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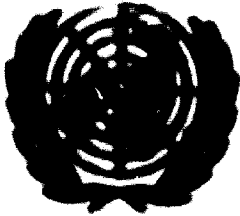
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Expert Group Meeting on Transfer of Knowledge
in Production and Use of Catalysts

Tehran, Iran, 26 - 30 June 1972

REPORT OF ANALYTICAL AND CATALYTIC RESEARCH

BY PETROLEUM RESEARCH

by

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INTRODUCTION:

Eighty percent of benzene (1), ninety-six percent of toluene (2) and ninety-eight percent of C_8 aromatics (3) in the world are produced from petroleum fractions. Catalytic reforming of petroleum fractions over platinum catalyst is the main source of these products in petroleum industries. Much work has been carried out on preparation of benzene (4, 546), toluene (7, 105) and C_8 aromatics (10, 11412) from catalytic reforming of petroleum fractions.

In this work data are presented from a catalytic reforming pilot-plant on two fractions at different reaction temperatures and pressures to optimize process variables. Some correlation curves on the yield of hydrogen, methane, ethane, propane and heavier than hexane (C_6) useful for design of commercial catalytic reforming unit are obtained.

Based on the reaction models suggested previously, in this experiment using the specific feedstock compositions, a reaction model is presented.

It is learned, there is always a limit of low pressure for operation of reforming conditions beyond which platinum catalyst deactivates rapidly.

Among the total conversion taken place in the experiment dehydrocyclization of paraffins are investigated. Even under very severe catalytic reforming conditions a small portion of naphthene

hydrocarbons remains unchanged.

EXPERIMENTAL:

The two gasoline fractions containing C_5-C_7 and C_7-C_9 hydrocarbons were respectively prepared from Agp-Jari and Jhama crude oil in a packed column atmospheric distillation pilot-plant having a still capacity of 200 litres.

The impurities of each fraction were removed over a white-naphthene catalyst (physical and chemical properties of the catalyst are given in table 2) in a hydrocracking pilot-plant. The operating conditions of hydrocracking unit were adjusted to remove sulfur and other impurities such as metals, nitrogen and oxygen to the level which is desirable for our catalytic reforming catalyst. Several test runs were carried out over white-naphthene catalyst. The optimum conditions obtained for removing impurities were as follows :

Table 1. Properties of feedstocks before and after hydrocracking

	<u>Lighter Fraction</u>		<u>Heavier Fraction</u>	
	<u>Before H.T.</u>	<u>After H.T.</u>	<u>Before H.T.</u>	<u>After H.T.</u>
Sp. Gr. at 60/60°	0.720	0.726	0.7422	0.7432
Sulfur content ppm	212.0	17.0	155.0	0.0
Viscosity No. @ 100ps.	-	-	0.75	0.0
R. V. P. gal/g	2.5	4.5	2.0	1.5
Color no. IS clear	53.4	56.4	47.0	90.0
<u>ASTM Distillation °C</u>				
IBP	95.0	96.5	106.5	107.5
5 vol. % recovered	95.5	96.0	100.0	100.5
10	96.0	96.5	110.0	111.5
20	96.5	97.0	112.5	113.0
30	97.0	97.5	114.5	114.5
40	97.5	98.5	117.0	117.0
50	98.5	99.0	120.5	120.0
60	99.5	100.0	122.0	122.5
70	100.5	101.0	125.0	125.0
80	102.5	103.5	131.0	131.0
90	107.5	110.5	137.0	137.0
95	115.5	123.5	143.0	142.5
FBP	140.0	130.5	153.0	153.0
<u>Hydrocarbon-Type Analysis</u> Vol. %				
Naphthenes	36.5	37.5	-	10.0
Aromatics	7.0	7.5	-	11.0
Paraffins	-	-	-	(0.20)
Diene	-	-	-	(5.20)
Cyc	-	-	-	(7.60)
Paraffins	56.5	55.5	-	60.0
Olefins	4.0	0.0	-	0.0

**Table 1. Interactions and Molecular Weights toward
"PES-4151"**

		Hydroxy-terminated Catalyst	Acid-terminated Catalyst
		wt. %	wt. %
Physical Properties			
Surface area	m ² /g	240	120
Pore density	cm ³ /g	0.50	0.75
Pore volume	cm ³ /g	0.65	0.52
Crushing strength	kg	0.0	-
Chemical Composition			
H	wt. %	-	0.0
Cl		-	0.5
F		-	0.4
Aluminum		by diff.	by diff.
Na ₂ O		12.0	-
CaO		3.5	-
Na ₂ P		0.09	200 ppm
P ₂ O ₅		0.05	500 ppm
Moisture loss at 150°C		10	0.50

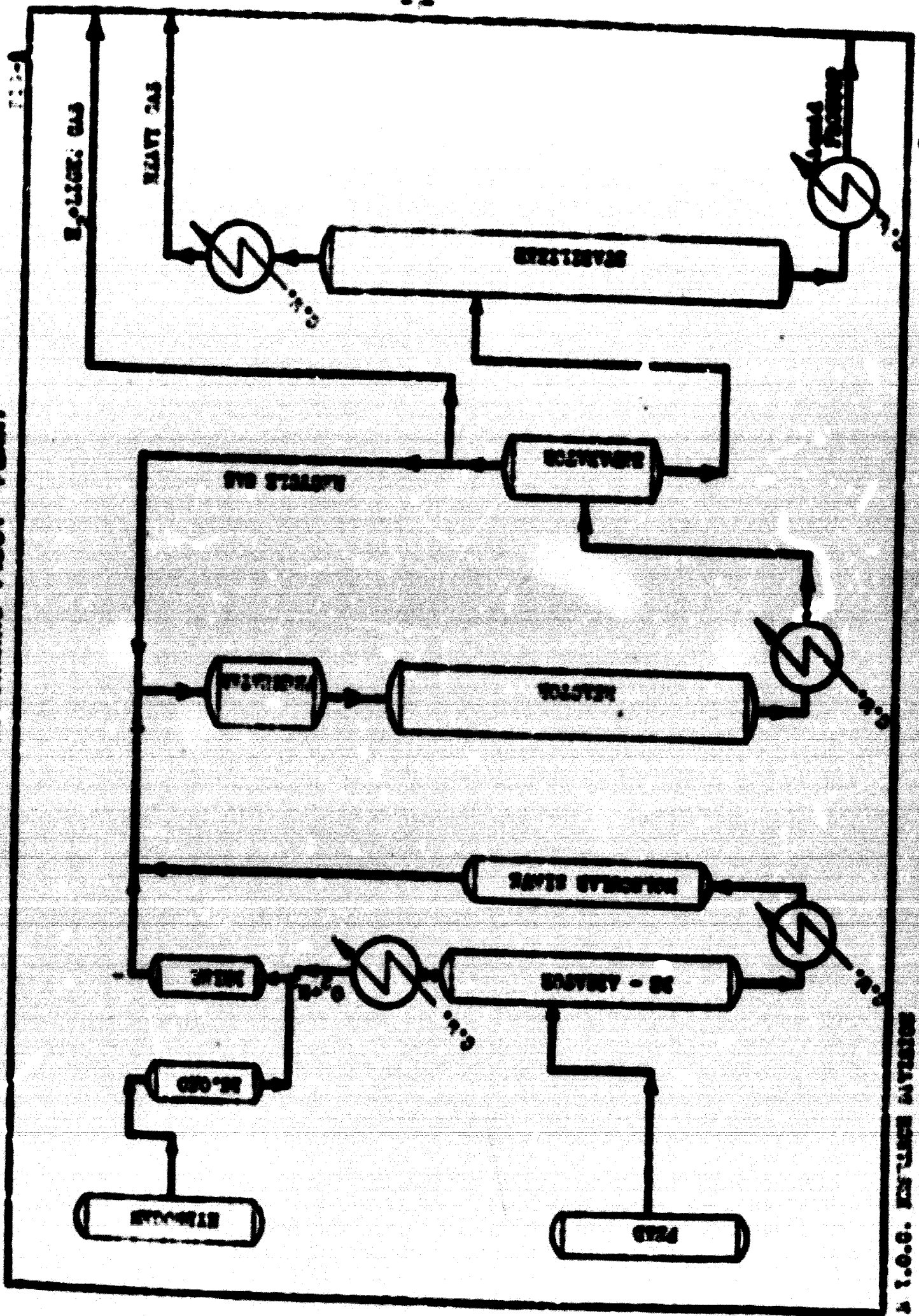
Reactor temperature	175°C
Reactor pressure	30 kg/cm ²
LHSV hr ⁻¹	1.2
Hydrogen to Hydrocarbon	70:1 v/v

The specifications of feedstock before and after hydrotreating are shown in table 1.

The reforming study was carried out over a platinum catalyst with 0.001% platinum (typical and chemical properties of the catalyst are given in table 2) in a catalytic reforming pilot-plant having capacity of 24 liters/day. A simplified process flowdiagram is given in Figure 1 (15). Fresh hydrogen with 99.999 percent purity was prepared from a hydrogen plant for start-up of this unit and also for operation of hydrotreating unit. The liquid feed after hydrotreating was continuously stripped of dissolved air in a packed column. The reactor was operated to maintain isothermal conditions throughout the catalyst bed.

Gas and liquid analyses were carried out by a Varian Aerograph with 20% 10% and glycol of 30% packed column and length of 16.5 and 9.0 ft respectively. Nitrogen was used as carrier gas for both analyses.

CATALYTIC REFORMING PILOT - PLANT



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RESULTS AND DISCUSSION

Different reforming conditions were studied for the two mentioned fractions. The range of 400 to 520°C temperature and 20 to 25 kg/cm² pressure with hydrogen to hydrocarbon mole ratio from 1.0:1.0 to 6.0:1.0 and liquid hourly space velocity around 2.0 and also specifications of products with 10-15 analysis of aromatic compositions are given in table 3 for 10-140°C fraction. The same data are given in the range of 400 to 520°C temperature and 20 to 25 kg/cm² pressure with hydrogen to hydrocarbon mole ratio from 7.0:1.0 to 9.0:1.0 and liquid hourly space velocity around 2.0 for 150 to 180°C fraction in table 4.

Calculation of material balances was carried out by the aid of a digital computer on the above test runs. Curves on the yield of C₁, C₂, C₃, C₄, iC₄, nC₄, iC₅, nC₅, and C₆+ are shown in Figure 2 & 3.

The yield of total aromatics, toluene, C₉ aromatics and yield-temperature relationship at different reforming conditions are given in Figure 4, 5 & 6.

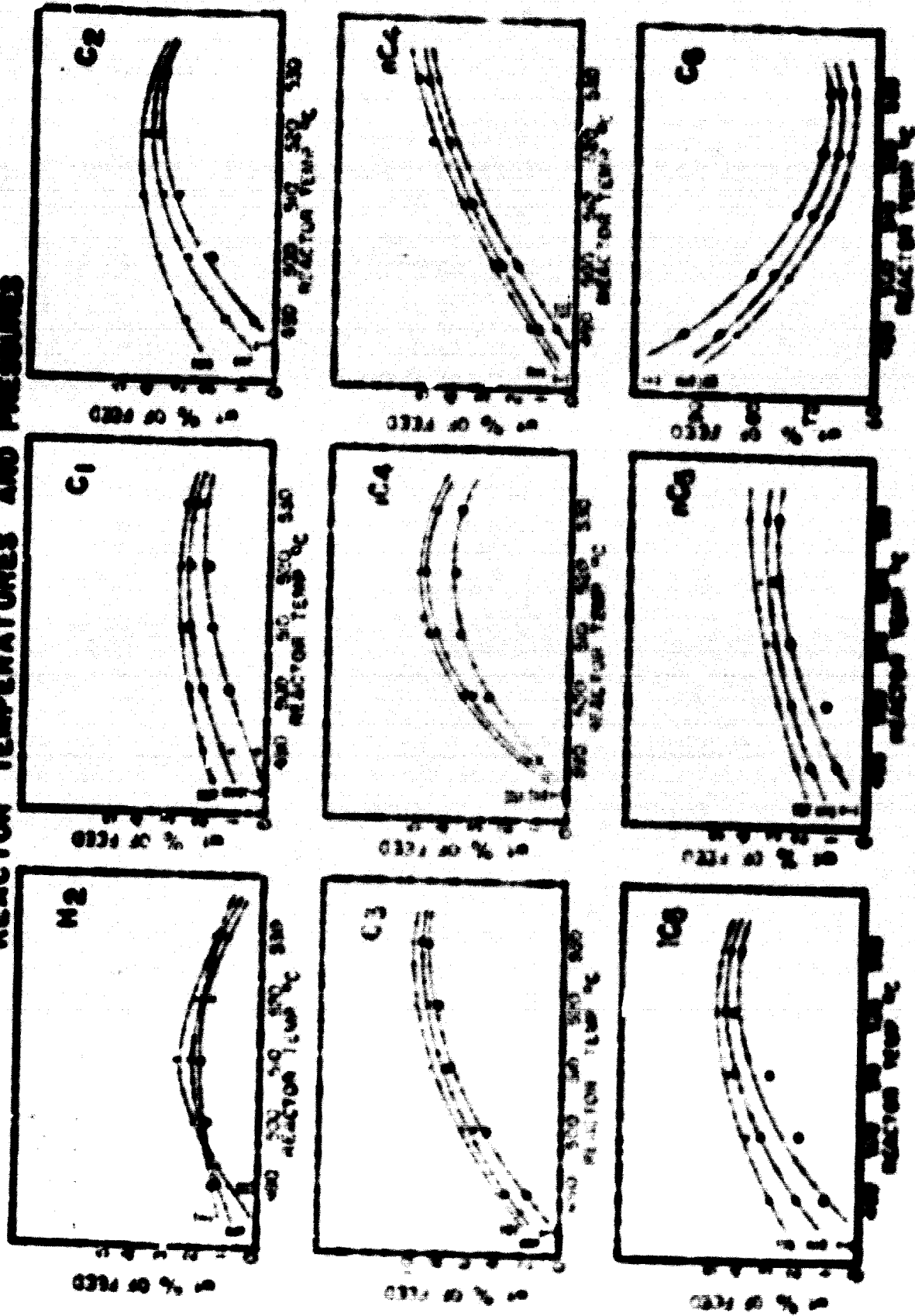
Production of hydrogen was maximum at 510°C temperature under experimental pressure for lighter fraction and temperature of 490°C for heavier fraction. However the maximum yield of hydrogen in all cases was 1700 vol./vol of feed at 510°C and 20 kg/cm² for lighter fraction.

Table 3 - Reactor Conditions and Products

CONDITIONS	Case 1					Case 2					Case 3				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
STARTING TEMPERATURE °C	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
REACTOR PRESSURE (kg/cm ²)	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
LIQUID BULKY SPACE															
W/CRTG hr ⁻¹	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15	2.15
DIAPHRAGM TO REACTOR	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
DIAPHRAGM	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
SPUR. at 60/100°	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733
WATER NUMBER P2 above	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3	70.3
60% DIAPHRAGM															
10%	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0	48.0
20%	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
30%	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0
40%	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5	95.5
50%	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
60%	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5	100.5
70%	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7	105.7
80%	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5
90%	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0	102.0
100%	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Volume	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.7
Volume - Diaphragms	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
C ₂ Armatage	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Total Armatage	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
Total Diaphragms	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
Total Porosity	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7

FIGURE 2

YIELDS OF H_2 , C_1 , C_2 , ... AND C_6^+ AT VARIOUS REACTOR TEMPERATURES AND PRESSURES



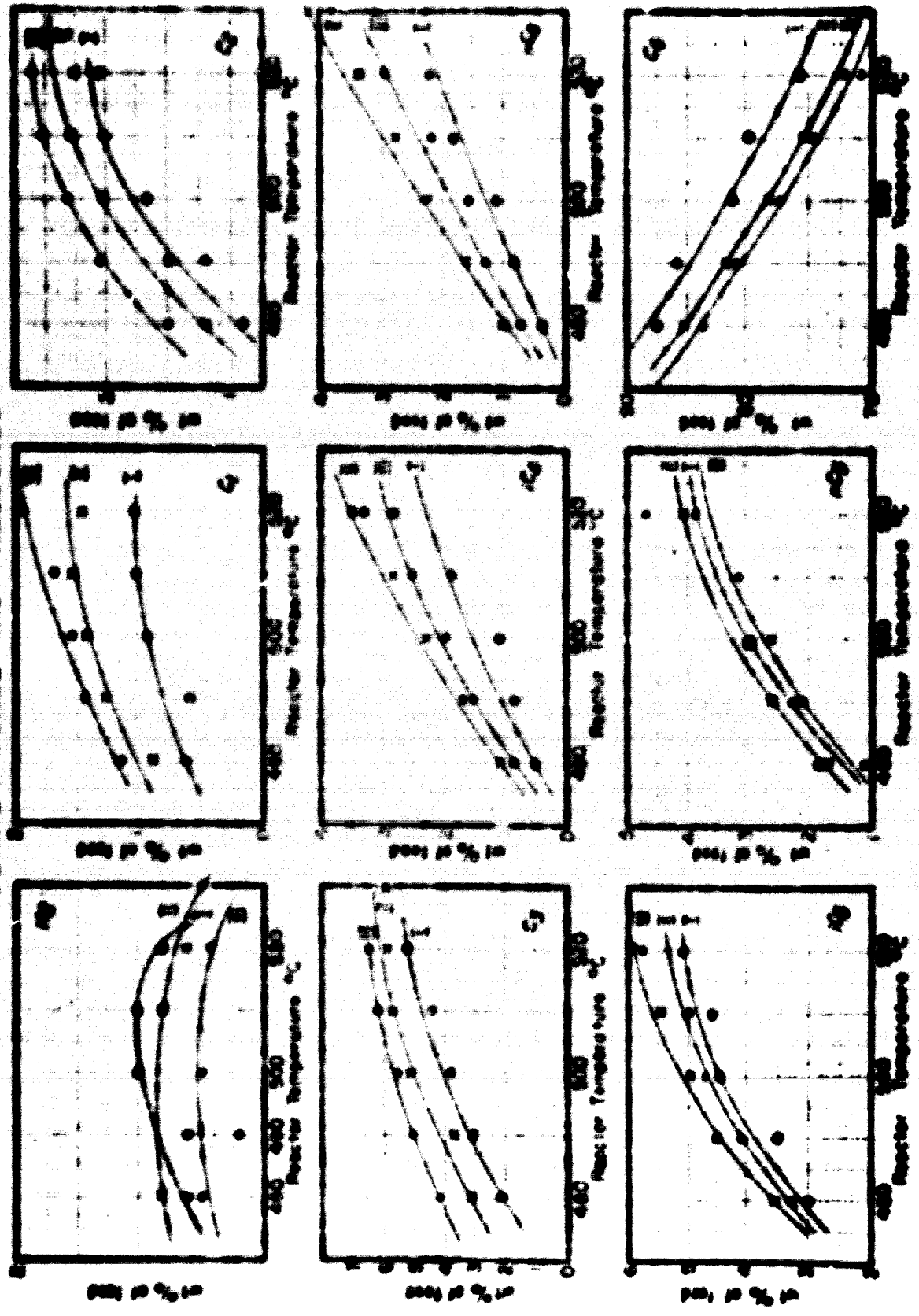
LEGEND

- I. 10 atm
- II. 20 atm
- III. 30 atm

1.00 atm
2.00 atm
3.00 atm

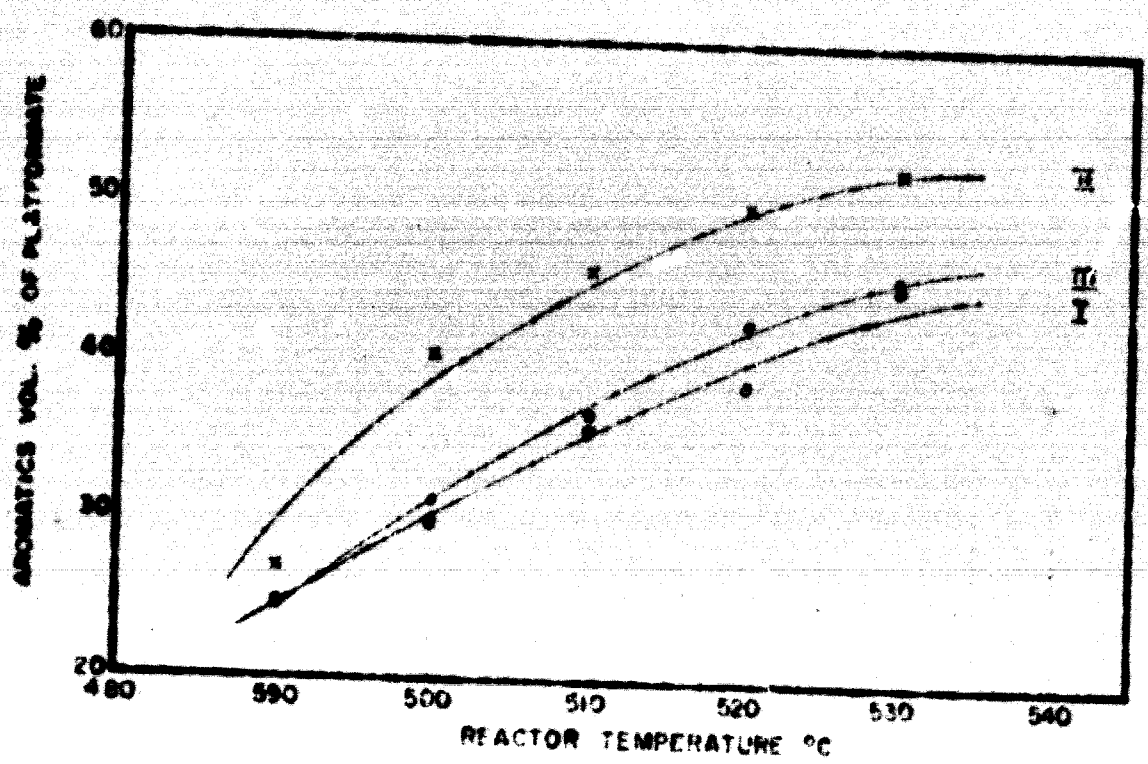
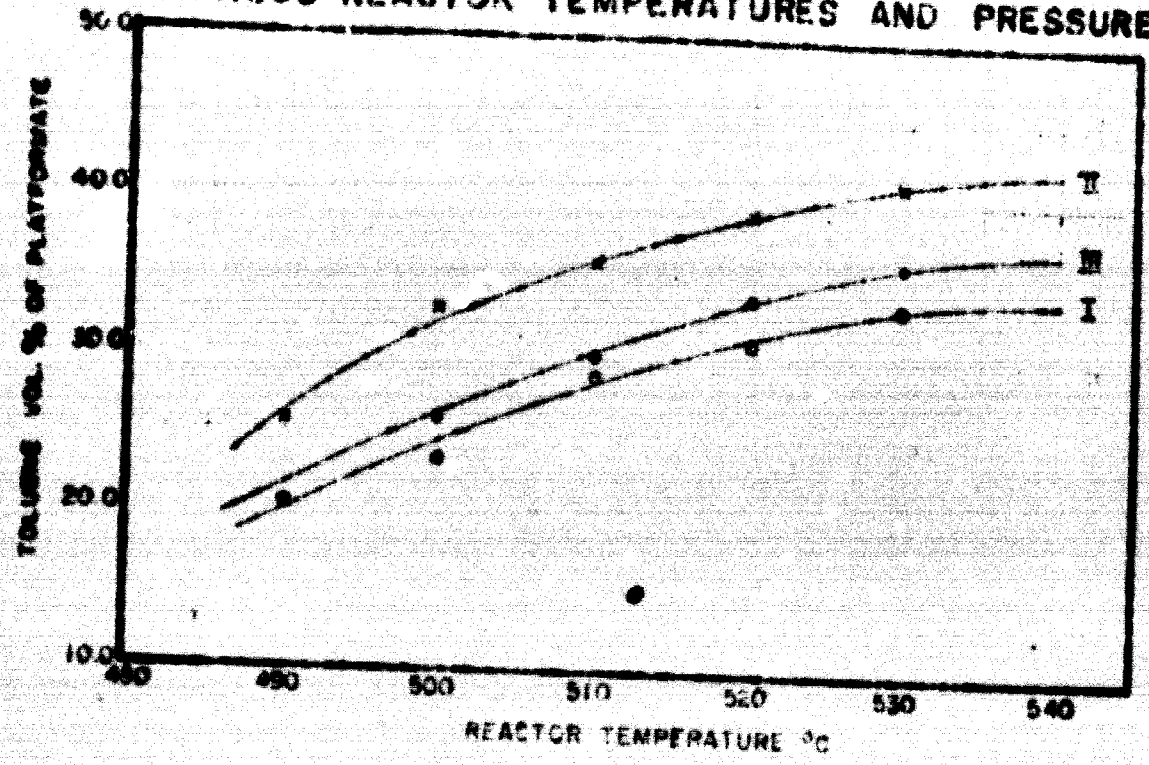
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DATE: May 1951
FIG. 2

YIELD OF H_2 , C_1 , C_2 AND C_3 AT VARIOUS REACTOR TEMPERATURES AND PRESSURES



I = 20 kg/cm² II = 25 kg/cm² III = 30 kg/cm²

YIELDS OF TOLUENE AND TOTAL AROMATICS AT VARIOUS REACTOR TEMPERATURES AND PRESSURES



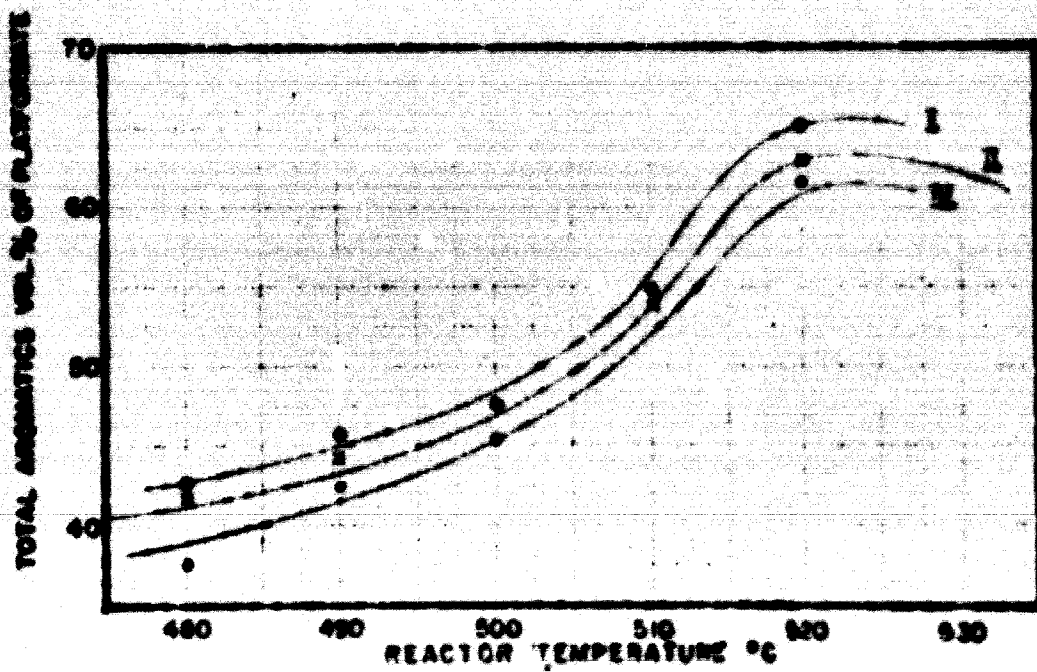
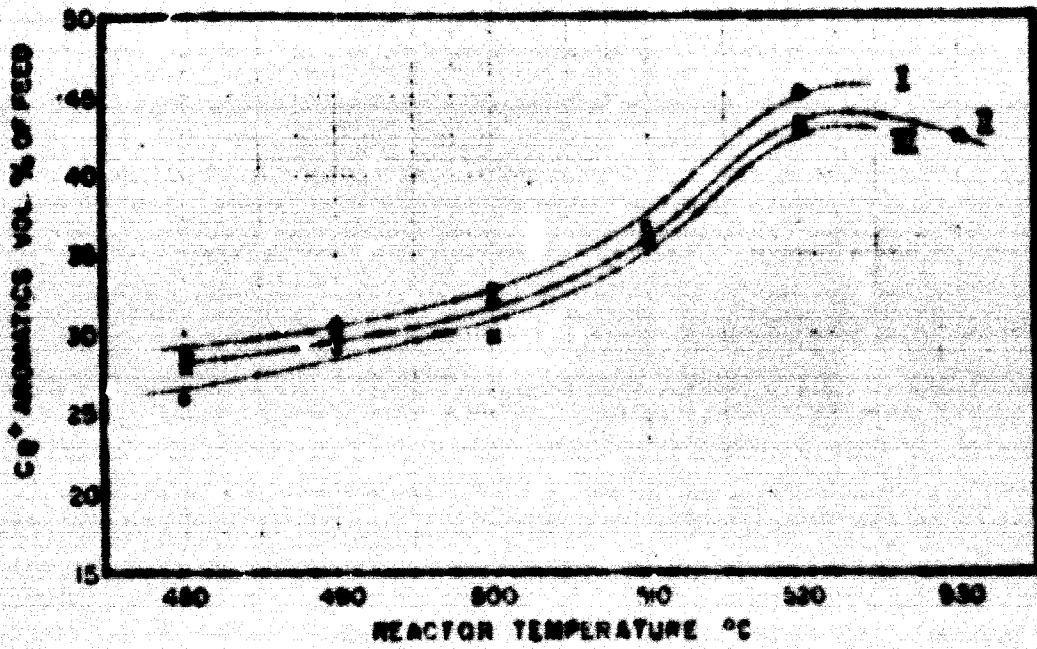
LEGEND:

- I 15 kg/cm²
- II 20 kg/cm²
- III 25 kg/cm²

Flow hr⁻¹ 20
 H₂/HC mol ratio 5.0-6.0

Research Division	TEHRAN
Acad. Fuel Plant	May 1971
Fig. 3	Drawing No R-351

YIELD OF C₈⁺ AROMATICS AND TOTAL AROMATICS AT VARIOUS REACTOR PRESSURES AND TEMPERATURES



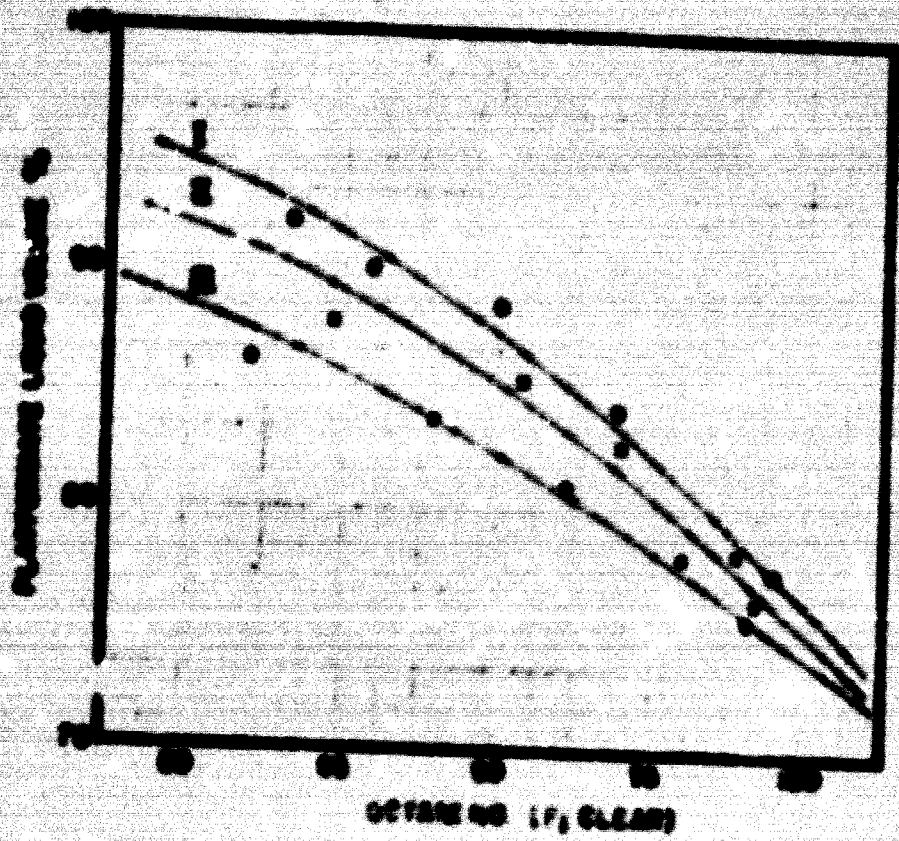
I = • 20 kg / Cm²

II = x 25 kg / Cm²

III = • 30 kg / Cm²

N.I.C.C. RESEARCH DIVISION		TEMPERATURE
Author	Pilot Plant	Date Aug 1957
Ref	Fig. 9	Drawing No. H-600

YIELD-OCTANE RELATIONSHIP AT EXPERIMENTED CONDITIONS



I - 2000/HR II - 2000/HR III - 2000/HR

N.I.C. RESEARCH DIVISION		PERMAN
Author: [Blank]	Date: Aug 1971	
Ref: [Blank]	Fig 2	Drawing No. G-000

refining temperature (530°C) a small portion of naphthene exists in the products.

Dehydrocyclization of paraffins to aromatics takes place under severe conditions. As the result of some experiments (15) production of benzene is much lower than production of heavier aromatics by dehydrocyclization reaction. The rate of dehydrocyclization is quite considerable on account of higher extent of this reaction on heavier paraffins. Aromatic hydrocarbons produced by dehydrocyclization reaction and also conversion rate of paraffins to aromatics is shown in table (5) for heavier fraction. Rate of dehydrocyclization reaction is actually higher than what is calculated on the account of the fact that some aromatics undergo reversible reactions to non-aromatics and conversion of naphthene to aromatics is not always 100% under all conditions experienced in practice. The maximum conversion is 37.9% at 520°C and 20 kg/cm^2 .

Table I: The rate of conversion of dehydrocyclization reaction at various conditions

						Case I					
Run no.	1	2	3	4	5						
Total aromatic Product, Vol. %	29.2	41.0	49.3	46.3	50.7						
Aromatic by dehydro-cyclization reaction Vol. %	7.2	9.0	10.3	10.3	10.7						
Conversion rate of dehydrocyclization reaction	10.4	13.2	15.0	21.0	27.5						
						Case II					
Run no.	6	7	8	9	10	11					
Total aromatic Product, Vol. %	26.7	27.0	27.3	41.0	40.3	43.7					
Aromatic by dehydro-cyclization reaction Vol. %	4.7	5.0	5.3	10.0	10.3	11.7					
Conversion rate of dehydrocyclization reaction	6.9	6.5	7.0	14.7	21.0	17.3					
						Case III					
Run no.	11	12	13	14	15						
Total aromatic Product, Vol. %	22.3	25.5	28.9	45.4	47.7						
Aromatic by dehydro-cyclization reaction Vol. %	0.3	1.5	6.9	13.4	15.7						
Conversion rate of dehydrocyclization reaction	0.4	5.1	19.1	19.7	23.1						

DISCUSSION

Toluene and C_6 aromatics were the highest amount of products in the reforming of 90-100°C fraction of Ags-Bari crude oil and the reforming of 110-115°C fraction of same crude oil respectively, under different conditions.

With respect to the feedstock composition, a reaction model for the performed experiment is given.

The yield of hydrogen was on average at 100-110°C of reaction temperature for all used promoters. The maximum yield of hydrogen was 110 vol% of feed at 110°C and 20 kg/cm² for the lighter fraction.

Even at very severe reforming conditions a small portion of naphthenic hydrocarbons remained unconverted.

Dehydrocyclization reaction extended to a maximum amount of 27.5 vol% for the heavier fraction.

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LITERATURE CITED

1. Stobough, R.B., Hydrocarbon Processing 44 (9) Sep, 1965.
2. Stobough, R.B., *ibid* 45 (4) April, 1966.
3. Stobough, R.B., " 45 (2) Feb, 1966.
4. Coley, J.R., Evering, B.L., McCollum J.D. (to Standard Oil Co.) U.S. Patent 2,861,944, Nov 25, 1958
5. Beckman, L.E., Hupp, Hupp, H.J. (to Phillips Petroleum Co.), U.S. Patent 3,259,501 June 28, 1966.
6. Maslyanski, G.M., Barkan, S.A. Int. Chem. Eng. 8 (2), 213-20, 1969.
7. KISS, H.C., Claymont, Jr. (to Sun Oil Co.) U.S. Patent 3,499,945 May 1970.
8. Kopf, F.W., Ducker, W.P., Pfefferle, W.C., Danson, N.H., Harrison J.A., Hydrocarbon Processing, 111-15 May, 1969.
9. Shurba, A.S., Bryanskaya, E.K., Sundar, A.F., Spol'nib, Yu. F., Yampolski, N.G., Che dnichenko, G.I., Khim. I. Tekhnol. Toplivi. Masel. 14 (13) 1-3, 1969.
10. Aliyev, V.S., and Aliyev, A.M., Azerb. Neft Khov 39-41, 1967.
11. Doup, L.C., Brenner, W., and Meius, A.M., IASC Process Design and Dev. 4 (1) 92-6, Jan. 1965.
12. Nakamura, E., Noguchi, K., Sekiyu Gakkai Shi 12 (8) 620-26, 1969.
13. Krane, H.G., Groh, A.B., Schulman, B.L., Siefert, J.H. proceeding of the Eighth World Pet. Congr. Section 111 Paper 4, 1959.
14. Henningsen, J., Bundgaard-Nielson, N., British Chem. Eng. 15 (11) Nov. 1970.
15. Badakhshan, A., Azimipour, A.M., Kamali, P., Norossian, A., Nashedi, M., Alizadeh, N., Sarram, P., Ind and Eng. Chem. Prod. Res. Dev. 10,330, 1971.



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