FISCHER-TROPSCH NAPHTHA UPGRADING

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INTRODUCTION

UOP* is in the final phase of the Light Fischer-Tropsch Product Upgrading Program sponsored by the U.S. Department of Energy. Being evaluated is the potential for new petroleum-refining technologies used within a Fischer-Tropsch (F-T) upgrading complex. The goal is to maximize the yield of transportation fuel. The upgraded product may also find applications as petrochemical products.

Pilot-plant and economic studies were designed to evaluate two new commercial processes. Each process upgrades a different portion of the light products produced by an F-T reactor. The experimental program involves the Cyclar* and low-pressure CCR Platforming* processes. The Cyclar process is a one-step conversion of LPG into aromatics (1). The first commercial Cyclar unit is expected on-stream before the end of 1989. The low-pressure CCR Platforming process is an extension of existing commercial technology that is used to upgrade naphtha (2). Because this second-generation process operates at half the pressure of a typical first-generation unit, it achieves higher liquid-product yield for a given product octane.

RESULTS OF THE CYCLAR PROCESS STUDY

A separate topical report documents an 18-run Cyclar pilot-plant study completed within this program (3). The study demonstrates that the Cyclar process is a technically viable option up to a limit of about 65 wt-% olefins in the fresh feed. Olefins are desirable because they give higher liquid-product yields than do LPG paraffins. This higher yield permits more flexibility in choosing process conditions, particularly with respect to process pressure. The economic evaluation is based on yield, capital, and operating-cost estimates. In one case (a 5,675 MT/day F-T upgrading complex), a Cyclar unit contributes more than 640 MT/day (4,500 BPSD) of a high-octane (106 R+M/2), low-RVP (1.6 psia) aromatic product. This Cyclar unit also provides 1,200 SCF of hydrogen coproduct per barrel of LPG feed, or about 14 MM SCFD of hydrogen production at 95 vol-% purity. This volume of hydrogen is sufficient to change the upgrading complex from a consumer to a net exporter of hydrogen.

NAPHTHA UPGRADING

As shown in Table 1, straight-run F-T naphtha has low octane, is olefinic, and has high levels of oxygenates (4). Oxygenates would be acceptable in the finished gasoline, but they are not compatible with commercial reforming or isomerization technologies. Therefore, the first naphtha-upgrading step is hydrotreating to convert olefins and oxygenates to paraffins. This procedure differs from the typical petroleum refinery rationale of hydrotreating naphtha primarily to remove sulfur and nitrogen as well as trace olefins and oxygenates.

The two dominant processes for upgrading hydrotreated naphtha into high-octane gasoline are isomerization and reforming. Isomerization is most attractive when the naphtha has a large fraction of normal paraffins. Table 2 shows the differential between the pure-component octane of various hydrocarbons. Arge naphtha is a better isomerization feedstock than Synthol naphtha because the latter is already highly branched when it is produced in the F-T reactor (Table 1). Information in Table 2 also suggests why reforming naphtha to aromatics benefits the gasoline pool. All aromatics have high octane, but some isoparaffins are too low in octane to be useful for blending. Even if normal paraffins are recycled to the isomerization reactor, the gasoline pool still needs an aromatics source to meet today's octane requirements.

Reformer feed typically contains paraffins, naphthenes, and aromatics from petroleum naphtha. The higher the paraffin content, the more difficult the feed is to reform. Hydrotreated F-T naphtha is an extreme example of a lean naphtha. The leaner, or more paraffinic, the naphtha, the more difficult the maintenance of good liquid-volume yields at high octane.

UOP investigated two methods of improving F-T reforming yields. One method is to lower the operating pressure of the unit. Lower pressure improves yields, but it also increases catalyst-coking rates. Low-pressure CCR Platforming is specifically designed to accommodate higher catalyst-coking rates. The second method involves splitting the naphtha into two fractions and processing each portion in the most efficient process for that specific fraction. The C_6-C_8 portion is charged to a light-naphtha Platforming unit. This technology is tailored to convert light paraffins into aromatics. The two alternatives are illustrated in Figures 1 and 2.

Pilot-Plant Program

Raw naphtha was obtained from a commercial F-T facility. The naphtha was hydrotreated in a pilot plant and then batch fractionated in the laboratory. Full-boiling-range (FBR), heavy, and light naphtha cuts were produced (Table 3). Cutpoints were adjusted to give the desired carbon-number distribution. A branched FBR naphtha was prepared by blending hydrocracked naphtha from a previous program into a portion of the FBR naphtha described in the preceding section (5).

Ten pilot-plant runs were conducted (Table 4). One objective of this program is to quantify the C_5+ and hydrogen yield advantage obtained at lower reforming pressure. Yield advantages at low pressure are illustrated for the FBR (Figures 3 and 4) and heavy naphthas (Figures 5 and 6). Catalyst stability for the heavy-naphtha cut was tested at each pressure (Figure 7). At a similar deactivation rate, the higher-pressure operation had an octane-number advantage of 2, and 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 No. 3 in Figure 7 would be greater.

The effect of molecular weight on yields was as expected (Figures 8 and 9). 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 10). At the same octane, this differential translates 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. However, the branched feedstock blend has a lower yield compared with FBR naphtha when octane is pushed over 96 RONC (Figures 11 and 12).

Yields produced by the light-naphtha Platforming and low-pressure CCR Platforming processes with the same light feed are compared in Table 5. The light-naphtha Platforming process makes a more-aromatic, higher-octane product than does the low-pressure CCR Platforming process. The light-naphtha Platforming process also provides higher hydrogen and C_5+ 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, which is obtained by multiplying the product octane and volumetric yield, is of course greater for the light-naphtha Platforming process.

Current Efforts

Pilot-plant data are being used to generate commercial yield, capital, and operating estimates. These estimates will be integrated to help the refiner choose between the two naphtha-processing options illustrated in Figures 1 and 2. Splitting the naphtha will result in higher octane and/or yield, but no one knows yet whether the additional capital is justified. Economic recommendations will be made at the end of the program.

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* CCR, CCR Platforming, Cyclar, Platforming, and UOP are trademarks and/or servicemarks of UOP.

REFERENCES

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2. R. W. Bennett, R. L. Peer, and S. T. Bakas, "Advances in CCR Platforming: The Second Generation," presented at the NPRA Annual Meeting, San Antonio, TX, Mar. 20-22, 1988.

3. J. H. Gregor, C. D. Gosling, and H. E. Fullerton, "Cyclar Topical Report," Contract DE-AC22-86PC90014, Dec. 1989.

4. M. E. Dry, "Sasol's Fischer-Tropsch Experience," Hydrocarbon Processing (Aug. 1982):121-24.

5. "Fischer-Tropsch Wax Characterization and Upgrading Final Report," Contract No. DE-AC22-85PC80017, June 6, 1988.

Table 1

Commercial F-T Naphtha Descriptions

	Arge	Synthol
Product, Wt-%		
Normal Paraffins	57.0	7.7
Branched Paraffins	3.0	6.3
Olefins	32.0	65.0
Aromatics	0.0	7.0
Alcohols	7.0	6.0
Ketones	0.6	6.0
Acids	0.4	2.0
	100.0	100.0

Paraffin Breakdown, Wt-%

	Arge	Synthol
Normal Paraffins	95	55
Branched Paraffins	5	45
	100	100

Table 2

Pure-Component Octane Values

Carbon No.	Compound	Normal Paraffin	Branched Paraffin	Aromatic
5	n-Pentane	61.7	-	-
5	2-Methylbutane	-	92.3	-
5	2,2-Dimethylpropane	-	85.5	-
6	n-Hexane	24.8	-	-
6	2-Methylpentane	-	73.4	-
6	3-Methylpentane	-	74.5	-
6	2,2-Dimethylbutane	-	91.8	-
6	2,3-Dimethylbutane	-	103.5	-
6	Benzene	-	-	115.0
7	n-Heptane	0.0	-	-
7	2-Methylhexane	-	42.4	-
7	3-Methylhexane	-	52.0	-
7	2,2-Dimethylpentane	-	92.8	-
7	2,4-Dimethylpentane	-	83.1	-
7	2,2,3-Trimethylbutane	-	112.1	-
7	Toluene	-	-	120.1
8	n-Octane	-19.0	-	-
8	2-Methylheptane	-	21.7	-
8	4-Methylheptane	-	26.7	-
8	2,2-Dimethylhexane	-	72.5	-
8	2,5-Dimethylhexane	-	55.5	-
8	2,2,4-Trimethylpentane	-	100.0	-
8	Ethylbenzene	-	-	107.4
8	1,3-Dimethylbenzene	-	-	117.5
8	1,4-Dimethylbenzene	-	-	116.4
8	1,2-Dimethylbenzene	-	-	100.0
9	n-Nonane	-17.0	-	-
9	2 Methyl Octane	-	0.0	-
9	4 Methyl Octane	-	4.8	-
9	2,2 Dimethyl Heptane	-	50.3	-
9	2,2,5 Trimethyl Hexane	-	92.0	-
9	Tetramethyl Pentane	-	116.8	-
9	n-Propylbenzene	-	-	111.0
9	i-Propylbenzene	-	-	113.1

Source: J. E. Brown, K. W. Greenlee, and E. M. Tindall, "Octane Numbers of Pure Hydrocarbon Blends and Their Relationship to Precombustion Reactions," May 16, 1962.

Table 3

Pilot-Plant Feedstock Summary

	Arge FBR	Arge Heavy	Arge Light	Branched FBR
Properties				
Carbon No. Target	C_6-C_{11}	C_9-C_{11}	C_6-C_8	C_6-C_{11}
Relative Density, g/ml	0.7070	0.7317	0.6899	0.7032
API Density	68.6	61.9	73.6	69.7
RONC	<40	<40	<40	<40
MONC	<40	<40	<40	<40
Distillation, °C				
IBP	81	153	72	5
10%	97	157	88	77
25%	110	159	93	100
50%	129	163	103	123
75%	158	170	114	150
90%	175	178	122	169
EP	194	197	143	198

Table 4

Pilot-Plant Program Description

Run No.	Feedstock	Pressure, psig	Test Type
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	Arge Light	-	Light-Naphtha Platforming

Note: Runs 1-9 were Platforming process pilot-plant runs.
Run 10 was a light-naphtha Platforming pilot-plant run.

Table 5

	Low-Pressure Platforming Process	Light-Naphtha Platforming Process
Run No.	7	10
Product RONC	101.1	103.9
C_5+ Yield, Wt-%	76.5	85.7
C_5+ Yield, Vol-%	71.8	71.1
H_2 Yield, SCFB	1,326	2,431

FIGURE 1

FULL-BOILING-RANGE NAPHTHA PROCESSING

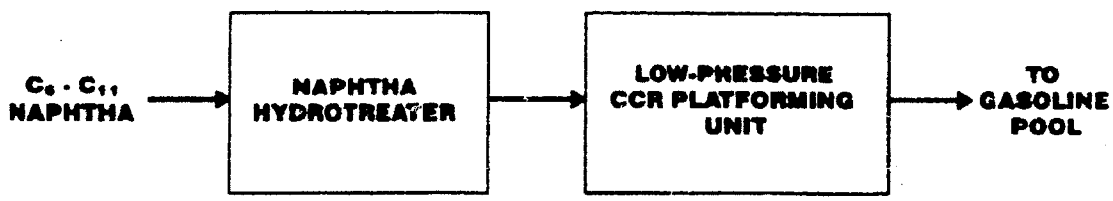

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FIGURE 2

SPLIT-NAPHTHA PROCESSING

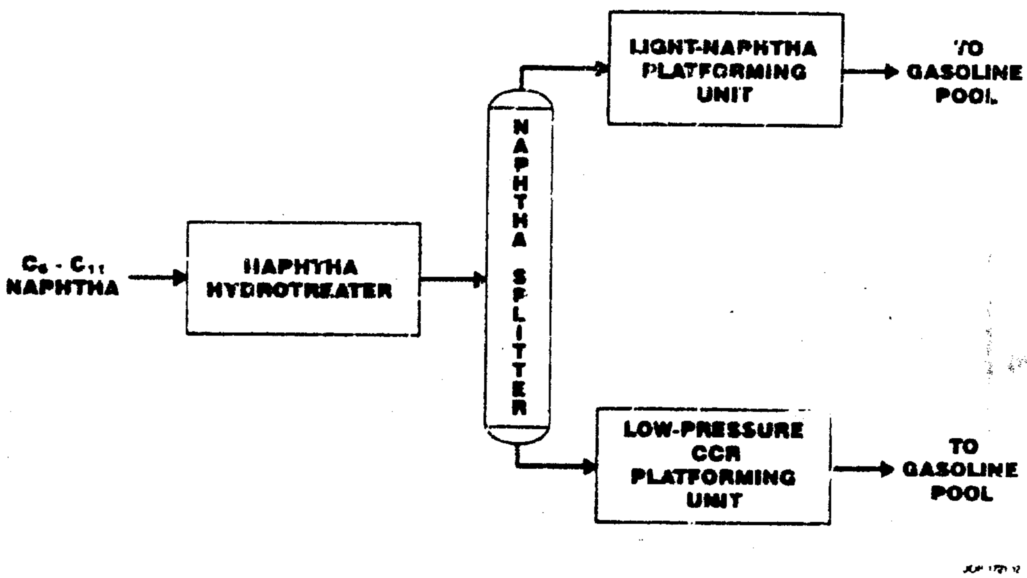


FIGURE 3

LIQUID-PRODUCT YIELDS FOR FBR ARGE NAPHTHA

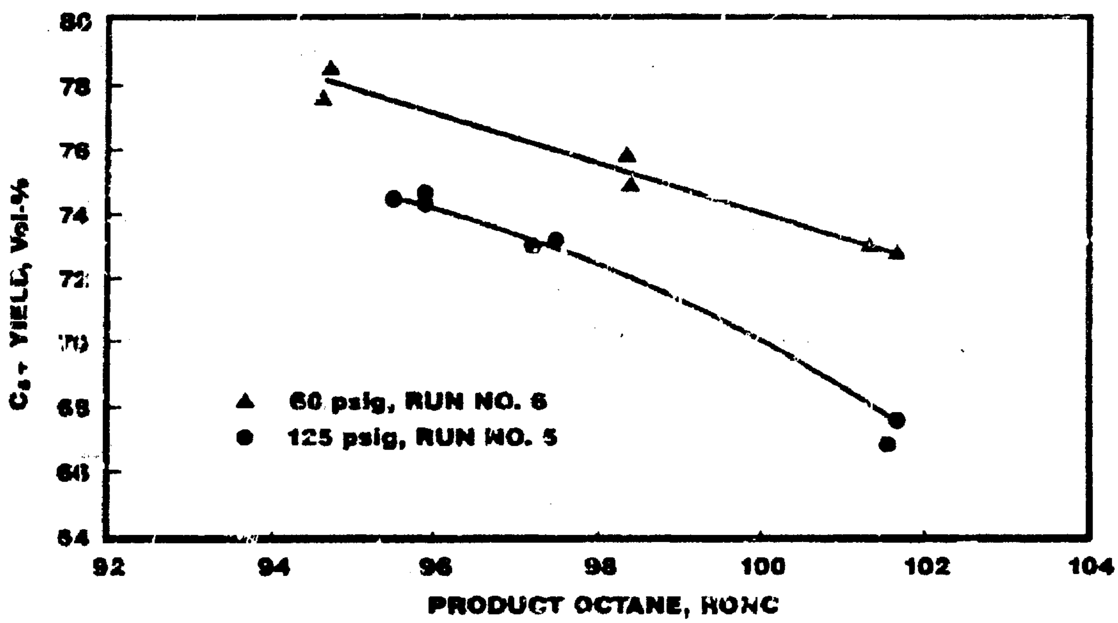


FIGURE 4

HYDROGEN YIELDS FOR FBR ARGE NAPHTHA

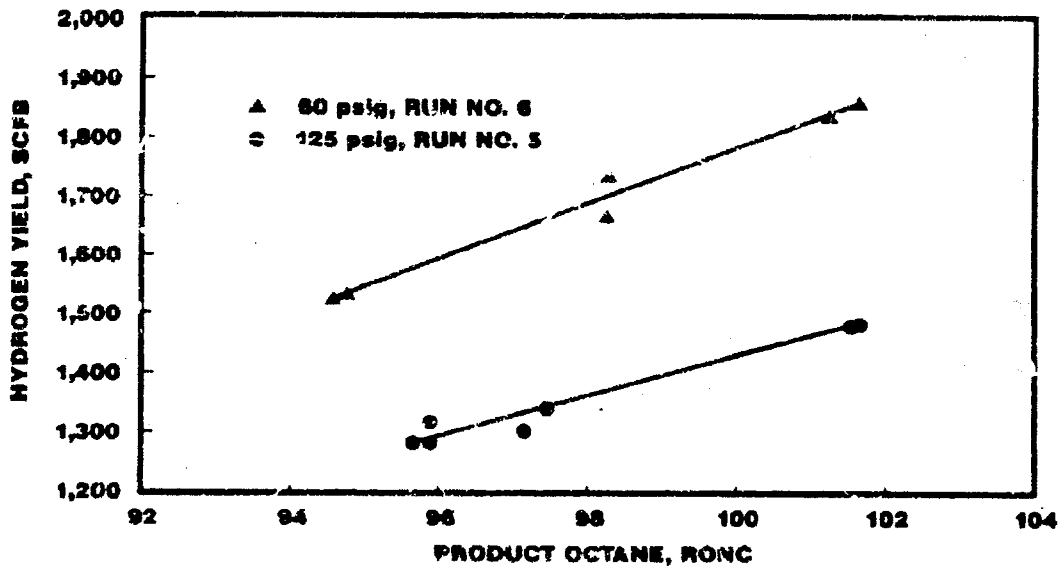


FIGURE 5

LIQUID-PRODUCT YIELDS FOR HEAVY ARGE NAPHTHA

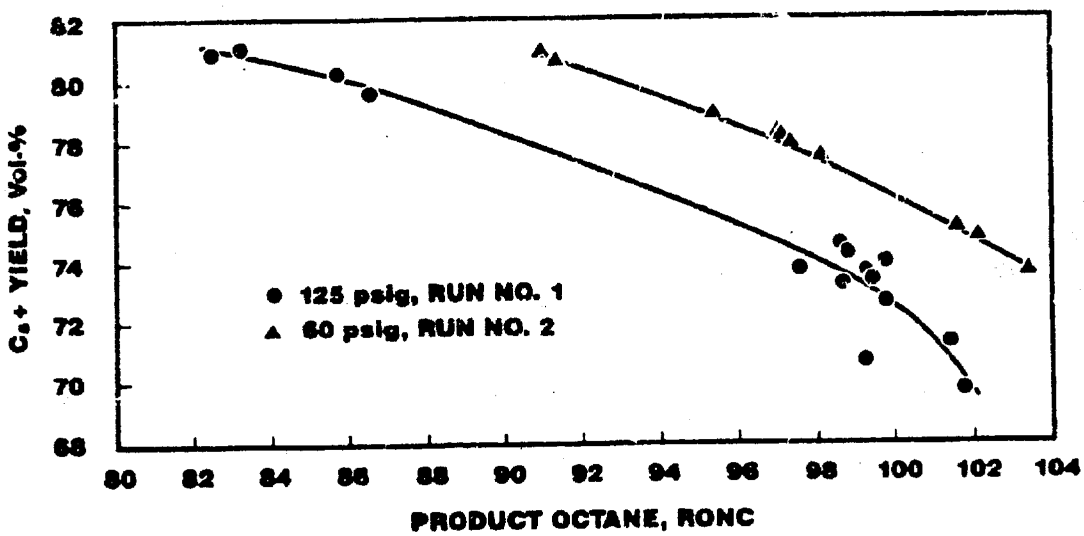


FIGURE 6

HYDROGEN YIELDS FOR HEAVY ARGE NAPHTHA

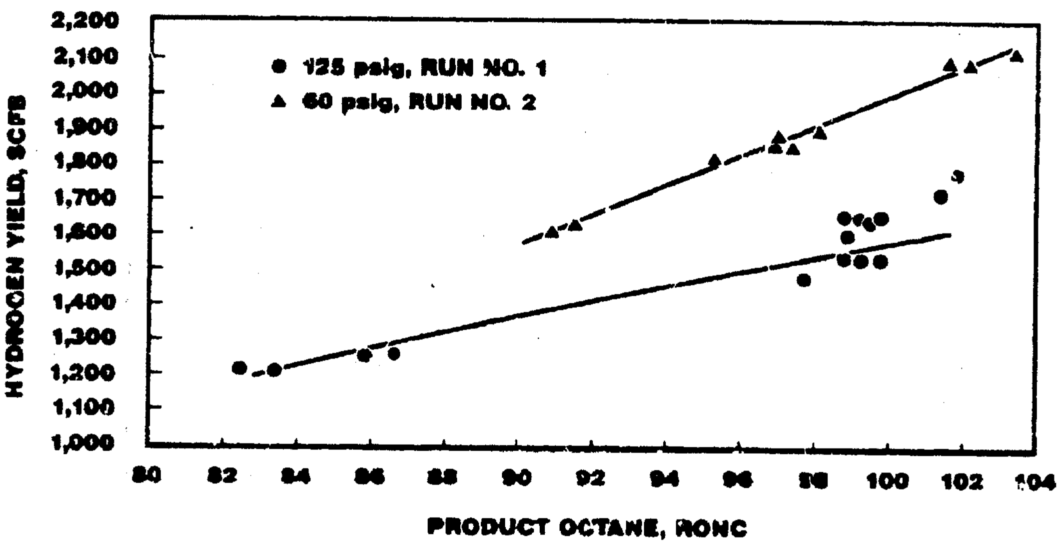


FIGURE 7

STABILITY TESTS FOR HEAVY ARGE NAPHTHA

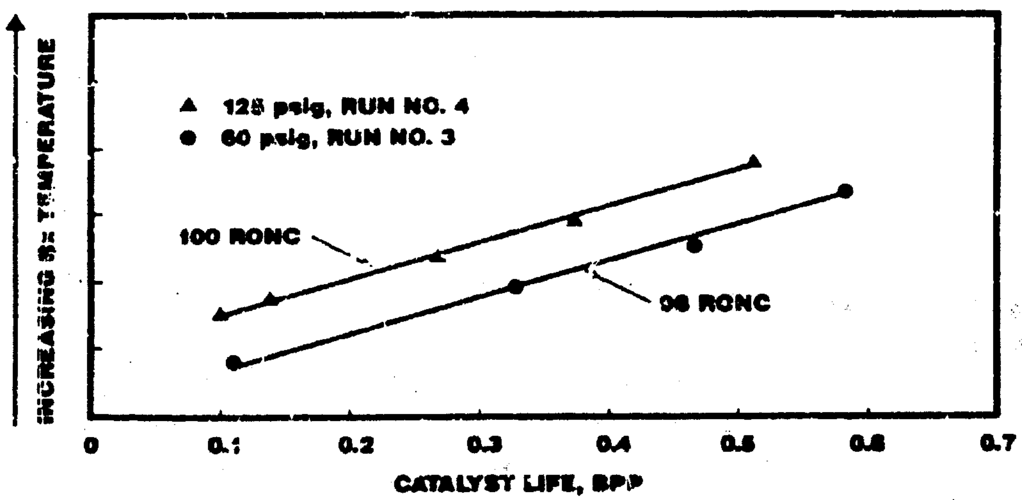
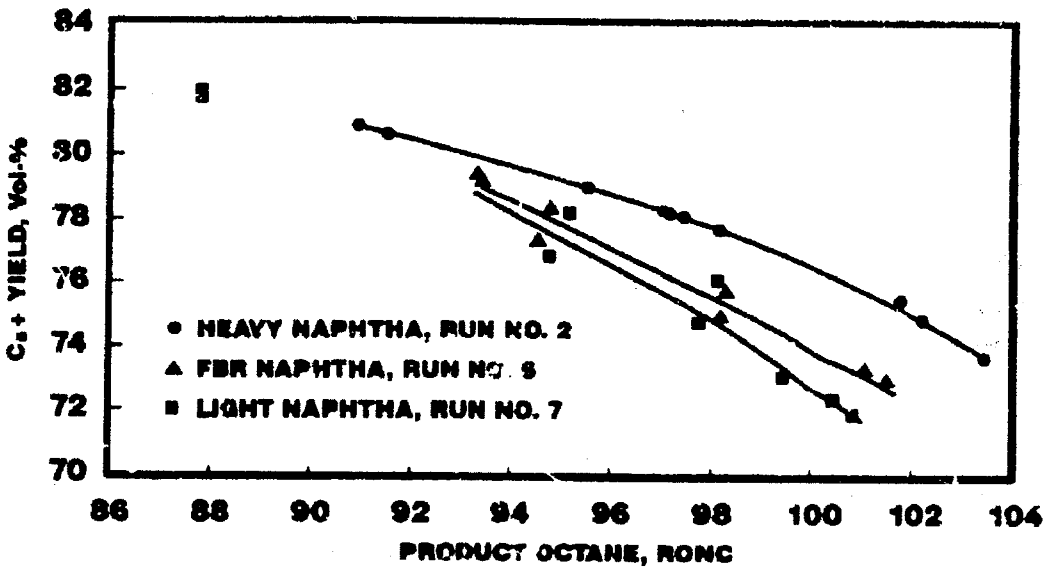


FIGURE 8

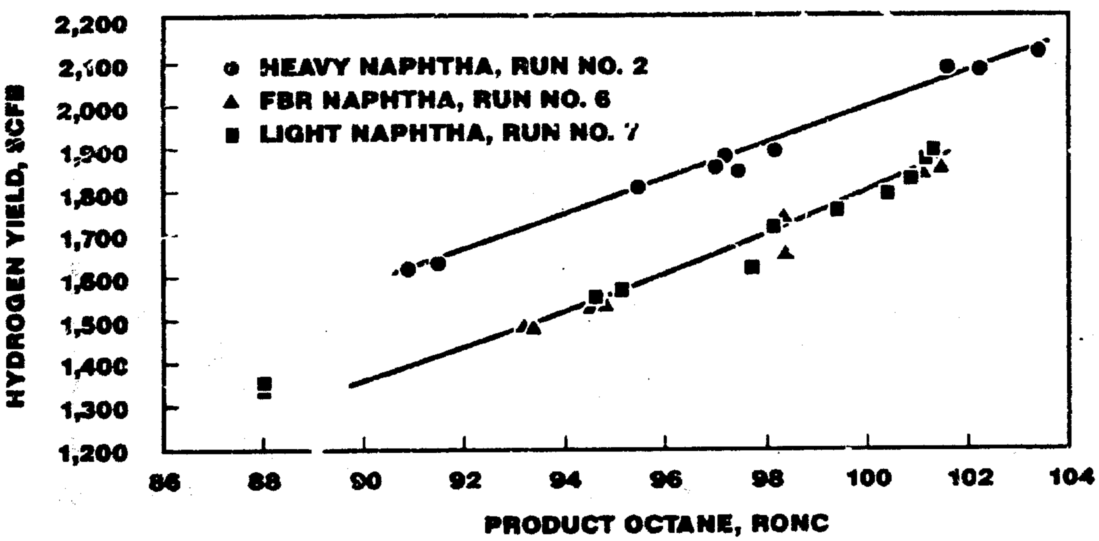
LIQUID-PRODUCT YIELDS FOR THREE ARGE NAPHTHAS



ALL DATA AT 60 psig

FIGURE 9

HYDROGEN YIELD FOR THREE ARGE NAPHTHAS



ALL DATA AT 60 psig

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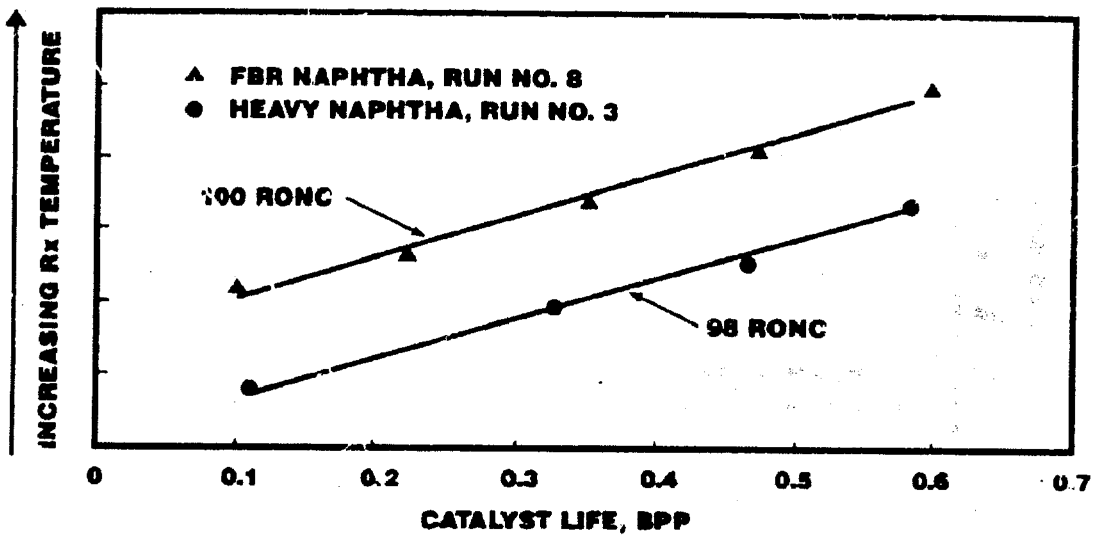
FIGURE 10

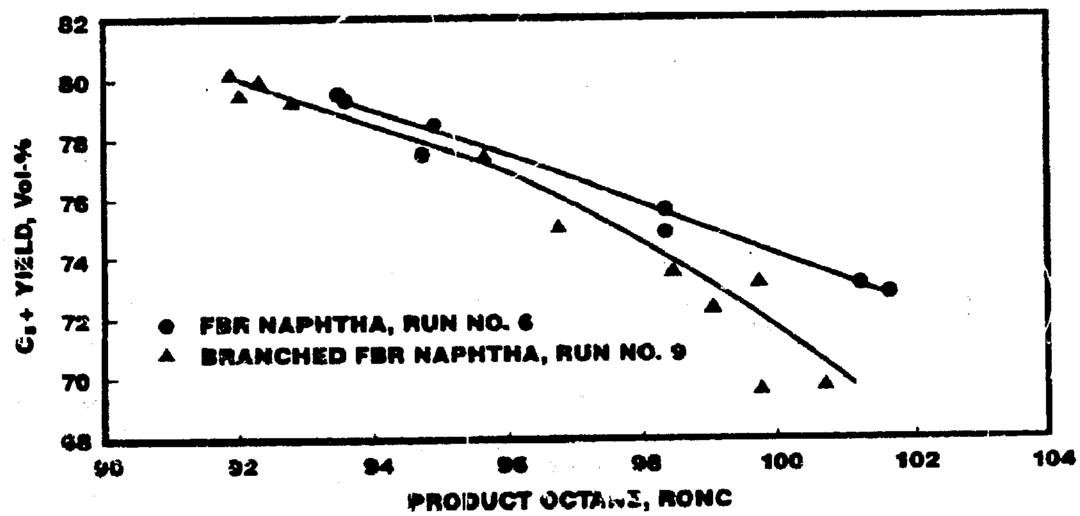
ARGE NAPHTHA STABILITY TESTS



ALL DATA AT 60 psig

FIGURE 11

EFFECT OF BRANCHING ON LIQUID-PRODUCT YIELD



ALL DATA AT 60 psig

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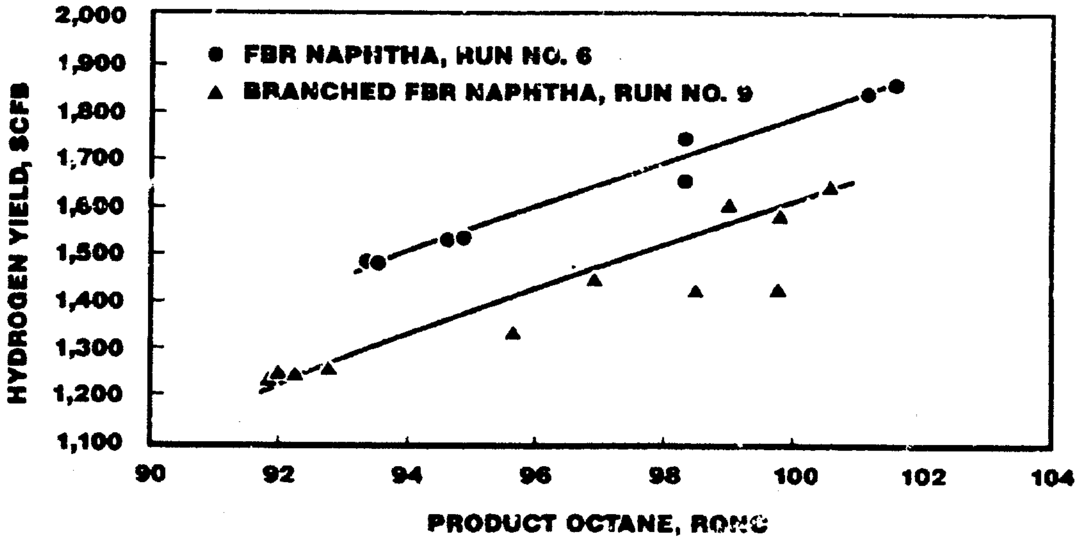
FIGURE 12

EFFECT OF BRANCHING ON HYDROGEN YIELD



ALL DATA AT 60 psig