REFORMING OF LOW SULFUR FEED STOCKS

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ABSTRACT

Four Egyptian SR-naphtha feed stocks were evaluated and carefully studied for hydrodesulfurization in a bench-scale unit under industrial conditions using commercial CoMo catalyst. The results show that the sulfur content decreased with increasing temperature down to a minimum. Increasing space velocity slightly increased product sulfur, while the hydrogen gas rate had an insignificant effect. The produced naphtha contains sulfur below 0.5 ppm at temperature range of $320°-380°C$ whatever its type.

An optimum condition for naphtha hydrotreating was selected in order to prepare a reformer feedstock. The reforming reactions were carried out using a prepared Pt/ γ-Al_2O_3 reforming catalyst and research octane number (RON) was calculated theoretically as a function of the reformate composition and the tested refinery conditions. The octane numbers were 94(RON) and 91(MON) due to the higher concentrations of aromatics in the reformate. Therefore, the octane rating of the investigated naphtha was upgraded ,i.e. from 54 to 94 (RON).

Key words: : Hydrodesulfurization(HDS), sulfur removal, mercaptan, hydrotreating catalyst, reforming catalysts, octane number,straight run(SR)-naphtha.

INTRODUCTION

Tomorrow's main gasoline challenges, as a motor fuel, deal with sulfur, aromatics and olefins contents together with a possible ban of ethers, hampering future octane demand and its technical feasibility [1]. The sulfur compounds in straight run naphthas are responsible of reducing the performance of engines using such fuels, and poisoning the reforming catalysts which can cause shorttering in their cycle length and deactivation.

Selection of a hydrodesulfurization (HDS) catalyst is dependent on several factors, including feedstock properties, product specifications, catalyst characteristics, and process economics [2-7].

However, for refiners at the high end of sulfur in heavy SR-naphtha, high HDS conversion is needed to meet the environmental specifications. After sulfur

conversions of greater than 90%, conventional fixed-bed hydrotreated results in olefin losses of 99% or 100% due to saturation reactions [2,3,8].

Catalytic reforming is an important process for conversion of low octane naphthas into high octane motor fuels. Naphtha consists of a mixture of hydrocarbons (C_5-C_{10}) and the low octane components should be converted to components with better octane rating, mainly aromatics and iso-paraffins, in the same boiling range. The process of naphtha reforming in presence of monometallic or bimetallic reforming catalysts (such as Pt or Pt-Re), has been the subject of extensive research and development since 1930s till now[9-12]. The improvements in these types showed much more effects with naphtha feeds containing sulfur more than 1 ppmw.

This study addresses the hydrodesulfurization of different types of SR-naphtha feeds used for reforming feedstock preparation. Reforming reactions were also studied using prepared Pt/ γ-Al_2O_3 reforming catalyst in order to obtain high octane gasoline under operating conditions close to industrial applications .

EXPERIMENTAL

Catalysts

-Hydrodesulfurization catalyst: a commercial CoO-MoO_3/Al_2O_3 (UOP-S12) catalyst was used and contains: 3.1 wt% Co and 10.5 wt% Mo as oxides.
-Reforming catalyst: a γ-alumina supported catalyst containing 0.35 wt% Pt was prepared as described elsewhere[13] and used as a conventional reforming catalyst.

Feedstocks

A- The feedstocks used in hydrodesulfurization runs were four straight-run naphthas (SRN's) originated from four different Egyptian crude oils, namely: Marine Balayem(1), Land Balayem(2), Ras Shoukair(3) and Morgan(4). The main characteristics of the feedstocks are given in Table (1).

B- Straight- run naphtha from Land Balayem(type 2) was hydrotreated under an optimum operating conditions (i.e.320^{0}C reaction temperature, 42 bar hydrogen pressure, 5 h^{-1} LHSV and 125 L/L hydrogen- to-feed ratio) and the hydrotreated naphtha was used as the reforming feedstock.

Experimental Techniques

A- The hydrodesulfurization (HDS) experiments were conducted in a fixed-bed micro-reactor unit (cata-test unit) with once through hydrogen [14] using the SR-naphthas as feeds. The catalyst was presulfided *in-situ* using 8 wt% dimethyldisulfide(DMDS) diluted in SR-naphtha at 320^{0}C ,1.5h^{-1},and 15 bar for 12 hours. After presulfiding, conditions for each run were adjusted to the desired operating temperature (240^0 to380^{0}C), space velocity (1 to 9 h^{-1}) and hydrogen-to-feed ratio (70 to 160 L/L) while hydrogen pressure was kept constant at 45 bar. At each HDS conditions, liquid products were collected after the catalyst steady state had been reached. These liquids were analysed for sulfur and PONA according to the standard methods.

B- The reforming test was carried out in the same cata-test unit [14] using the prepared Pt/ γ-Al$_2$O$_3$ reforming catalyst. The reforming reaction conditions were nearly close to the industrial ones; 30 bar hydrogen pressure, 500^{0}C reaction temperature, 4 h^{-1} LHSV and 5 hydrogen-to-feed mole ratio. Prior to the catalytic test , the catalyst (50 Cm^3) was heated to 500^{0}C in dry hydrogen stream (15 ml/min) and reduced at this temperature for 7 h. The reactor was used in isothermal mode and the reforming reactions were carried out at 500^{0}C. After 45 min. of steady state operation, liquid and gas samples were collected during the next 3 h. The gaseous and liquid products were analyzed by gas chromatography using a column (3.5m length and 1/8" diameter) packed with tetra-cyanoethylated-penta-erithretol(TCEPE) on chromosorb-P(80-100). A Pye-Unicom GLC model 4550 was used and FID program with temperature integration of 40^0-90^{0}C and 90^0-140^{0}C.

From the chromatographic results, the composition of the reformate as well as the treated feedstock were determined.

C- Octane Number Determinations: The theoretical and predicting research octane number of different types of naphtha have been proposed by Anderson et al.[15] by the aid of the chromatographic analysis of the naphtha and based on the hypothesis that to each individual naphtha component corresponds a particular effective octane factor. This was adapted by Moljord et al.[16],Lugo[17],Cherepitsa[18],Arandes et al.[19] and Astapov[20] according to the equation:

$$\text{Octane Number} = \sum_{i=1}^{31} \left(a_i\ c_i \right)$$

where a_i is the octane number of group i and c_i is the mass proportion of group i identified by GLC. All the calculated values of octane numbers were in the $\pm$ 0.6 range of the RON values and in the $\pm$ 0.4 range of the MON values determined by the ASTM D-2699 method[17].
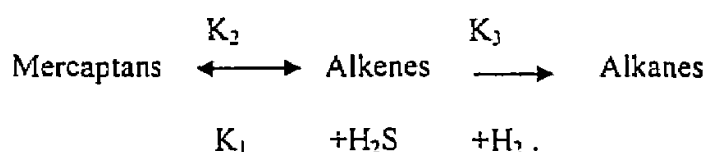
RESULTS AND DISCUSSION

- Feedstock Analysis

Analysis of the four feedstocks, shown in Table (1) indicates that the density, RVP, RON, PONA and boiling point distribution are nearly identical except the total sulfur and mercaptans. To study the effect of catalyst activity on the hydrotreating process, the feedstocks and products were characterized by chemical analysis for total sulfur, mercaptan and PONA analysis according to standard methods;ASTM: D-4045, D-3227/UOP-212 and D-1319/UOP-273 respectively.

-Effect of Temperature

The total sulfur in the hydrotreated products is shown in Figure (1). The hydrodesulfurization runs were done under constant hydrogen pressure, 45 bar, 6 h^{-1} LHSV and 125 L/L hydrogen-to-feed ratio. The total sulfur for all hydrotreated products, using the catalyst under investigation, decreased from 2.5ppm at 240°C to a

minimum of 0.25ppm at 380°C. The extent of HDS reactions increased with temperature increase. The mercaptans in the feedstocks, which were between 40 to 55% of the total sulfur, were greatly eliminated in the liquid products by the effects of temperatures and catalyst activity, and hence no mercaptan forming reactions along with hydrodesulfurization due to H_2S-alkene recombination reactions [3]. Therefore, the hydrotreating reactions has been operated at higher temperature ranges (240°-380°C), then alkenes were produced, and via the reaction with the formed H_2S, alkanes rather than mercaptans were formed as indicated by the forward reaction [3,6,21-22]:

$$\text{Mercaptans} \underset{K_1}{\overset{K_2}{\rightleftharpoons}} \text{Alkenes} \quad \underset{+H_2}{\overset{K_3}{\longrightarrow}} \text{Alkanes}$$

$$+H_2S \quad +H_2 .$$

The reversible reaction, i.e H_2S-alkene recombination to form mercaptans is an exothermic reaction and dependent on temperature, feedstock type, total sulfur, hydrogen partial pressure, space velocity and catalyst type[21].

Hydrogen sulfide has a strong retarding effect on HDS at moderate conditions, due to inhibition caused by adsorption of H_2S on catalytic sites in competition with the sulfur compounds. Therefore, the HDS inhibiting effect on the catalyst under study was observed to be decreased with rising temperature and was more pronounced in the bench-scale (cata-test) unit rather than commercial units[6,7]. In commercial hydrotreater units, the hydrogen sulfide was observed to be recombined with alkene to form mercaptans in the reactor outlet piping and heat exchangers systems as the fluid cool down, leading to higher product mercaptan contents [22].

The alkanes were also increased with temperature increase (Fig.2) due to ring opening reactions of the naphthenic content. It is clear that increasing reaction temperature results in slightly an increase in the aromatic content, which may be due to naphthenes dehydrogenation reactions [8].

- Effect of Space Velocity and Hydrogen-to-Feed-Ratio

The effect of space velocity on HDS was studied at the range of 1 to 9 h^{-1} at contant reaction temperature, 320^0C, hydrogen pressure, 45 bar, and 125 L/L hydrogen-to-feed ratio. In all the SR-naphthas, the total sulfur content in the hydrotreated products were slightly increased from less than o.25 to 1ppm as the space velocity increased from 1 to 7 h^{-1} as shown in Figure.(3). Raising the space velocity, a sharp increase in the sulfur content was observed, i.e. from 1 to 4 ppm at 7 to 9 h^{-1} respectively due to the decrease in hydrogenation and hydrogenolysis extents.

The effect of hydrogen-to-feed ratio on HDS was also investigated from 70 to 160 L/L .The data shown in Figure (4), indicated that the effect of hydrogen gas rate on the desulfurization of the four SR-naphthas was increased within the range of operating conditions used.

The HDS extent improved with increasing the hydrogen-to-feed ratio from 70 to .130 L/L, above which, there was a slight increase in HDS. It means that the hydrogen partial pressure is increased, leading to the HDS reaction rates increase and suppresses H_2S-alkene recombination reactions to mercaptan formation The alkane formation was increased and observed in the PONA analysis as shown in Figure(5).

-Reforming Reactions by Platinum Catalyst

The hydrotreated naphtha (using SR-naphtha feed type-2, contained 0.3ppm sulfur was produced under optimum operating conditions; 320^0C reaction temperature,42 bar hydrogen pressure, 5 h^{-1} LHSV and 125 L/L hydrogen-to-feed ratio) was reformed under the reforming conditions. Deyhdrocyclization of paraffins is one of the main reactions during naphtha reforming, because it increases the octane number and produces valuable aromatic hydrocarbons (benzene, toluene and xylenes). Table (2) shows the conversion of the treated naphtha to the most interesting reforming products under the effect of 0.35 wt% Pt/ γ-Al_2O_3 catalyst. The reforming reactions rate was observed to be favored at high temperature (500^0C) and mild pressure (30 bar). These conditions are necessary for the traditional monometallic Pt/Al_2O_3 catalyst stability and to increase the selectivity to aromatics, which in turn increased the octane number of the reformate. These results were attributed to the high activity of the catalyst and

to the Lewis acidity of the alumina support. The catalyst is a bifunctional type and the presence of the acid function adds isomerization and cracking capacity to its function.

The formation of light hydrocarbons such as C_1 to C_4 (26 wt%) can be taken as a measure of the activity in hydrogenolysis of the metallic function of the catalyst. Therefore, the data in Table (2) indicates that the activity in hydrogenolysis of Pt/γ-Al_2O_3 is high, producing large amounts of C_1 and C_2 (i.e 4.51 and 2.8 wt%) and also of benzene and toluene (4.6 and 9.0 wt%) which are products of the hydrogenolysis of naphtha under study. On the other hand, cracking reactions occurred on the acid sites of the catalyst, and C_3 and C_4 hydrocarbons are produced. Paraffin isomerization is a very rapid reaction when compared to dehydrocyclization and hydrocracking over bifunctional catalysts [11]. The higher paraffins in the naphtha are first isomerized, the isomers being then dehydrocyclized over bifunctional catalyst and the cyclization of the carbon chain which occurs mainly on the acid function cause the formation of a five-carbon or a six-carbon ring intermediate [11,12]. The data also shows that Pt/γ-Al_2O_3 has a high activity in dehydrogenation reaction which reflects on the production of aromatics (51wt%).

Determination of Octane Number of the Reformate

The data in Table (3) indicates that the octane number, either RON or MON have a certain correlation with the content of aromatics in the reformate. Moljord et al. [16] have found this correlation as linear and independent of the reaction conditions. A given concentration of aromatics in the reformate is needed to achieve a certain RON value. However, the relative amount of the different aromatic components depends on the operating conditions. The aromatic components produced in our study were attained at severe condition of reaction temperature (500°C) and mild pressure (30 bar), and reached the most favorite value that obtained, i.e higher octane values, 93.5 (RON) and 91 (MON). Since the iso-paraffins crack much easier than the corresponding n-paraffins, it is not obvious that the iso-to-normal(i/n) ratio for all paraffins are defined by their thermodynamic equilibrium at high-severity reforming. As the paraffin isomerization reactions are slightly exothermic, the equilibrium ratio i/n of paraffins diminishes slightly with increasing reaction temperature. Therefore,

less isomers were produced, with increasing reaction temperature, which were responsible for higher values of RON.

CONCLUSIONS

The study investigated in this text included the naphthas HDS followed by reforming the hydrotreated naphtha in bench-scale cata-test reactor. The hydrotreated naphtha sulfur content decreased to a minimum, i.e. less than 0.5 ppm, with increasing temperature (within the limit of 340-360°C) or decreasing LHSV to the range of 6 to $1h^{-1}$. At nearly higher H_2-to-feed ratio of 120-150 L/L, the product sulfur content was also decreased from 0.5 to 0.4 ppm. .

It can be stated that the CoMo/alumina catalyst used in the hydrotreating process has high HDS activity and not favor mercaptan formation by H_2S-alkene recombination reactions under the higher hydrotreating conditions, Of temperatures and hydrogen partial pressure.

The RON of the reformate was calculated using a simplified and fast method which is very applicable and accepted in many international laboratories depending on the GLC analysis of naphtha.

The prepared Pt/γ-Al_2O_3 was active toward dehydrocyclization reactions of paraffins and their reaction rate were favored at the severe reaction temperature, i.e. 500°C.

The RON of the reformate produced on the conventional Pt/γ-Al_2O_3 catalyst after naphtha hydrotreated was nearly high (93.5). Less iso-paraffins , more aromatic hydrocarbons and 26% of lighter products were found in the liquid reformate, which means the higher selectivity of the catalyst towards aromatization rather than isomerization.

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Table (1) : Analytical Results of SR-Naphta Feedstocks

Property	SRN-Types			
	1 o	2 ●	3 Δ	4 □
Desnity @ 15°C	0.7125	0.7215	0.7155	0.7015
RVP, psi@ 100°F	8.9	8.4	8.8	9.4
RON	55	51	53	56
Total sulfur, ppm	366	640	350	162
Mercaptans, ppm	200	265	194	90
PONA analysis, vol%:				
Paraffins	64.85	64.17	67.47	64.97
Olefins	0.15	0.13	0.13	0.13
Naphthenes	29.08	29.90	27.40	28.20
Aromatics	5.92	5.80	5.00	6.70
ASTM-Distillation:				
IBP @ °C	39	43	40	37
50% vol @ °C	100	105	102	98
FBP @ °C	164	168	166	163

Table (2) : Naphtha Composition (wt%) as Distributed by GLC Analysis of the Treated Naphtha Feed and Reforming Product.

Carbon No	Treated Naphtha				Reformate			
	P	N	Ar	Total	P	N	Ar	Total
C_5	1.34	---	---	1.34	0.81	---	---	0.81
C_6	9.96	0.15	0.30	10.41	1.20	0.16	4.59	5.95
C_7	16.65	3.00	2.50	22.15	5.58	1.75	8.95	16.28
C_8	26.14	13.80	5.00	44.94	7.79	3.03	25.18	36.00
C_9	13.50	4.60	---	18.10	2.17	0.07	12.60	14.84
C_{10}	2.80	0.26	---	3.06	0.47	0.04	---	0.51
Total	70.39	21.81	7.80	100.00	18.02	5.05	51.32	74.39

Hydrocracking, wt% (C_1-C_4):	25.61
C_1 4.51%	
C_2 2.80%	
C_3 10.80%	
C_4 7.50%	
Total Isomerization, wt%	9.04

Table (3) Calculated Octane Number of the Treated Naphtha and Reformate

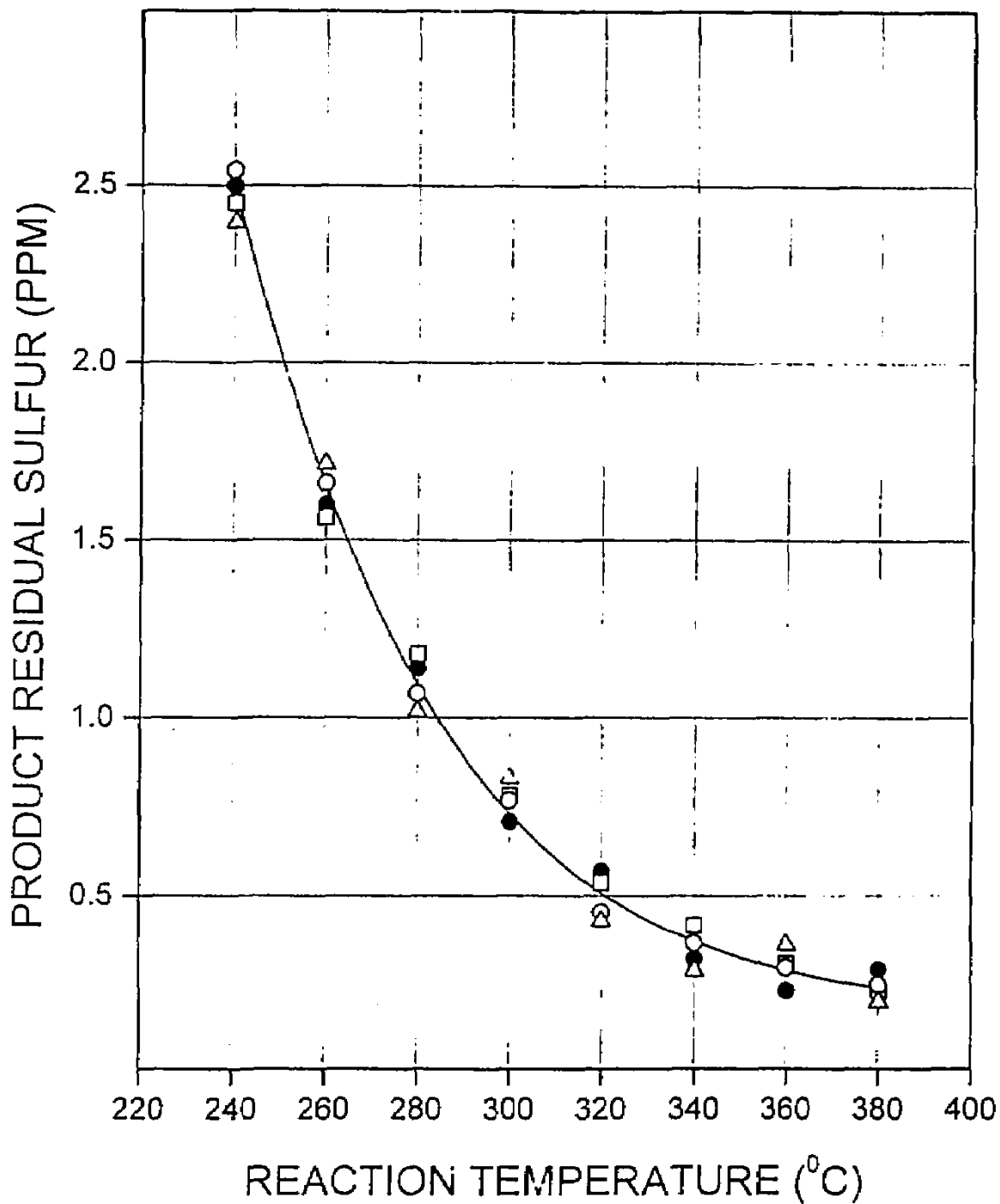| Characteristics	Treated Naphtha	Reformate
RON	54.09 ± 0.6	93.47 ± 0.6
MON	53.28 ± 0.4	90.88 ± 0.4
Aromatic content, wt%		
Benzene	0.30	4.59
Toluene	2.50	8.95
m-xylene	1.81	7.98
o-xylene	1.39	6.10
p-xylene	0.60	2.62
Ethyl benzene	1.20	8.48
Higher aromatics	---	12.60

Fig. (1): Effect of Temperature on Naphtha Hydrodesulfurization Under Constant H_2 Pressure, 45 bar; LHSV, 6h^{-1} and H_2-to-Feed Ratio 125 L/L
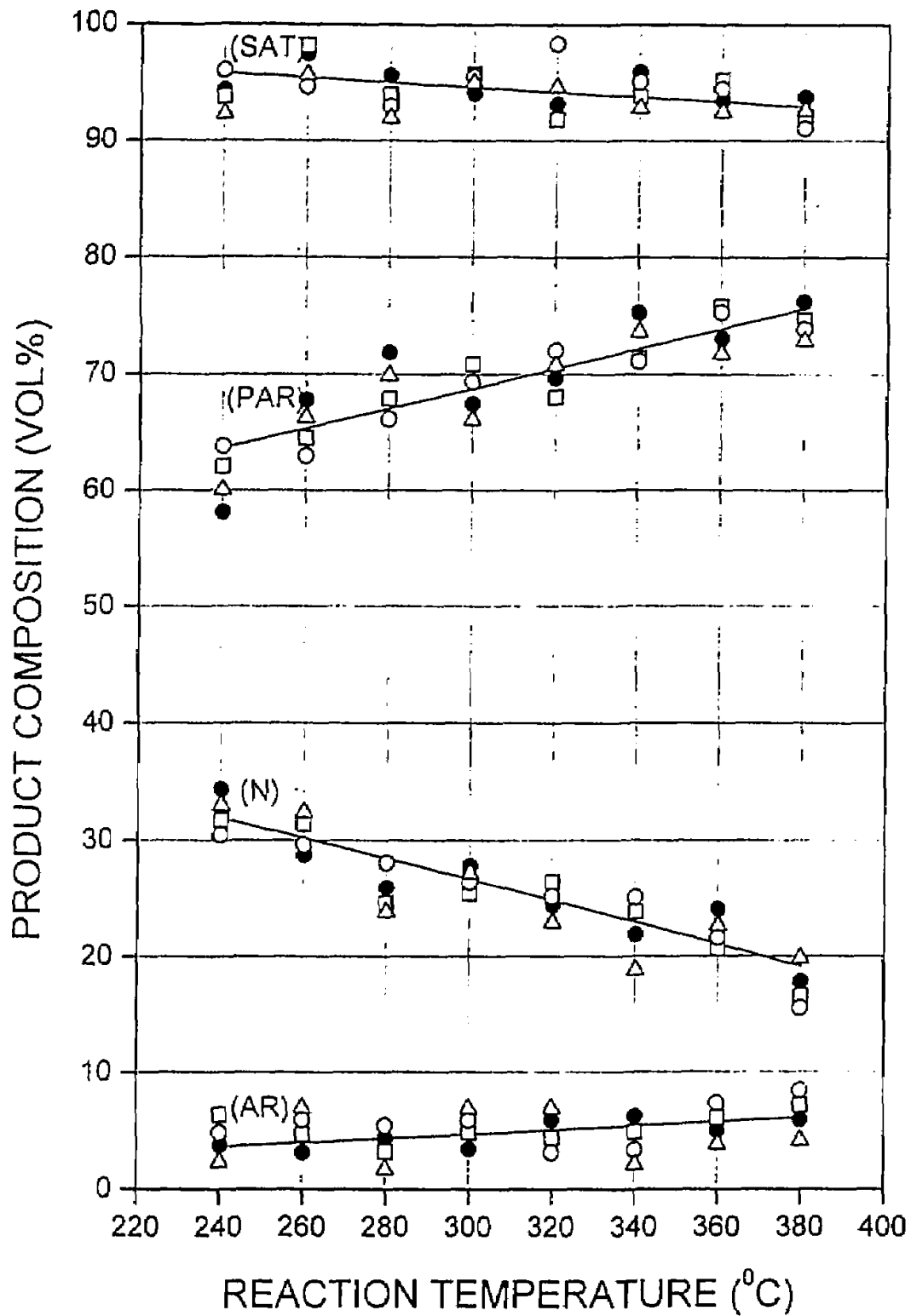
Fig.(2): Effect of Temperature on Hydrotreated Naphtha Composition
Under Constant H_2 Pressure, 45 bar; LHSV, 6h^{-1} and
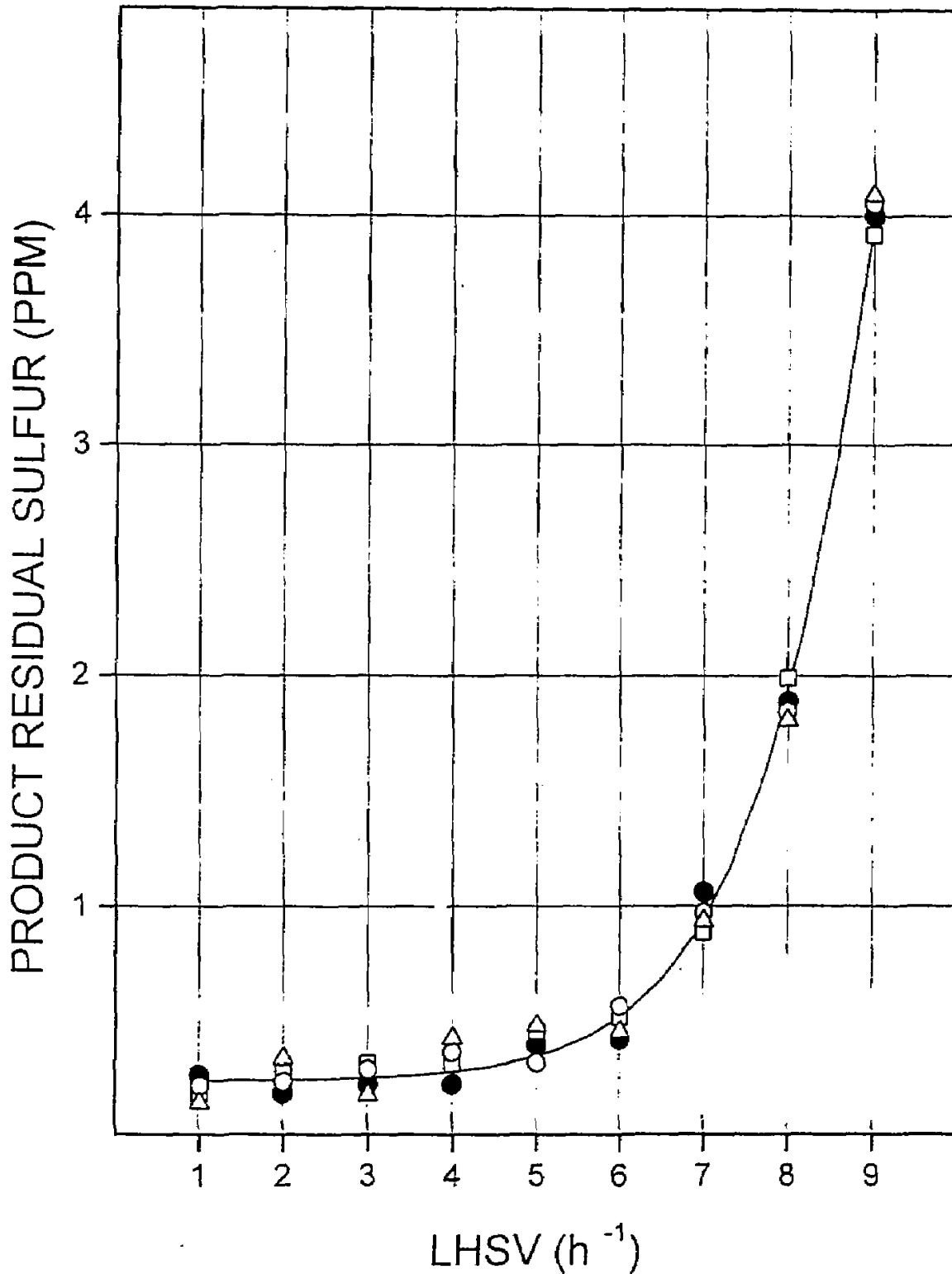H_2 to Feed Ratio 125 L/L.

Fig.(3): Effect of LHSV on Naphtha Hydrodesulfurization Under Constant Reaction Temperature, 320°C, H_2 Pressure, 45 bar, and H_2-to-Feed Ratio, 125 L/L.
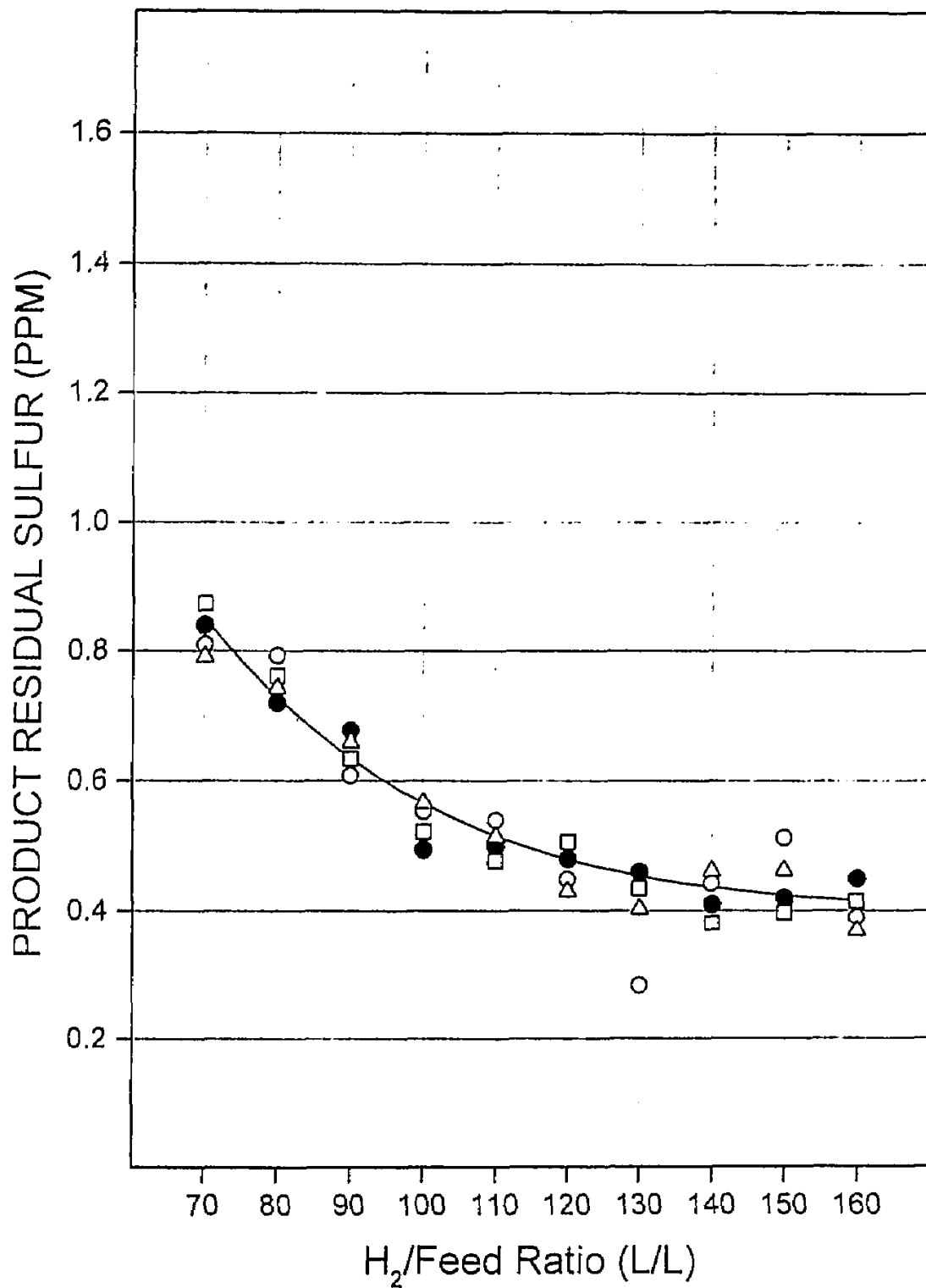
Fig.(4): Effect of H_2/Feed Ratio on Naphtha Hydrodesulfurization Under Constant Reaction Temperature, 320^0C, H_2 Pressure, 45 bar, and LHSV, $6h^{-1}$.
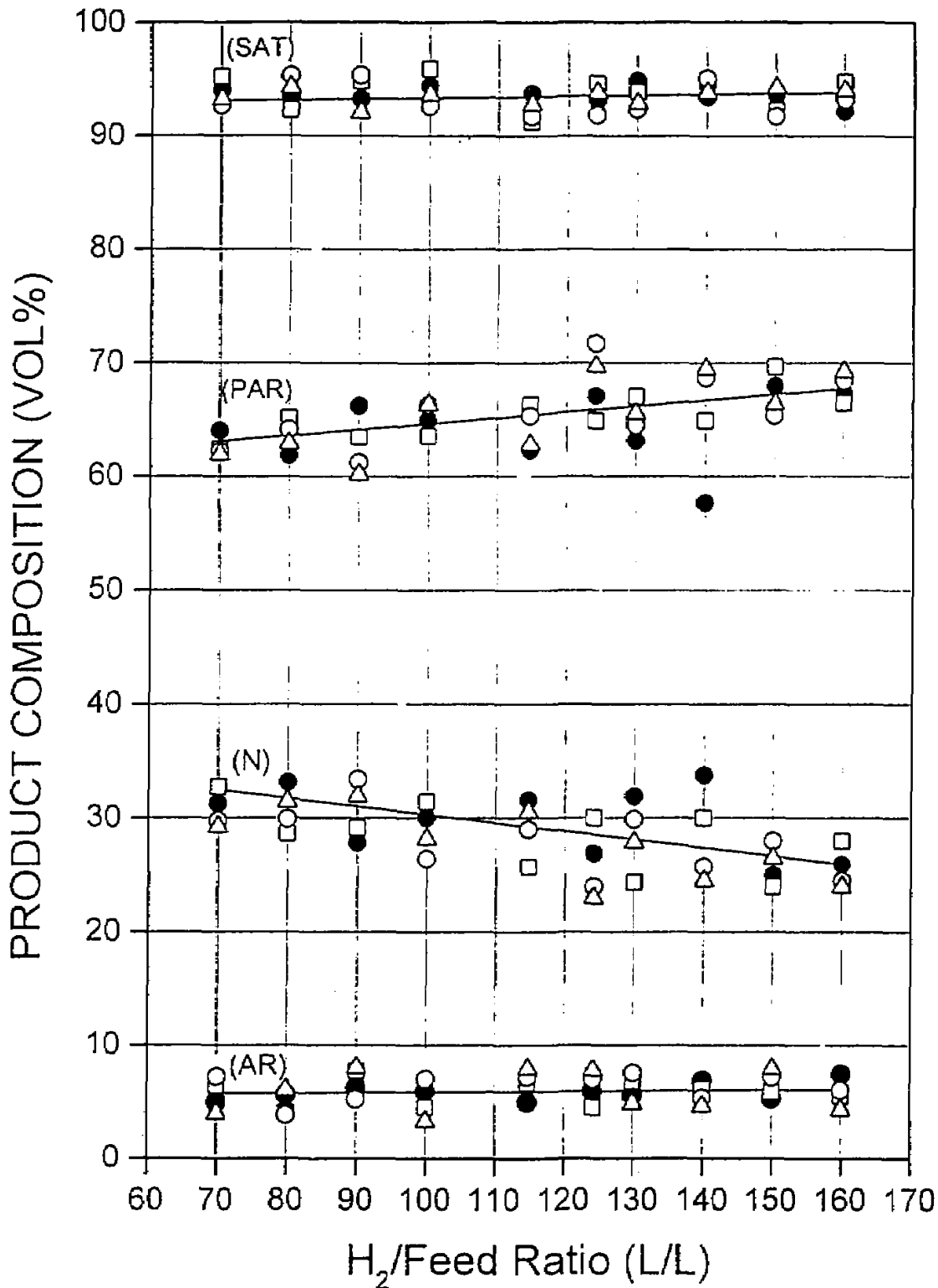
Fig.(5): Effect of H_2/Feed Ratio on Hydrotreated Naphtha Coposition Under
Constant Reaction Temperature, 320^0C, H_2 Pressure, 45 bar,
and LHSV, $6h^{-1}$.