

INFLUENCE OF HYDROCARBON COMPOSITION OF NAPHTHA FEED ON THE YIELD AND OCTANE NUMBER OF REFORMATE

by
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I. INTRODUCTION

The rapidly increasing demand for high octane number gasoline and aromatic hydrocarbon as a petrochemical feedstock has promoted refiners to seek methods of improving yields of these valuable products.

The purpose of catalytic reforming is to convert a low-octane distillate fraction boiling within the gasoline range into high-octane blending stock and low aromatic hydrocarbons^{3,5}. The increase in the octane number of low-octane naphtha reformer feed can therefore be regarded as the transformation of naphthenes and paraffins into aromatics; resulting in the highest octane improvement^{6,11}. Paraffin and C₃ ring naphthene aromatization are guided by the metal and acid sites of bifunctional reforming catalyst^{1,2,4}.

In order to obtain more information about the influence of hydrocarbon composition of naphtha reformer feed on the yield and research octane number of reformate, an experiment has been carried out to study the conversion of pure hydrocarbon (i.e. cyclohexane, methylcyclopentane and n.hexane); and naphthenes, and paraffins of three types of naphtha feeds with various hydrocarbon compositions using bifunctional reforming catalyst. The operating conditions: temperatures: 400° to 500°C, pressure: 10 to 30 bars and H₂/HC ratio = 8 mole/mole. A Catatest Unit operated in a continuous system was used in this experiment. Gas and liquid product samplers taken from gas and liquid samplers, respectively, were analyzed for their hydrocarbon using a Gas Liquid Chromatography.

II. EXPERIMENTAL

Pure hydrocarbons, i.e. cyclohexane, methylpentane and n.hexane with a purity >99.5 mole % and naphtha with the specification shown on the Table 1 have been used as feedstocks. The operating conditions of this experiment are shown on the Table 2. The electrolytic

hydrogen used has been purified from oxygen compound by passing into deoxo catalyst followed by drying in molecular sieve. The purified hydrogen has a purity >99.5 by volume. Industrial bifunctional reforming catalyst was used in this experiment.

The experimental work was carried out in a Catatest Unit which can be operated in a continuous system, with flow scheme given on the Figure 1. The reactor assembly consisted of a microreactor placed in an electric furnace and joined to an inlet and outlet fittings, temperature control panel (not-shown), for measuring gas flow and pressures, continuous high pressure oil feeding pump. The microreactor was constructed from stainless steel tubing, 220 cc volume, 19 mm inside diameter and 7 mm outside diameter thermo couple well tubing.

Feedstock and hydrogen were feed from the upper part of the reactor. The products were moved from the cooler to high pressure receiver, where separated into gas and liquid. Gas was released after its volume was measured by a wet gas meter. The operating conditions are temperature: 400° to 510°C, Pressure: 10 to 30 kg/cm², and H₂/HC ratio = 8 mole/mole.

Gas and liquid products samples taken from gas and liquid samples, respectively, were analyzed by using a Gas-Liquid Chromatography.

Initial reaction rate ($r = \text{mole/hour, g.catalyst}$) is proportional to the feedstock conversion ($X = \text{mole/mole}$) and the ratio between the rate of hydrocarbon feedstock ($F = \text{mole/hour}$) and the catalyst weight ($W = \text{g}$)¹¹ or

$$r = X F/W \quad 1$$

And this initial rate is nearly proportional with the reaction rate constant (k) or

$$r \approx k = A \exp(-E/RT) \quad 2$$

The reaction rate can be also written as follows

$$r = k \cdot p_{HC}^a \cdot P_{H_2}^b \quad 3$$

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If H₂/HC ratio is kept constant, this reaction rate becomes:

$$r = k_2 P_T^{(a+\beta)} \quad 4$$

or

$$\log r = (a+\beta) \log P_T + \log k_2 \quad 5$$

III. RESULT AND DISCUSSIONS

A. Influence of Operating Condition

1. Temperature

Influence of operating temperature on the aromatization of pure hydrocarbon and naphtha feedstock are shown on the Figure 2, 3, and 5

Aromatization of cyclohexane, methylcyclopentane and n. hexane are observed as follows.

- Dehydrogenation of cyclohexane to benzene ceews very rapidly.
- Methylcyclopentane reacts at a much slower rate and undergoes both dehydroisomerization to form benzene as well as hydrocyclization to form hexane.
- The most difficult aromatization reaction is the dehydrocyclization of n. hexane to benzene.

Activation energies of aromatization reaction of these three hydrocarbon i.e. cyclohexane, methylcyclopentane and hexane, are observed at the values of 19.230; 21.96 and 37.682 kcal/mole, respectively.

By increasing the operating temperature from 490° to 510°C, the yield of reformats decreases and the conversion of naphthenes and paraffins to aromatics increases, i.e. 62.95 to 75.39% vol. and 9.18 to 59.86% vol., respectively.

Therefore a higher operating temperature clearly favors the harmful reactions more than the sought-after

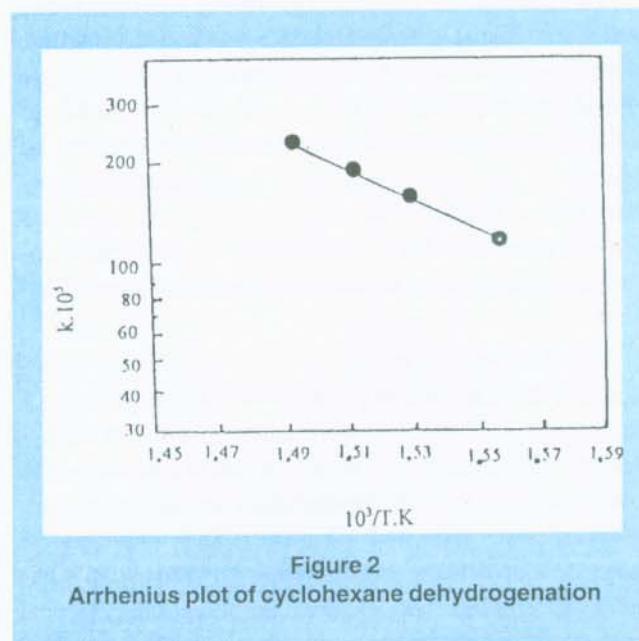
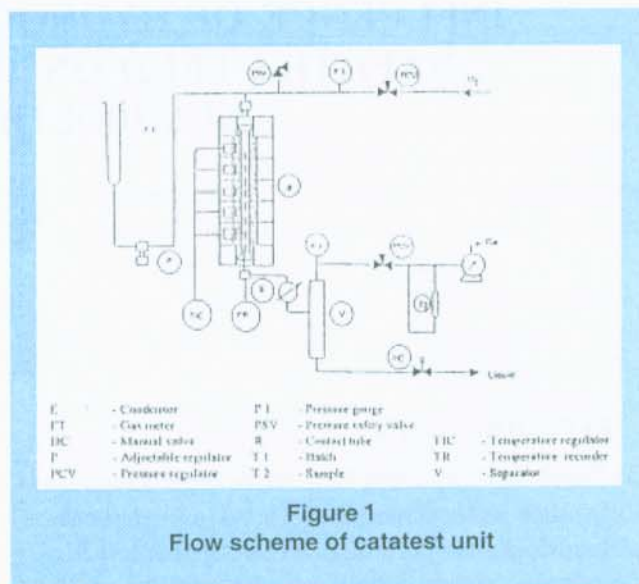


Table 1
Characteristics of naphtha feedstocks

No	Characteristic	Naphtha Feedstocks		
		1	11	111
1	Boiling range °C	85° - 180°	85° - 185°	85° - 190°
2	Hydrocarbon composition vol%			
	Paraffins	72.7	75.2	41.2
	Naphthenes	24.1	32.7	46.5
	Aromatics	13.2	10.1	12.3

reactions^{6,8}. An increase in operating temperature favours thermodynamics, but accelerates the degradation reactions even more; consequently an increase in temperature leads to a loss in reformat yield^{8,9}.

2. Pressure

Influence of operating pressure on the aromatiza-

tion of pure hydrocarbon and naphtha feedstock are given on the Figure 4 and 6. The negative order of the total pressure had -0.408 and -1,330 for the aromatization of methylcyclopentane and n.hexane, respectively.

The conversion of naphthenes and paraffins of naphtha feed had decreased from 79.02 to 53.37% vol. and

Table 2
Operating conditions

Operating conditions		Feedstocks			
		Pure hydrocarbons			Naphthas
		Cyclohexane	Methylcyclopentane	Normal hexane	
Catalyst	gr	5	5	5	60
H ₂ /HC	mole/mole	8	8	8	8
Pressure	bar	20	30-Oct	30-Oct	30-Oct
Temperature	°C	400° - 430°	450° - 490°	450° - 490°	490° - 510°

Figure 3
Arrhenius plot of aromatization of N-Hexane, and methyleyclopentane

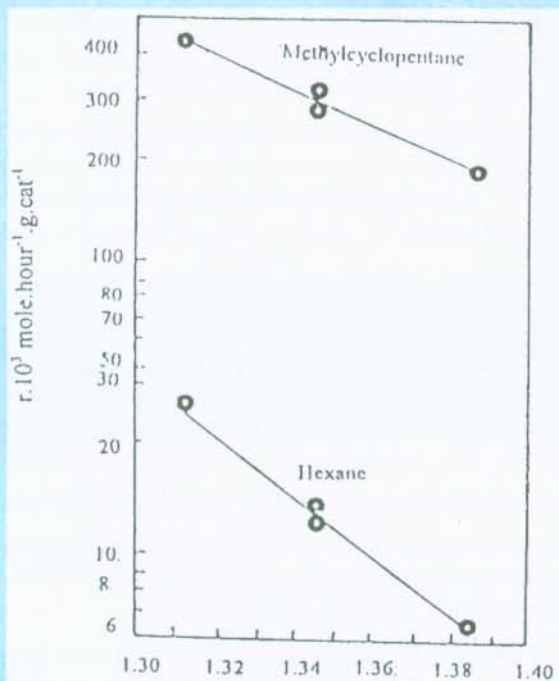
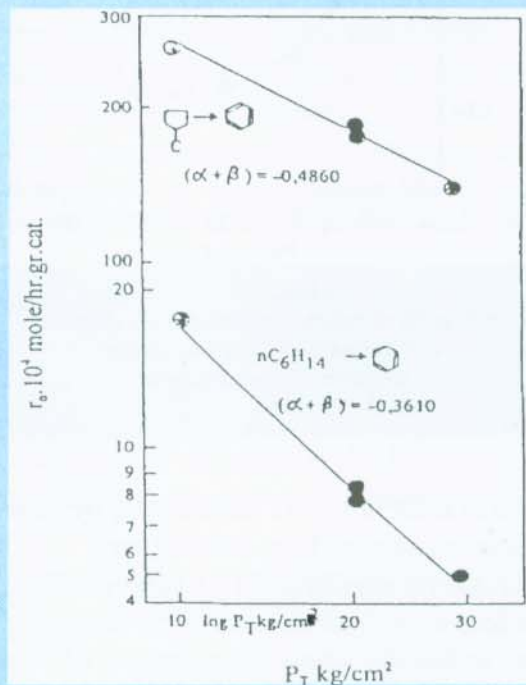


Figure 4
Influence of total pressure on the aromatization of N.Hexane and methyclopentane



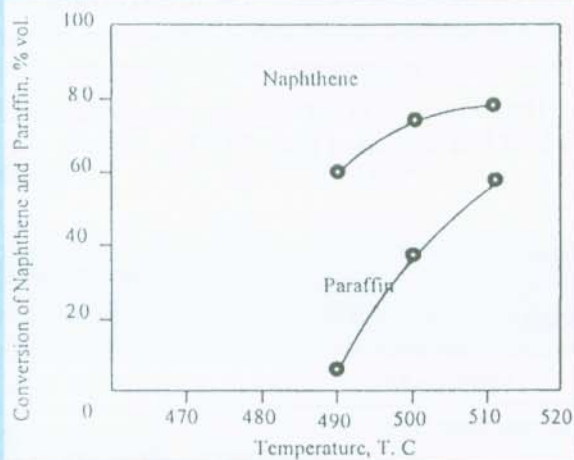


Figure 5
Influence of operating temperature
on conversion of Naphthene and
paraffin of Naphtha feed

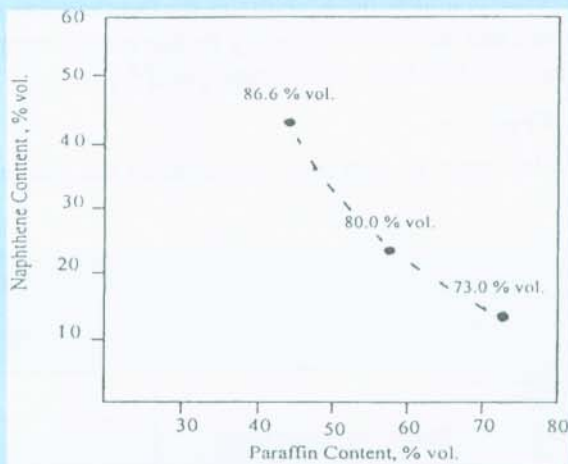


Figure 7
Influence of hydrocarbon
composition of Naphtha feed
on the yield of reformate

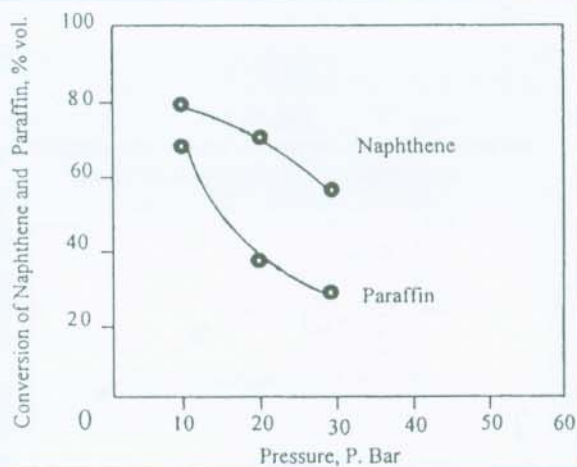


Figure 6
Influence of operating pressure on the
conversion of Naphthene and
paraffin of Naphtha feed

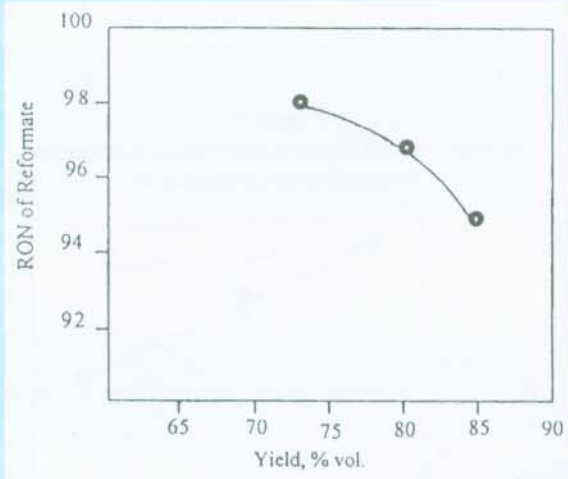


Figure 8
Influence of yield on the RON reformate

from 70.31 to 27.59% vol., respectively, by increasing the operating pressure from 10 to 30 bars.

Because the aromatization of naphthenes and paraffins occurs with an increase in the number of molecules, so that the lowest concentrations of aromatics occur at high operating pressure^{5,10}. Paraffins hydrocarbon is relatively rapid and is favored by high pressure

and high temperature^{6,12}. The disappearance of paraffins through hydrocracking concentrates aromatics in the reformate but produces low value light paraffins and consumes hydrogen^{7,8}.

The catalyst and operating conditions must be properly chosen in order to minimize hydrocracking and provide maximum aromatic yields, and relative rate of par-

affin dehydrocyclization to hydrocracking is a critical measure of reforming selectivity.

B. Influence of Hydrocarbon Composition of Naphtha Feedstock

Influence of hydrocarbon composition of naphtha feedstock on the yield and research octane number (RON) of reformat are shown on the Figure 7 and 8.

A naphthenic feed (N = 46.5% vol.) gives a volume yield consistently about 13.6% points higher than a paraffinic feed (N = 24.1% vol.) even though the research octane number of reformat varies from 96 to 98.

Increasing the RON of reformats from 95 to 98 given by paraffinic feed causes a drop of about 11.43% point in yield of these reformates.

This is because naphthenes are easily transformed into aromatics, while the aromatization of paraffins is more difficult and is accompanied also racking^{6,8}.

Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms so conversion these paraffins and naphthenes to aromatics reduces the volume of reformat. Because the boiling points of aromatics are higher than the paraffins and naphthenes, the end point of this reformat obtained from paraffinic naphtha feed increases relatively higher than paraffinic feed.

IV CONCLUSION

Dehydrogenation of C₆-ring naphthenes occurs very rapidly, dehydroisomerization of C5-ring reacts at much slower, but the most difficult aromatization is the dehydrocyclization of paraffins. Under optimum conditions the yield of reformat from fresh catalysts depends on hydrocarbon composition naphtha feed, operating conditions and the octane number of reformat.

From now on it appears that catalytic reforming for high octane gasoline and petrochemicals (i.e. low aromatic) production will be used more and more.

Thus extensive researches must be carried out for improving catalyst selectivity, stability or even activity in order to finally achieve a catalyst that will transform any feed into aromatics and hydrogen alone.

NOTATION

A = frequency factor
 E = activation energy-kcal/mole
 H₂/HC and H₂/HC = hydrogen, hydrocarbons and mole ratio between H₂ and

HC, respectively

k, k₁, k₂ = rate constants
 P_{HC}, P_{H₂}, P_T = partial pressure of hydrocarbon, hydrogen, and the total pressure respectively
 R = the gas constants
 r = reaction rate
 α and β = partial order of reaction with respect to hydrocarbon and hydrogen, respectively

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