content is reduced.

A commercial F-T naphtha hydrotreater is depicted in Figure 2.1. The same flow scheme is used at Sasol II and III (8). At Sasol, fresh feed and recycle hydrogen are preheated in a combined feed exchanger and then a charge heater. A multiple reactor system with heat exchangers between reactors copes with heat released by olefin

hydrogenation. The amount of interstage heat removal sets the inlet temperature for the next reactor. This arrangement permits olefin saturation at mild conditions (low temperature) followed by oxygenate removal at high severity (high temperature). The hydrotreated product is condensed and cooled. The non-condensables (mostly hydrogen) are sent to a recycle compressor before mixing with fresh feed. Olefin saturation, oxygen removal, and solution losses all consume hydrogen, so makeup hydrogen is added to maintain system pressure. Liquid product from the separator is sent to a cold-flash drum, and then to a product fractionator.

The pilot plant flow scheme used in this program differs from the commercial flow scheme described above. The pilot plant operation was conducted with two separate process steps as discussed in Section 3.1.

## 2.2 PLATFORMING PROCESS

The conventional semi-regenerative Platforming unit (Figure 2.2) consists of either three or four reactors arranged in series with interstage heating by fired furnaces. The feed is combined with recycle hydrogen and heated to reaction temperature with heat exchangers and a charge heater. Reactor product is condensed, cooled, and sent to the product separator. Separator gas is recycled to the reactors and net hydrogen product is sent to the hydrogen distribution system. Separator liquid is directed to product stabilization facilities.

Semi-regenerative units need periodic catalyst regeneration, which requires shutting the unit down for at least five days. A significant advancement in reforming technology was achieved with the development of continuous Platforming technology. A Platforming unit with CCR\* Catalyst Regeneration technology is able to maintain catalyst performance by continuously regenerating catalyst while the unit is on stream. In a CCR Platforming\* unit (Figure 2.3), catalyst is transported through the reactors to the regeneration section where a small



quantity is continually regenerated. Product yields are essentially equivalent to those expected from fresh catalyst as a result of CCR technology.

The CCR Platforming process has significant advantages over a conventional fixed-bed system. This process can operate at lower pressure, leading to improved hydrogen and reformat yields. High catalyst coking rates resulting from these severe operating conditions are accommodated by continuous catalyst regeneration. A recent development in the design of the CCR unit has made operation at 50 psig possible. This is approximately half the pressure of first generation CCR technology.

The light naphtha Platforming process is highly selective for the conversion of light C<sub>6</sub>-C<sub>8</sub> paraffins to aromatics. Light paraffin feeds are the most difficult for conventional Platforming units to convert to aromatics. The high selectivity of a light naphtha Platforming unit permits the utilization of process streams such as light Fischer-Tropsch naphtha, which may otherwise not be considered for reforming.

**FIGURE 2.1**  
**F-T NAPHTHA HYDROTREATING UNIT**

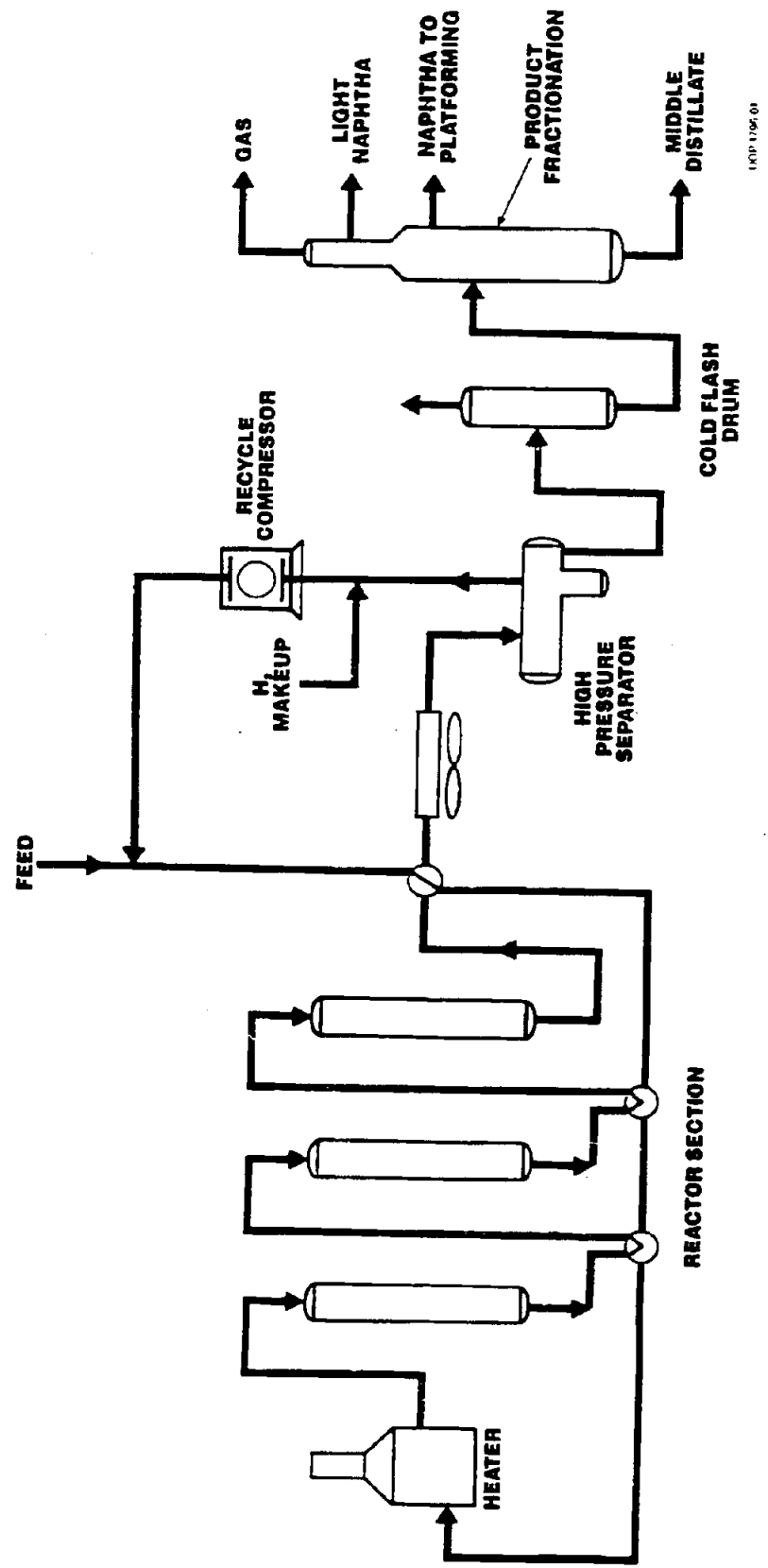
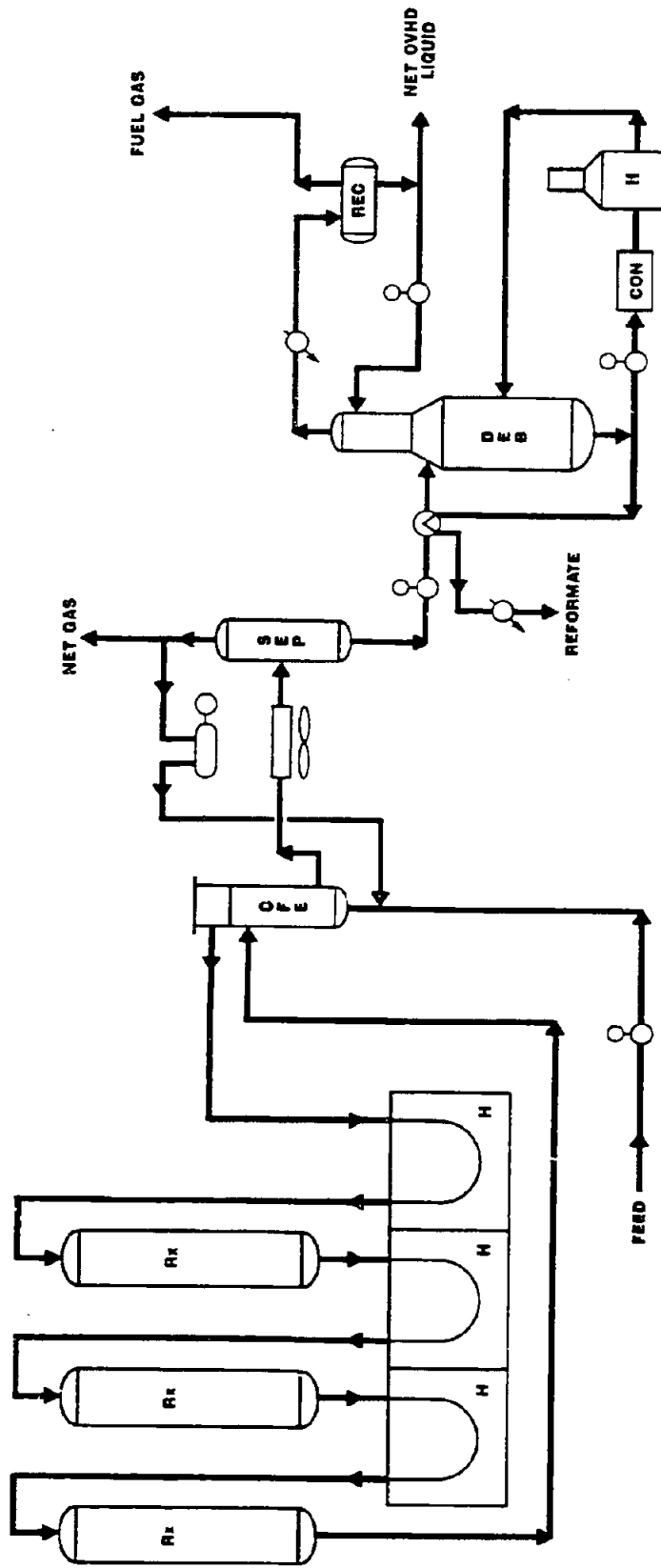


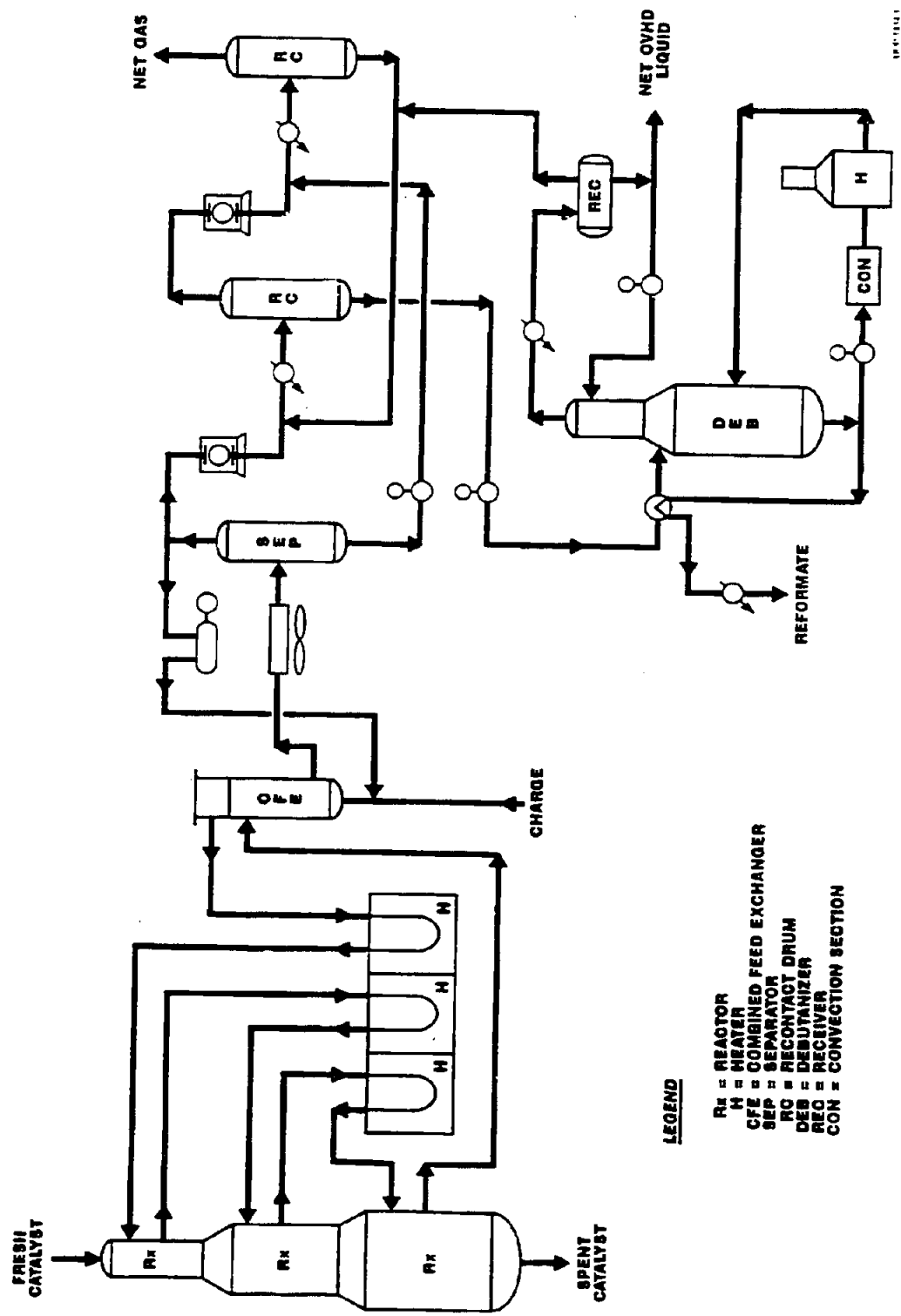
FIGURE 2.2  
**UOP SEMIREGENERATIVE PLATFORMING PROCESS**



**LEGEND**  
 R = REACTOR  
 H = HEATER  
 CFE = COMBINED FEED EXCHANGER  
 SEP = SEPARATOR  
 DET = DEUTANIZER  
 REC = RECEIVER  
 CON = CONVECTION SECTION

**UOP CCF PLATFORMING PROCESS  
WITH TWO-STAGE COUNTERCURRENT RECONTACT**

FIGURE 2.3



- LEGEND**
- Rx = REACTOR
  - H = HEATER
  - CFE = COMBINED FEED EXCHANGER
  - SEP = SEPARATOR
  - RC = RECONTACT DRUM
  - DEB = DEBUTANIZER
  - REC = RECEIVER
  - CON = CONVECTION SECTION

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### 3.0 PILOT PLANT DESCRIPTION

Two types of pilot plants were used to complete this program. A hydrotreating pilot plant was used to saturate olefins, dehydrate oxygenates, and remove trace contaminants. Platforming pilot plants were used to reform the hydrotreated naphtha into reformat.

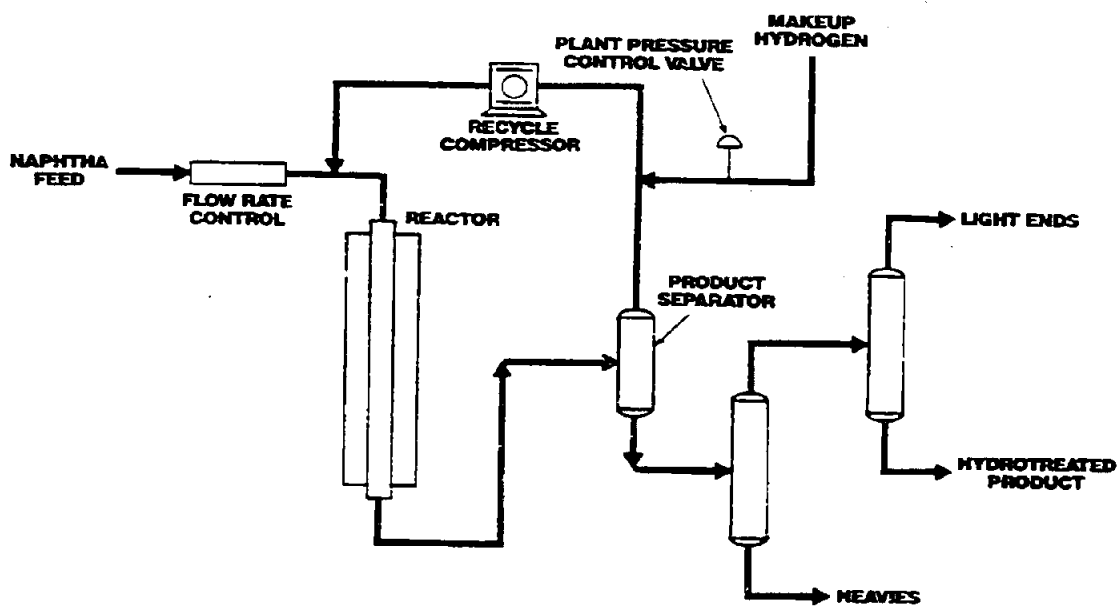
#### 3.1 HYDROTREATING PILOT PLANT

Raw naphtha was combined with recycle hydrogen (Figure 3.1) and charged to a reactor. Reaction temperature was controlled with heating elements surrounding the reactor. Reactor effluent was sent to a product separator where the light gas, primarily hydrogen, was compressed then recycled. Plant pressure was maintained by adding makeup hydrogen. Separator liquid was sent to a fractionation column where heavy (C<sub>12</sub>+) material was removed from the column bottom. Fractionator overhead was sent to a debutanizer to remove C<sub>4</sub>- products.

#### 3.2 PLATFORMING PROCESS PILOT PLANT

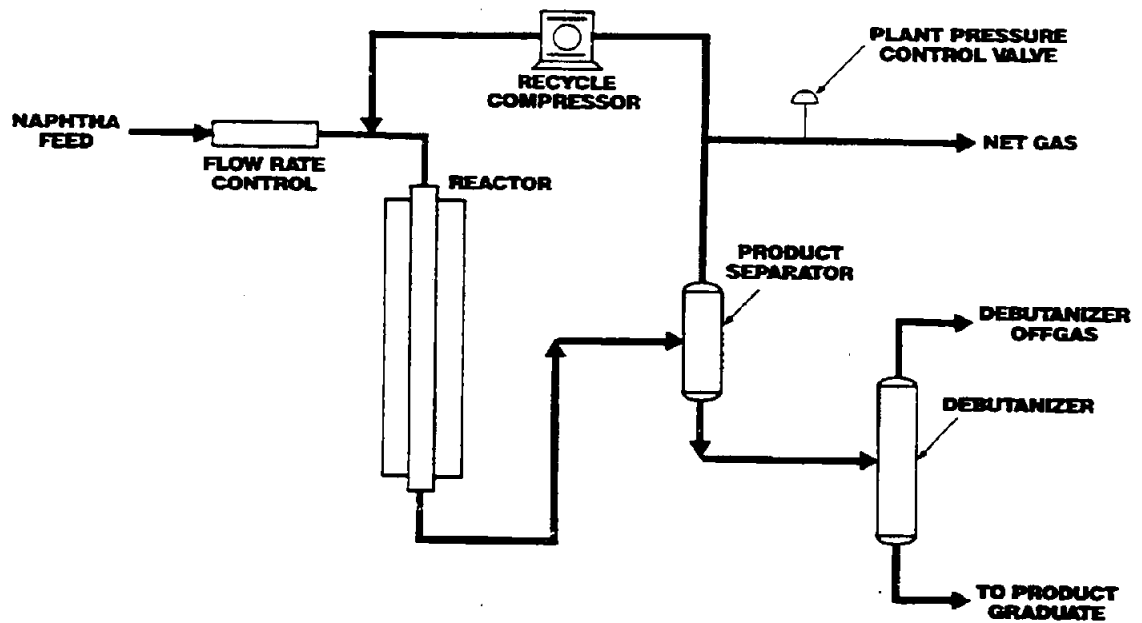
Hydrotreated naphtha was combined with recycle hydrogen (Figure 3.2) and charged to the Platforming reactor. Reaction temperature was controlled with heating elements surrounding the reactor. Reactor effluent was sent to a product separator where the light gas, primarily hydrogen, was compressed then recycled. Unlike the hydrotreater, the Platforming process pilot plant has to export hydrogen from the gas loop to maintain plant pressure. Separator liquid was sent to a debutanizer where any C<sub>4</sub>- gases were removed.

FIGURE 3.1  
**HYDROTREATING PILOT PLANT**



UOP 1760-6

**FIGURE 3.2**  
**PLATFORMING PILOT PLANT**



UOP 1798-05

#### 4.0 FEEDSTOCKS

Feedstock was procured from a commercial F-T facility. The raw naphtha was hydrotreated in a pilot plant as the first step in feed preparation. Two-stage hydrotreating was conducted in separate operations (Table 4.1). First, the naphtha was hydrotreated over a noble-metal catalyst at low temperature to saturate olefins. The liquid product was collected, then charged to a second hydrotreating operation. The second operation used a base-metal catalyst at high temperature to remove oxygenates and any trace contaminants. Reactor effluent was rerun in a fractionator, then stripped in a debutanizer.

The hydrotreated naphtha was batch fractionated in the laboratory. Full-boiling-range (FBR), heavy, and light naphtha cuts were produced. Cut points were adjusted to give the desired carbon number distribution. A branched FBR naphtha was prepared by blending hydrocracked naphtha from a previous program (4) into a portion of the FBR naphtha described above. The four pilot plant feedstocks are summarized in Table 4.2.



TABLE 4.1

Hydrotreating Process Conditions

	<u>First Stage</u>	<u>Second Stage</u>
Catalyst	Noble Metal	Base Metal
LHSV, hr <sup>-1</sup>	4	4
Pressure, psig	800	800
H <sub>2</sub> Recycle, SCFB	1500	1500
Rx Peak Temperature, °C	160	380

TABLE 4.2

Pilot Plant Feedstock Summary

	<u>Arge FBR</u>	<u>Arge Heavy</u>	<u>Arge Light</u>	<u>Branched FBR</u>	<u>Branched Light</u>
<u>Properties</u>					
Carbon No. Target	C <sub>6</sub> -C <sub>11</sub>	C <sub>9</sub> -C <sub>11</sub>	C <sub>6</sub> -C <sub>8</sub>	C <sub>6</sub> -C <sub>11</sub>	C <sub>6</sub> -C <sub>8</sub>
Relative Density, g/ml	0.7070	0.7317	0.6899	0.7032	0.6894
API Density	68.6	61.9	73.6	69.7	73.8
RONC	<40	<40	<40	<40	<40
MONC	<40	<40	<40	<40	<40
<u>Distillation, °C</u>					
IBP	81	153	72	52	
10%	97	157	88	77	75
25%	110	159	93	100	--
50%	129	163	103	123	82
75%	158	170	114	150	--
90%	175	178	122	169	103
EP	194	197	143	198	118

## 5.0 PILOT PLANT RESULTS

This section presents an overview of the pilot plant tests. Detailed run results are in Appendix A.

### 5.1 LOW PRESSURE CCR PLATFORMING STUDY

Nine pilot plant runs were conducted (Table 5.1). One objective of this program is to quantify the C<sub>5</sub>+ and hydrogen yield advantage obtained at lower reforming pressure. Yield advantages at low pressure are illustrated for the FBR (Figures 5.1 and 5.2) and heavy naphthas (Figures 5.3 and 5.4). Catalyst stability for the heavy naphtha cut was tested at each pressure (Figure 5.5). At a similar deactivation rate, there is a 2 octane number advantage for the higher pressure operation, therefore it is more stable. If the 60 psig operation were forced to produce 100 RONC, the deactivation rate would increase by about 50%, and the slope of the curve for Run #3 in Figure 5.5 would be greater.

The effect of molecular weight on yields (Figures 5.6 and 5.7) was expected. Better yield is obtained from a heavier naphtha. Stability for the heavy naphtha cut at 98 RONC is the same as FBR naphtha at 100 RONC (Figure 5.8). At the same octane, this differential would translate into a 50% stability advantage for the FBR naphtha over the heavy naphtha cut.

The final feedstock property evaluated in this program is molecular branching. Highly branched FBR naphthas have similar yields at low octanes, but the branched feedstock blend has lower yield compared to FBR naphtha when octane is increased above 96 RONC (Figures 5.9 and 5.10).

### 5.2 LIGHT NAPHTHA PLATFORMING STUDY

Yields produced by the light naphtha Platforming and low

pressure CCR Platforming processes with the same light feed are compared in Table 5.2. The light naphtha Platforming process makes a more aromatic, higher octane product than the low pressure CCR Platforming process. The light naphtha Platforming process also provides higher hydrogen and C<sub>5</sub>+ wt-% yields. Volumetric yields for the two processes are similar because the more aromatic product from the light naphtha Platforming process has higher density. The octane-barrel yield, obtained by multiplying the product octane and volumetric yield, is of course greater for the light naphtha Platforming process.

TABLE 5.1

Pilot Plant Program Description

<u>Run #</u>	<u>Naphtha</u>	<u>Pressure, psig</u>	<u>Test Type</u>
1	Arge Heavy	125	Yield, Octane
2	Arge Heavy	60	Yield, Octane
3	Arge Heavy	60	Stability
4	Arge Heavy	125	Stability
5	Arge FBR	125	Yield, Octane
6	Arge FBR	60	Yield, Octane
7	Arge Light	60	Yield, Octane
8	Arge FBR	60	Stability
9	Branched FBR	60	Yield, Octane
10 *	Branched Light	--	Stability
11 *	Arge Light	--	Yield, Octane

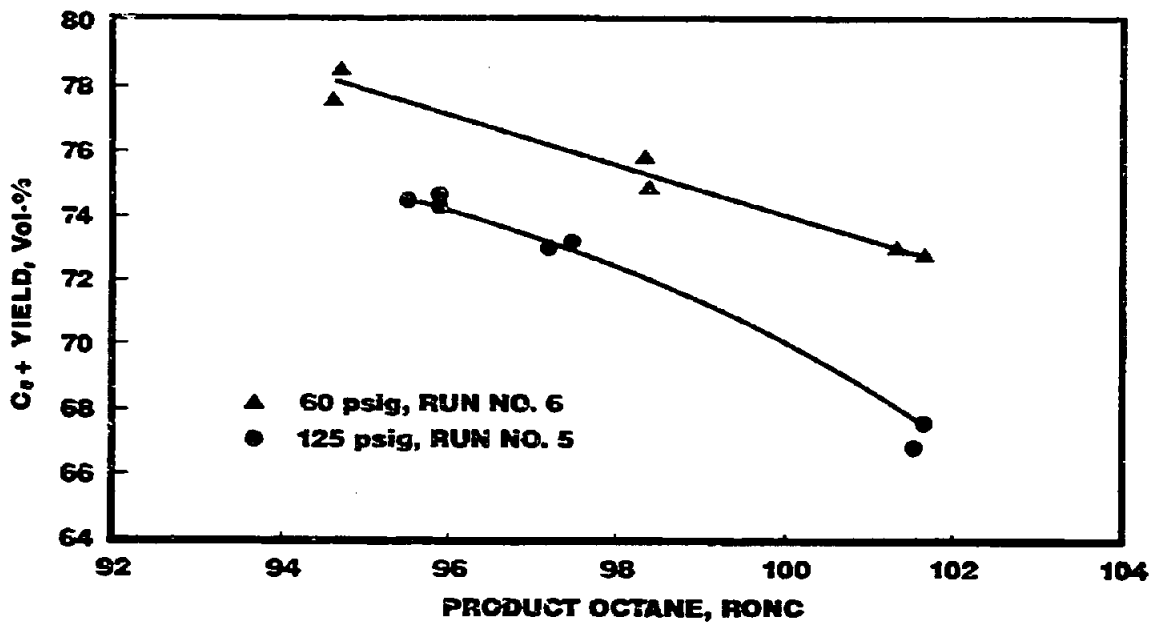
\* Runs 10 and 11 were light naphtha Platforming process runs.

TABLE 5.2

Comparison of Platforming Processes with Light Naphtha Feedstock

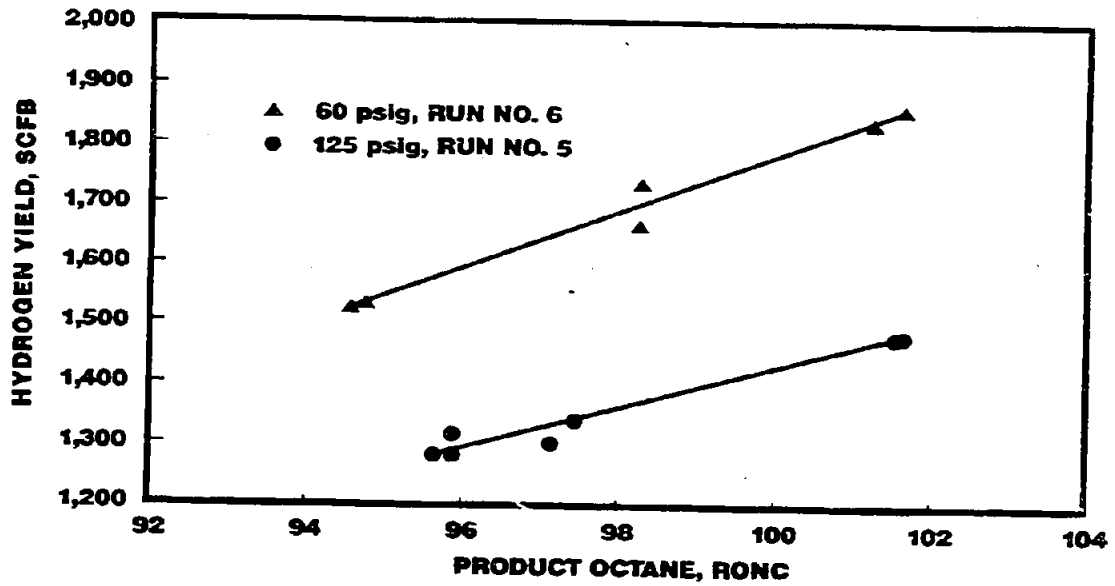
	<u>Low Pressure Platforming Process</u>	<u>Light Naphtha Platforming Process</u>
Run No.	7	11
Product RONC	101.1	104.3
C <sub>5</sub> + Yield, Wt-%	76.5	86.4
C <sub>5</sub> + Yield, Vol-%	71.8	70.9
H <sub>2</sub> Yield, SCFB	1,826	2,530

**FIGURE 5.1**  
**LIQUID-PRODUCT YIELDS**  
**FOR FBR ARGE NAPHTHA**



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UOP 1756-08

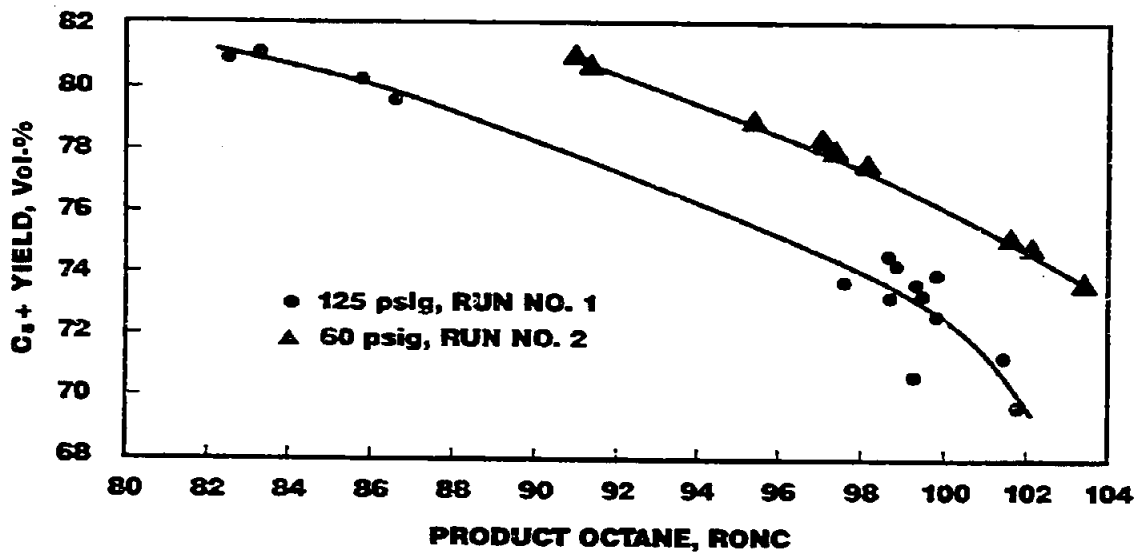
**FIGURE 5.2**  
**HYDROGEN YIELDS FOR FBR ARGE NAPHTHA**



UOP 177-15  
UOP 178-07

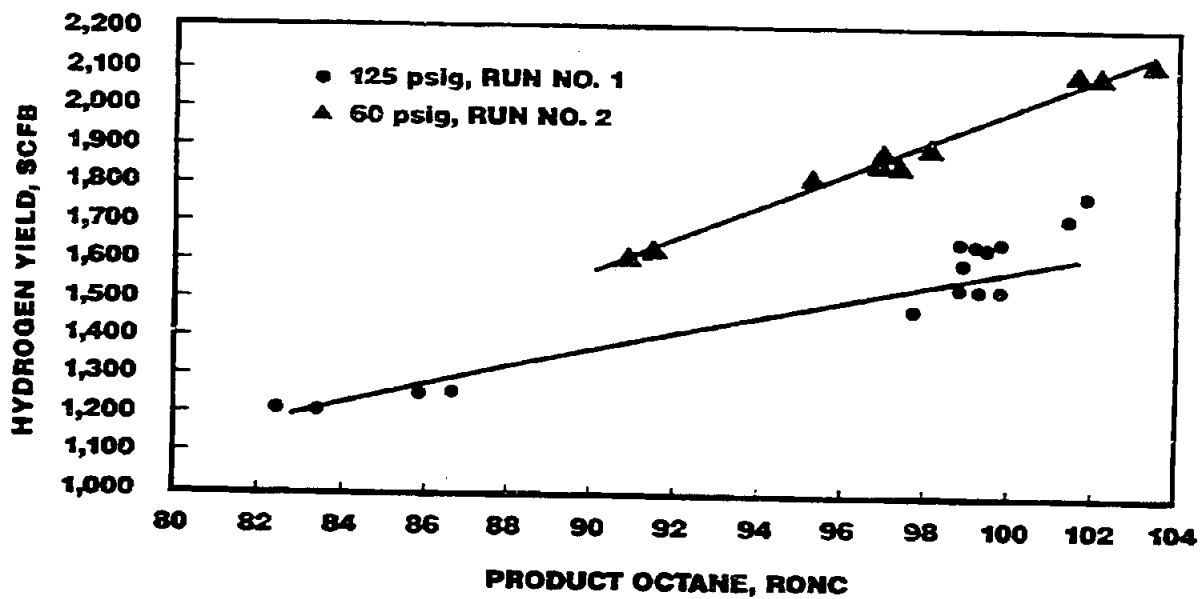


**FIGURE 5.3**  
**LIQUID-PRODUCT YIELDS**  
**FOR HEAVY ARGE NAPHTHA**



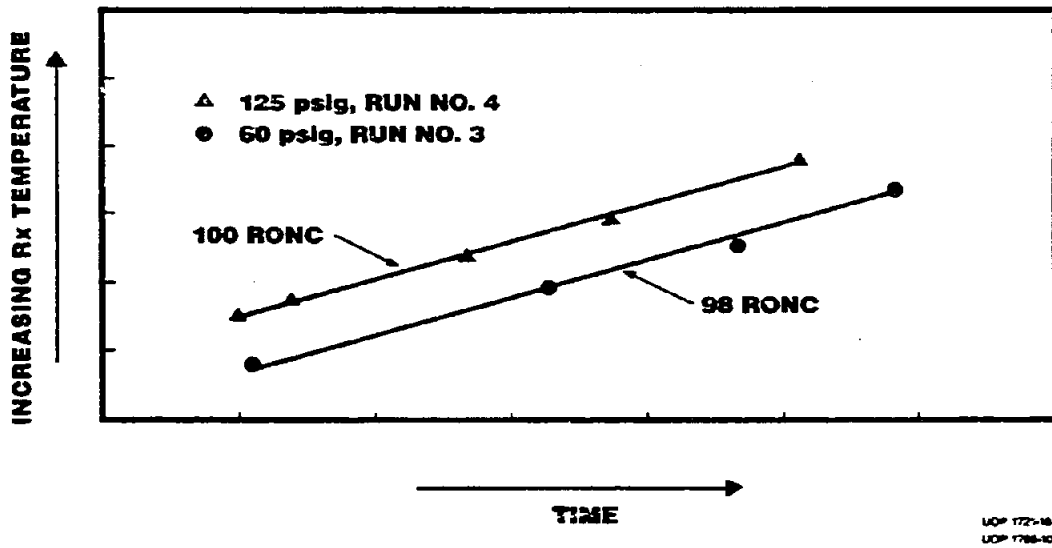
UOP 1721-35  
UOP 1726-06

**FIGURE 5.4**  
**HYDROGEN YIELDS**  
**FOR HEAVY ARGE NAPHTHA**

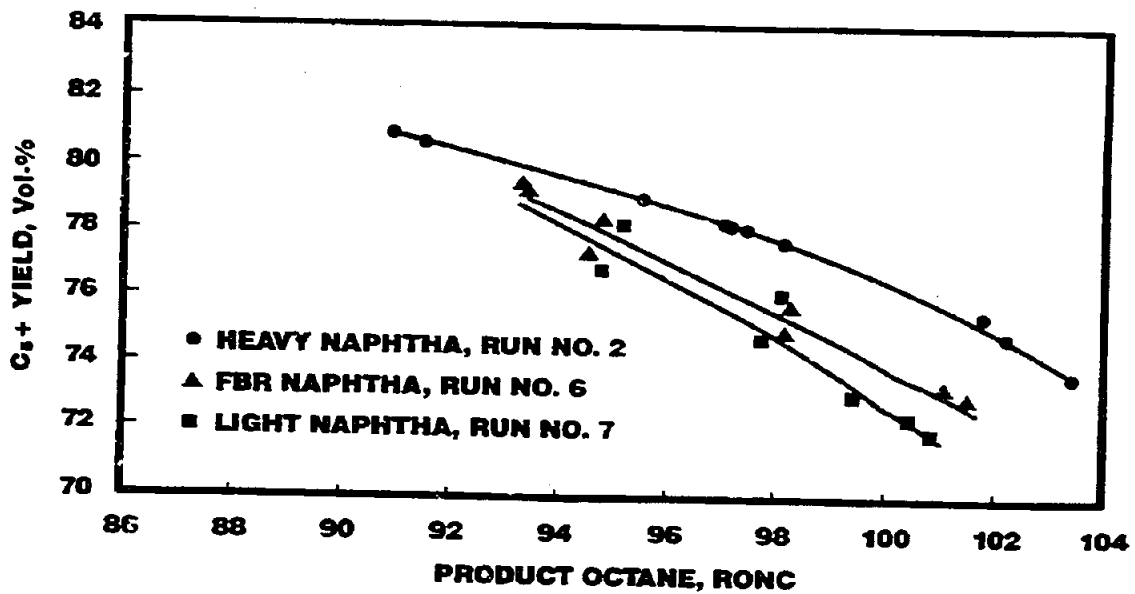


UOP 1724-27  
UOP 1796-06

**FIGURE 5.5**  
**STABILITY TESTS FOR HEAVY ARGE NAPHTHA**



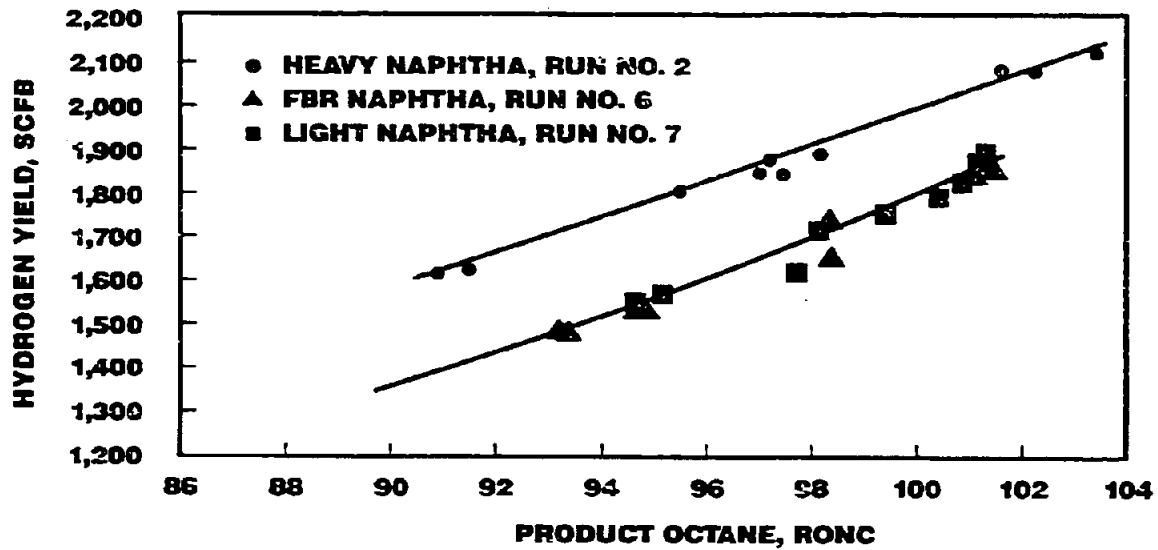
**FIGURE 5.6**  
**LIQUID-PRODUCT YIELDS**  
**FOR THREE ARGE NAPHTHAS**



ALL DATA AT 60 psig

UOP 1721-16  
UOP 1796-11

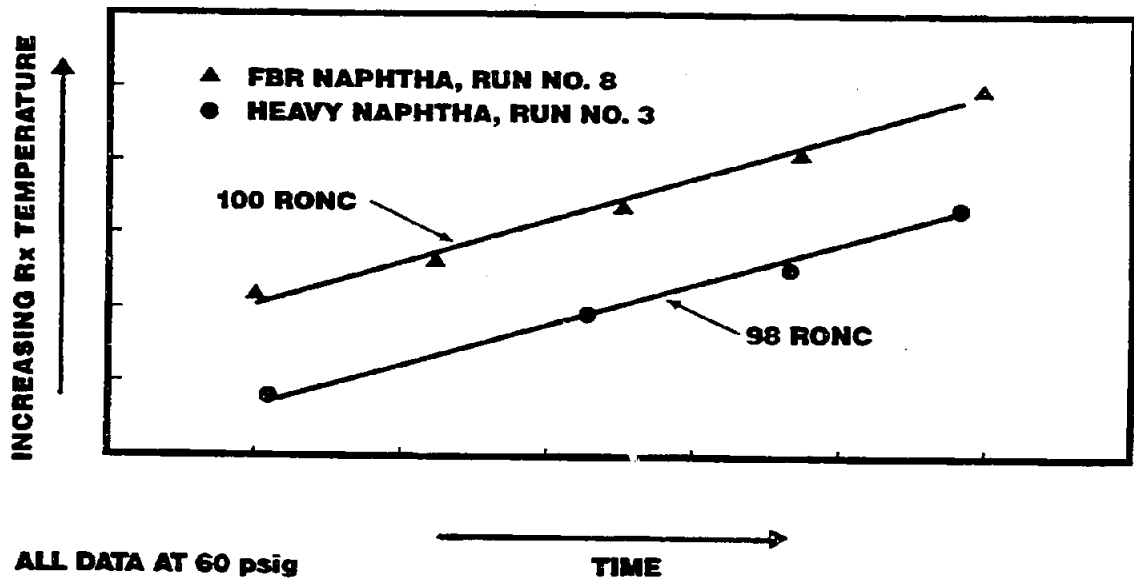
**FIGURE 5.7**  
**HYDROGEN YIELD**  
**FOR THREE ARGE NAPHTHAS**



ALL DATA AT 60 psig

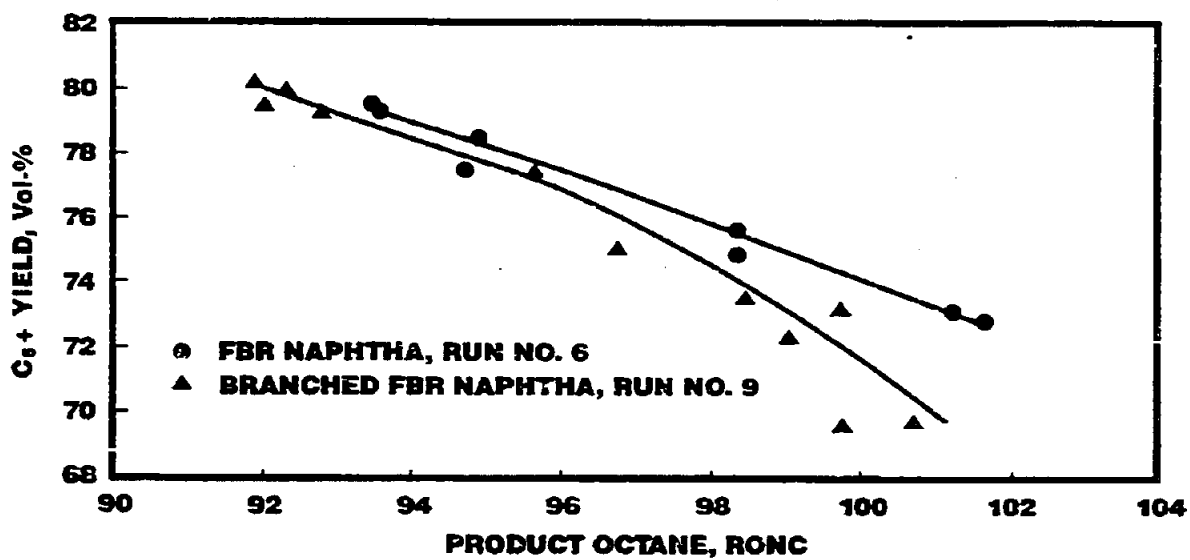
UOP 1721-25  
 UOP 1766-C

**FIGURE 5.8**  
**ARGE NAPHTHA STABILITY TESTS**



UOP 1721-B  
UOP 1785-C

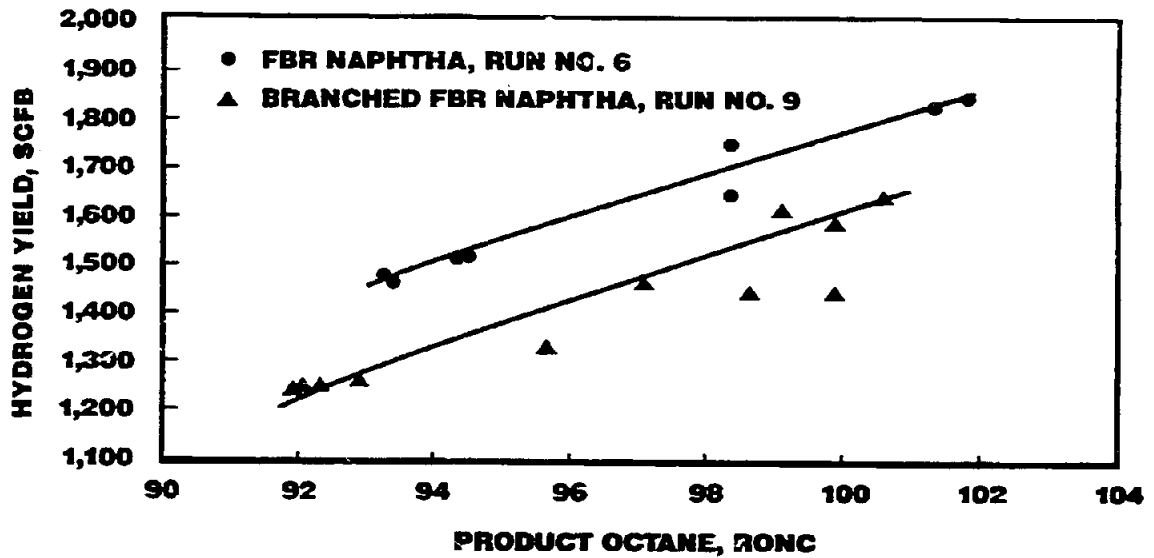
**FIGURE 5.9**  
**EFFECT OF BRANCHING**  
**ON LIQUID-PRODUCT YIELD**



ALL DATA AT 60 psig

UOP 172-17  
UOP 178-14

**FIGURE 5.10**  
**EFFECT OF BRANCHING**  
**ON HYDROGEN YIELD**



ALL DATA AT 60 psig

UOP 172-23  
UOP 179-15