STUDY IN CATALYTIC REFORMING OF HEAVY NAPHTHA

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ABSTRACT

Catalytic naphtha reforming is a refinary process to upgrade heavy naphtha into high octane reformate product for gasoline blending. The catalytic reforming reactions lead to hydrogen production which is used in the hydrotreatment of petroleum products. The effect of reforming reactions should be guided by a selective and an active catalyst under well defined operating conditions.

The aim of this work is to study the effect of process variables on the conversion of low octane number of heavy straight run naphtha into higher octane number gasoline

The hydroconversion reactions are carried out in a high pressure catalytic activity testing unit under different operating conditions; 400 to 500°C reaction temperature, liquid hourly space velocity (LHSV) from 1 to 3h^{-1}, hydrogen pressure varying from 8 to 16 kg/cm^2 gauge and hydrogen hydrocarbon mole ratio from 2 to 6, using a commercial reforming catalyst containing 0.375wt% Pt on alumina base. Upon raising the reactor temperature, the RON of the product increases where as the product yield decreases as a result of cracking reaction. The aromatic content, posseses a high octane number, increases with increasing temperature form 400 to 500°C.

The values of RON, aromatics and isoparaffins contents are boasted by increasing H$_2$/H.C mole ratio from 2 to 3, and diminished on further increasing the H$_2$/H.C ratio to 6.

The effect of liquid hourly space velocity parameter was investigated in this study. Lower LHSV enhances the reaction and formation of aromatics and isoparaffins whereas the concentration of naphthenes and paraffins decline.

The pressure factor influences the RON, aromatics and isoparaffins contents that increase upon raising the hydrogen pressure. This may be attributed to the decrease of coking which deactivate the catalyst.

The maximum RON (93.8) and aromatics (61.9 wt%) were obtained at 500°C reaction temperature, 16kg/cm^2 gauge hydrogen pressure, 1h^{-1} LHSV and 3 H$_2$/H.C mole ratio. At the same conditions but with hydrogen pressure 8kg/cm^{2}g, the product yield was very high (99.1 vol.%) and RON became (80.15).

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INTRODUCTION

Gasoline has many advantages (1) and is used to a greater extent than any other fuel in internal combustion engines having spark ignition. It has a better burning rate than other fuels, and because it vaporizes easily, it gives quick starting in cold weather, smooth acceleration and maximum power. High performance cars require high performance gasoline.

Some additives, such as tetraethyllead (TEL), methyle tertiary butyle ether (MTBE) (2), etc....., were used in gasoline to minimize or prevent knocking. However, these materials now has been reduced to non detectable level for health and environmental considerations (3,4). This was accompanied by the immediate introduction of many processes for improving the gasoline quality.

The octane number of gasoline increases linearly with the increment in isoparaffin and aromatic concentration (5). In catalytic reforming low octane hydrocarbons are converted into higher octane components. This is a key process in petroleum refining which makes high octane number unleaded gasoline a reality. The high octane number hydrocarbons in the gasoline boiling range, produced in reforming are primarily aromatic hydrocarbons. The aromatics are not only premium blending stocks for motor fuel but some are also in demand as petrochemicals, from which a wide range of plastic films and fibers are produced, as well as solvents and adhesives.

The light hydrocarbon gases, by-products of cracking reactions, were generally added to refinery fuel gas systems. Butanes and other cracked by-products were commonly used in adjusting vapor pressures of gasoline pools. Hydrogen, the by-product from aromatic producing reactions was found to be useful in supporting the operation of reformer feed preparation units as well as other hydrotreating units. Thus, most reformers and many petrochemicals manufactures have found the catalytic reforming process an increasingly valuable tool.

In the process, naphtha is fed to a catalytic reforming unit typically contains C_6 to C_{11} paraffins, naphthenes and aromatics.

Catalyst is the key to this process. Reforming catalyst is a marvel in its design and ability to perform specifically desired chemical reactions and to essentially

exclude undesirable reactions. Commercial catalyst is a dual function which consists of an acidic carrier and hydrogenation-dehydrogenation function, frequently a noble metal (Re, Pt) (6) supported on acidic carrier (γ-alumina)

In a single reaction system, the catalyst performs both dehydrogenation and hydrogenation, isomerization, hydrocracking and dehydrocyclization reactions with incredible efficiency and stability (7). The necessity for frequent catalyst regeneration arises from the fact that its activity declines with time (on reactions) owing to deposition of carbonaceous material on the catalyst (8).

The aim of this work is to study the effect of process variables on conversion of low octane number of heavy naphtha into high octane number gasoline, with maximum yield of reformate.

EXPERIMENTAL

A hydrotreated heavy straight-run naphtha provided from Suez Refinery Petroleum Co. is used as a feed stock. It consists of a mixture of hydrocarbons having from 6 to 10 carbon atoms per molecule, and specification depicted in table (1).

Catalyst:

The experimental work is carried out using a commercial platforming catalyst with alumina base, 0.375 wt% Pt/γAl₂O₃.

Experimental Set up and Procedure:-

Have been declared elsewhere (9). Liquid samples collected from the receiver were analyzed by Gas chromatograph (G.C). The research octane number (RON) values are calculated from the data obtained from G.C analysis (10). The gas chromatographic analyzer has specifications declared in (table 2)

Table (1) Feed Specifications

Test	Result
1- ASTM Distillation: °C	
I.B.P.	67
10%	91
30%	102
50%	115
70%	127
90%	146
F.B.P.	171
2- Density @ 15°C gm/cm^3	0.7404
3- R.V.P. @ 100°F psi	2.1
4- Total Sulphur ppm	0.3113
5- Octane Number (Research method)	52.2
6- GC Analysis: % Vol.	
P	60.02
N	30.06
A	9.92

Table (2): GC Analyzer Specifications

Model	Varian CP-3800
Carrier gas	Helium, linear velocity = 29 cm/sec @35°C
Detector	FID @ 300°C
Injection temperature	250°C
I.B.P.	35°C
F.B.P.	200°C
Column	Length: 100cm diameter: 0.25mm
	Name: fused silica coated with 0.5 microm methyle silicon pounded.

RESULTS AND DISCUSSIONS

Effect of Reaction Temperature:-

The reactor temperature is the most important parameter which affects the catalytic reforming reactions i.e with increasing the temperature of the reactor, the quality of product improves (11). But on the other hand, the product yield decreases Fig (1), because the higher temperature may cause thermal cracking reactions which increase the rate of coke lay down on the catalyst.

The hydroconversion of heavy naphtha were carried out under different reaction temperature ranging from 400-500°C, at 12kg/cm^{2}g hydrogen pressure, 2.5h^{-1} LHSV and 3H$_2$/H.C mole ratio.

Product distribution results from the hydroconversion are given in table (3) and Fig. (1). It is obvious from these data that increasing the temperature from 400°C to 450°C led to a high increase in aromatic content from 13 wt% to 31wt% accompanied by a decrease on the amount of cycloparaffins from 23-17wt%. On raising the temperature above 450°C up to 500°C, an insignificant increase in aromatics content (from 31wt% to 35wt%) with a slight decrease in naphthenes concentrations has occurred. This may be attributed mainly to the dehydrogenation of cycloparaffins to aromatics. The hydroisomerization is an important reaction for upgrading the octane number of n-paraffins. Fig (4) shows that, upon raising the temperature from 400 to 500°C, the percentage of isoparaffins in the produced naphtha has been improved whereas the amount of n-paraffins diminshed from 42 wt% to 20 wt%. This may be principally resulted from the isomerization and hydrocracking of n-paraffins (12).

From this situation, the effect of temperature on RON is obvious particularly at the range of 400-450°C, since the octane number increased from 70 to 80.

However, beyond this temperature, the amelioration of the knock quality is not valuable.

Effect of Hydrogen to Hydrocarbon Mole Ratio:-

Hydrogen is necessary in the platforming process for purposes of catalyst stability and decrease of coke (11).

The effect of H$_2$/H.C mole ratio on the hydroconversion of heavy naphtha over Pt/Al$_2$O$_3$ was carried out at H$_2$/H.C mole ratio of 2 to 6 and at constant reaction temperature 500°C, hydrogen pressure 12Kg/cm^{2}g and LHSV 2.5h^{-1}. Product distribution resulted are given in table (4) and Fig (2).

Higher RON can be obtained with increasing H$_2$/H.C mole ratio from 2 to 3, that may be due to preventing carbon deposition on the catalyst and increasing its stability and activity. This leads to enhance the rate of dehydrogenation,

hydroisomerization and dehydrocyclization reactions of paraffins and naphthenes. Therefore the aromatics and isoparaffins content increases. But when the H_2/H.C mole ratio increased from 3 to 6, the RON decreases. This may be due to the large amount of H_2 that will reverse the direction of positive reactions because these reactions are reversible and the H_2 will be a reactant. Therefore the RON decreased as a result of the drop in concentration of aromatics and isoparaffins in the product.

The Effect of Liquid Hour Space Velocity:-

The effect of space velocity on the hydroconversion of heavy naphtha at reaction temperature of 500°C, hydrogen pressure of $12 Kg/Cm^2$ gauge and H_2/H.C mole ratio 3 and different liquid hourly space velocity (LHSV) from 1 to $3h^{-1}$ was illustrated in table (5) and Fig (3). As the space velocity is lowered the residence time gets higher and the RON is improved owing to the conversion of naphthenes and paraffins to aromatics and isoparaffins. When LHSV increased from 1 to $3h^{-1}$, the RON reduced from 85 to 81.1.

The product liquid yield is affected by liquid hour space velocity. Fig (3) indicates that, the lower the space velocity, the lower the produced liquid yield, this may be attributed to the occurrence of the unfavorable cracking reaction.

Simultaneously, an improvement in the amount of isomers from 24 to 27 wt% and aromatics from 34 to 40 wt% accompained by a reduction in the paraffinic and naphthenic contents is observed upon reducing the LHSV from 3 to h^{-1}.

This mainly resulted from the isomerization and dehydrocyclization of n-paraffins and also for dehydrogenation of cycloparaffins reactions.

Effect of Hydrogen Pressure: (low pressure range)

The effect of operating hydrogen pressure on the hydroconversion of heavy naphtha was carried out. A hydrogen pressure of 8 to 16 Kg/cm^2 gauge was applied at a constant reaction temperature of 500°C, LHSV $1h^{-1}$ and H_2/H.C mole ratio of 3 table (6) and Fig (4).

The effect of low range pressure on the catalytic reforming reactions and RON is different from that at higher pressure. In the higher pressure range , with decreasing the pressure, the rate of the desired reactions increases as it is promoted with low pressure, and the RON is consequently increase. However, there is a limit of reducing the pressure, since it affects coke formation on the surface of the catalyst specially for a fixed bed catalyst reactor (12,13). Decreasing the pressure will increase the product liquid yield and increase the coke formation. Fig (4) indicate the effect of pressure on the product liquid yield .It is clear from this figure that pressure lower than $12Kg/cm^2$ gauge, has no clear effect on the yield of the liquid product, but higher pressure caused marked decrease in liquid yield from 98%to 85%. This may be due to some cracking that took place.

The effect of low pressure range on the RON is clear that increase from 80.15 to 93.6 upon raising the pressure from 8to 16 Kg /cm^2 gauge. This can be attributed to the decrease of catalyst deactivation by coking and production of aromatics and isoparaffins.

The relationship between the RON and the product yield at different reaction temperatures, hydrogen pressure and space velocity is depicted in fig (5). This relation generally indicates that when the RON increases the product liquid yield decreases at any operating conditions. The reason of this behavior might be that the RON (above 80) are usually obtained at severe operating condition (temp, P,S.V) where some cracking might occur leading to minimization of liquid yield.

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Table (3): The Effect of Temperature

(@ pressure = 12 Kg/cm^{2}g./ space velocity = 2.5 1/hr / H$_2$/HC molar ratio = 3)

Temp. °C	400	425	450	475	500
R.O.N.	70.66	75.21	80.03	80.60	82.50
Aromatics wt. %	13.10	17.70	31.23	32.89	34.86
Naphthenes wt. %	23.20	20.90	17.10	16.70	16.50
n-Paraffins wt. %	42.60	38.80	30.06	25.13	20.29
Iso-paraffins wt. %	17.90	19.70	20.50	23.60	25.60
Total Paraffins wt. %	60.50	58.50	50.56	48.73	45.89
Olefins wt. %	3.20	2.90	1.11	1.68	2.15
Product Liquid Yield vol. %	98.30	97.50	93.70	89.10	87.50

Table (4): The Effect of H$_2$/HC mole ratio

(@ Temp = 500°C/ Pressure = 12 Kg/cm^{2}g./ space velocity = 2.5 1/hr)

H$_2$/H.C mole ratio	2	3	4	5	6
R.O.N.	81.10	82.50	81.30	80.70	79.70
Aromatics wt. %	33.90	34.86	34.10	33.50	31.50
Naphthenes wt. %	17.90	16.50	17.60	18.10	18.50
n-Paraffins wt. %	21.90	20.29	23.00	24.50	27.60
Iso-paraffins wt.%	24.90	25.60	23.10	22.70	20.90
Total Paraffins wt. %	46.80	45.89	46.10	47.20	48.50
Olefins wt. %	1.40	2.75	2.20	1.20	1.50

Table (5): The Effect of LHSV
(@ Temp = 500°C/ Pressure = 12 Kg/cm²g. / H₂/HC molar ratio = 3)

LHSV 1/hr	1	1.5	2	2.5	3
R.O.N.	85.10	83.60	83.10	82.50	81.10
Aromatics wt. %	40.10	36.70	35.90	34.86	33.80
Naphthenes wt. %	13.50	14.10	15.70	16.50	17.10
n-Paraffins wt. %	16.90	17.91	19.40	20.29	22.60
Iso-paraffins wt. %	27.50	26.99	26.10	25.60	24.30
Total Paraffins wt. %	44.40	44.90	45.50	45.89	46.90
Olefins wt. %	2.00	4.30	2.90	2.75	2.20
Product Liquid Yield vol. %	81.00	85.30	86.00	87.50	88.10

Table (6): The Effect of Pressure
(@ Temp = 500°C space velocity = 1.0 1/hr / H₂/HC molar ratio = 3)

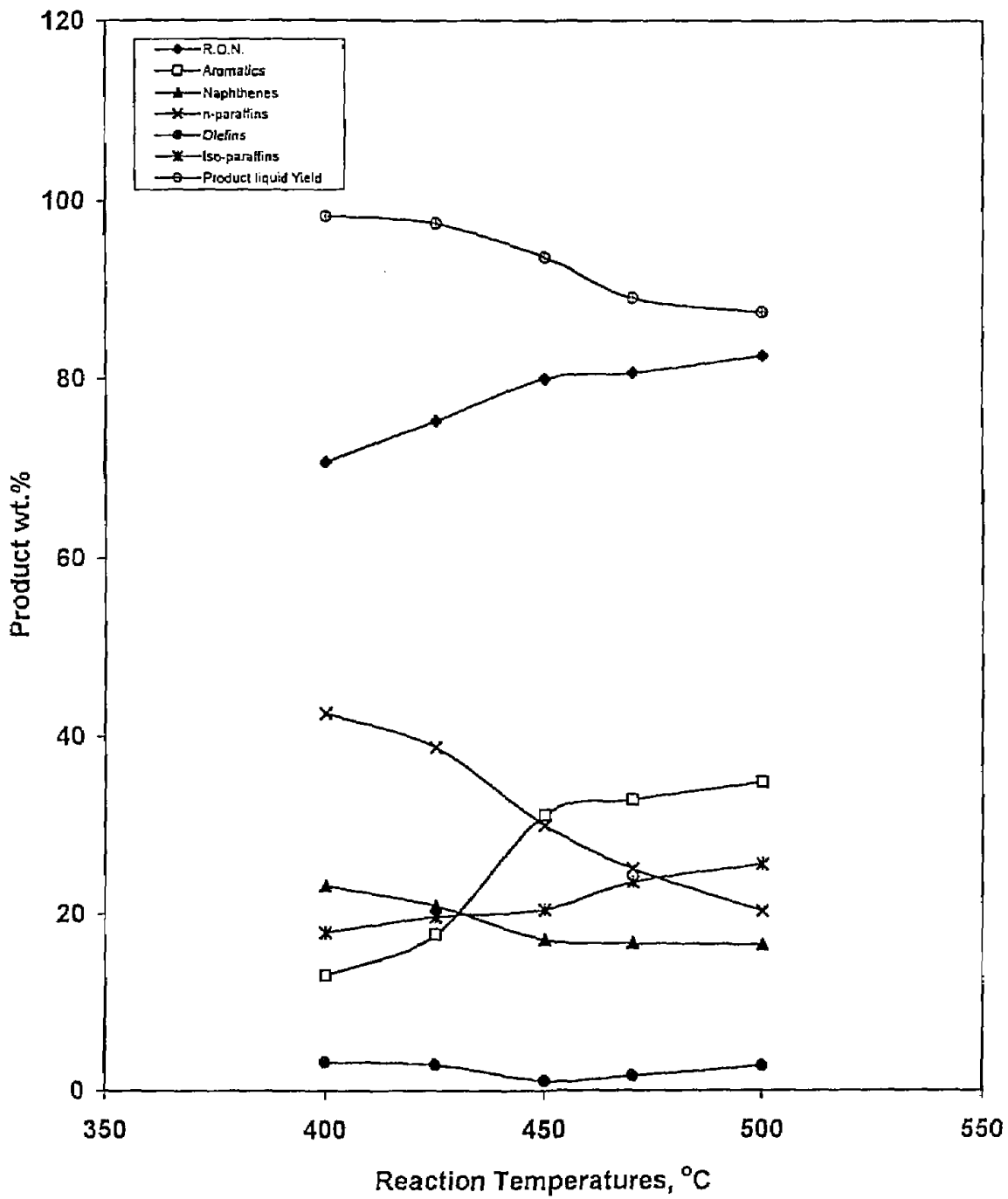| Pressure Kg/cm²g	8	10	12	14	16
R.O.N.	80.15	81.27	85.10	85.90	93.60
Aromatics wt. %	24.30	25.60	40.10	45.60	61.90
Naphthenes wt. %	22.80	21.90	13.50	11.90	6.20
n-Paraffins wt. %	30.50	24.90	16.90	13.20	2.10
Iso-paraffins wt. %	20.50	25.20	27.50	28.30	29.00
Total Paraffins wt. %	51.00	50.10	44.40	41.50	31.10
Olefins wt. %	1.90	2.40	2.00	1.00	0.80
Product Liquid Yield vol. %	99.10	98.40	98.00	90.90	84.90

Fig. (1): Distribution of Products of Heavy Naphtha
Hydroconversion at Different Temperatures Using
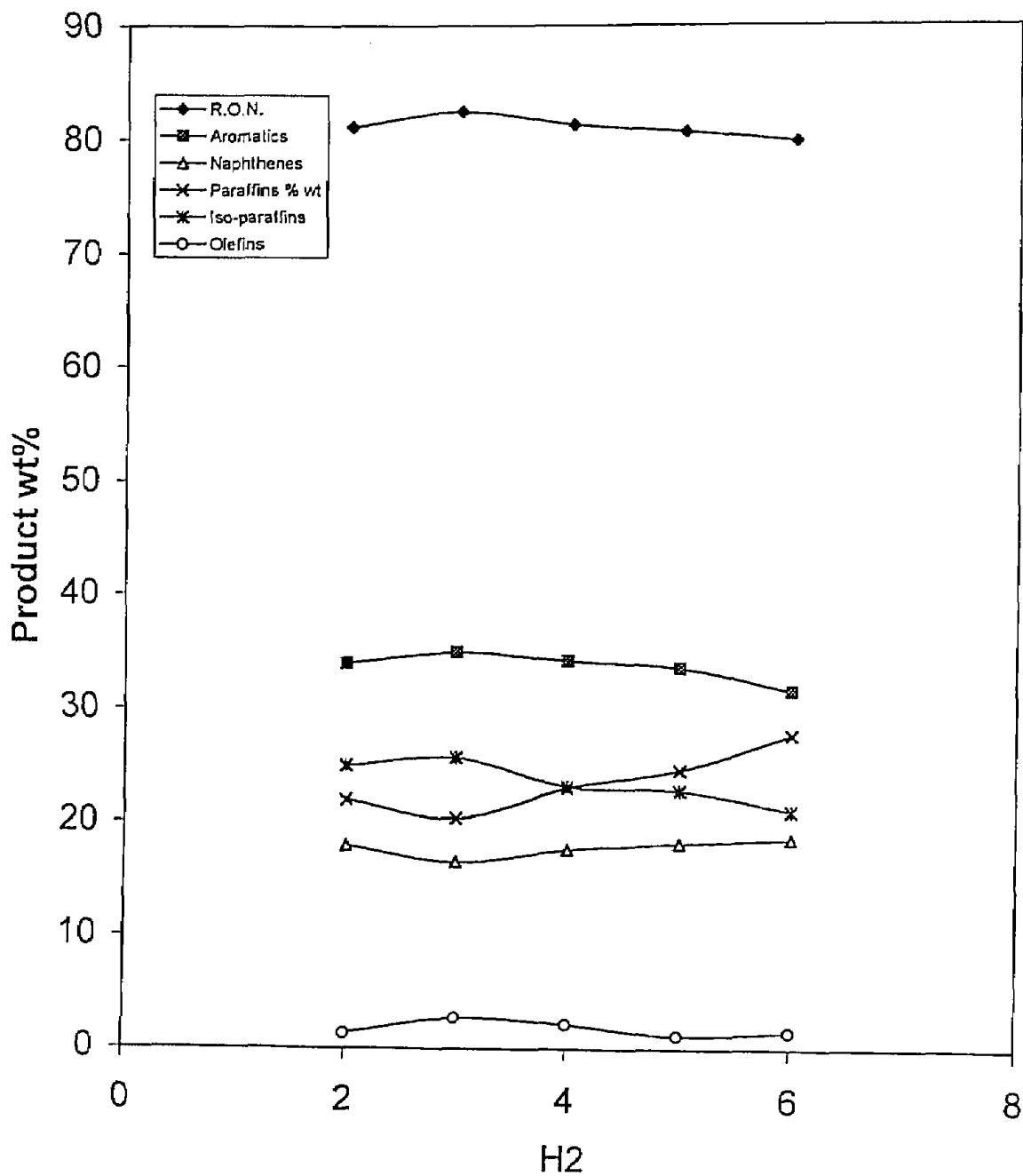Pt/Al₂O₃ Catalyst

Fig. (2):Distribution of Products of Heavy Naphtha
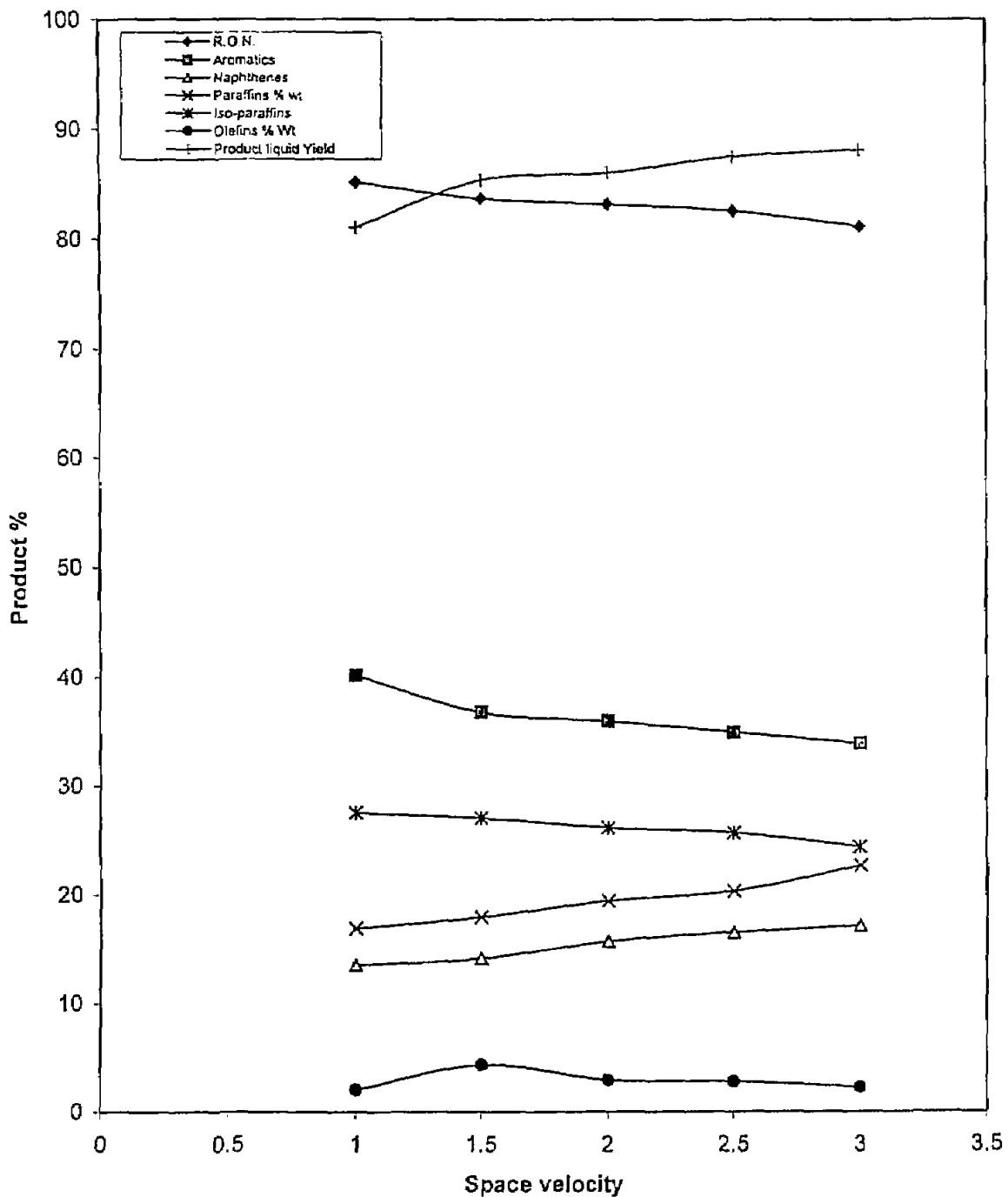Hydroconversion at Different H_2/H.C mole ratio Using
Pt/Al_2O_3 Catalyst

Fig. (3) Distribution of Products of Heavy Naphtha Hydroconversion
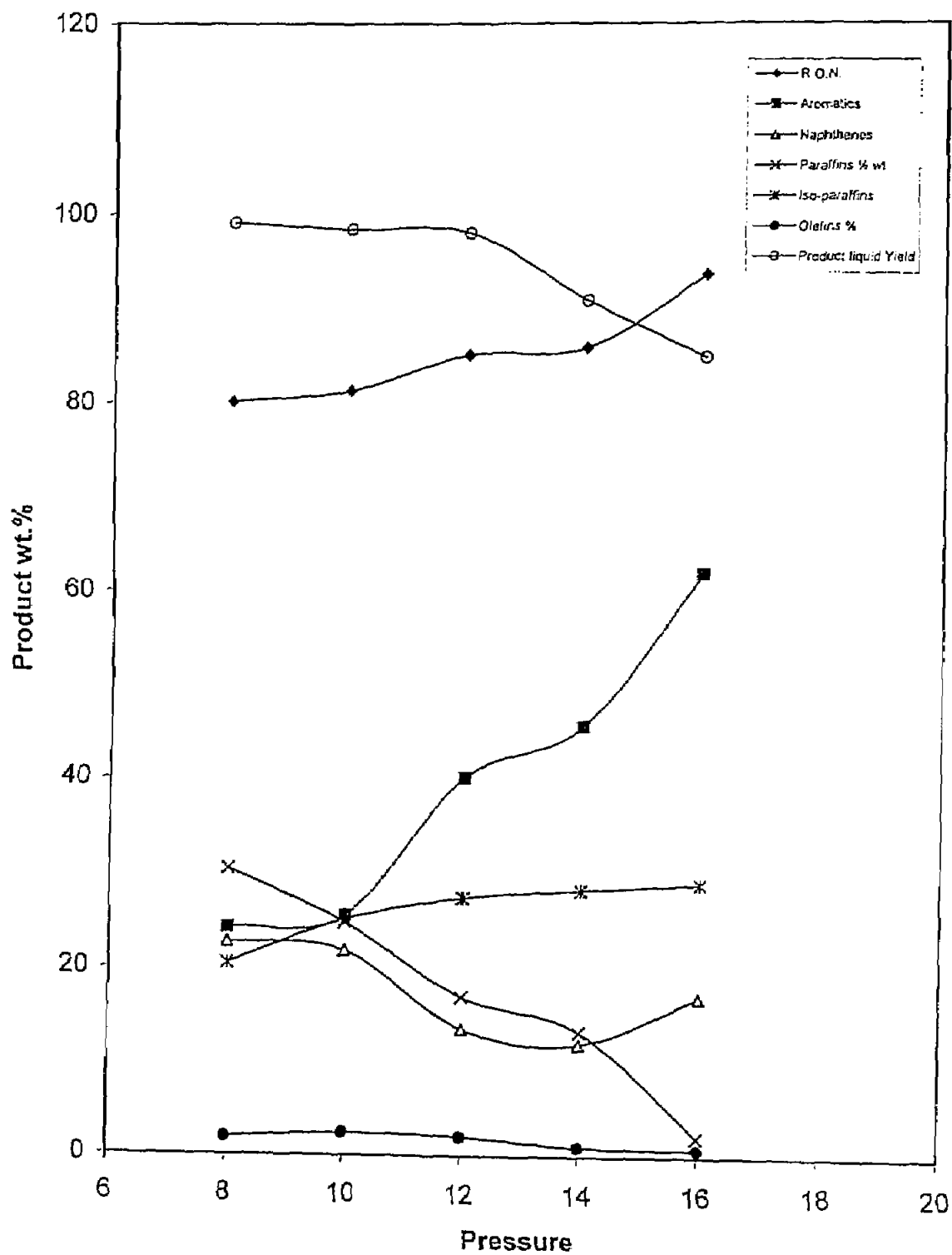at Different Space velocity Using
Pt/Al_2O_3 Catalyst

Fig. (4) Distribution of Products of Heavy Naphtha
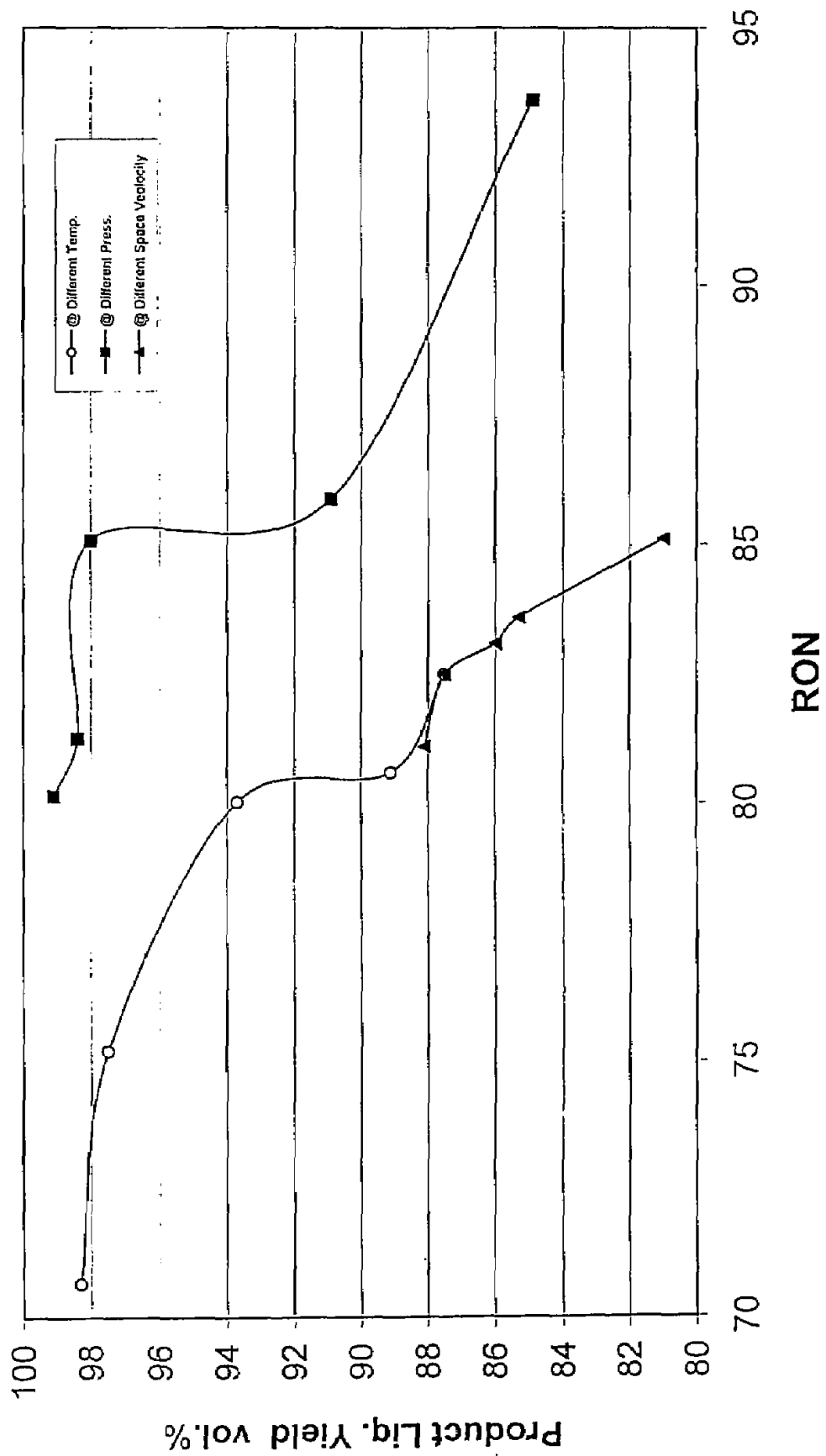Hydroconversion at Different Pressures Using
Pt/Al₂O₃ Catalyst

Fig. (5) The Effect of RON On Product Liquid Yield