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Effect of Operating Cconditions on Hydrodesulfurization of Vacuum Gas Oil

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Abstract

This study was conducted according to contract with the North Refineries Company-Baiji and deals with the hydrodesulphurization of vacuum gas oil of Kirkuk crude oil, boiling range 611-833 K. A trickle bed reactor packed with a commercial cobalt-molybdenum on alumina catalyst was used. The operating conditions were: temperature range 583-643 K, liquid hourly space velocity range 1.50-3.75 1/h, hydrogen to oil ratio about 250 l/l and pressure kept constant at 3.5MPa.

The results showed that the aromatic content decreased and sulfur removal increased with increasing temperature and decreasing space velocity. The properties (viscosity, density, flash point and carbon residue) of the products decrease with temperature increasing, but the aniline point increased.

Introduction

Hydrotreating process plays an important role in the refinery. It is a catalytic conversion for removal of organic sulfur, nitrogen, oxygen compounds and metals from petroleum fractions and residue at high hydrogen pressures and temperatures accompanied by hydrogenation of unsaturated and cracking of feedstock's to lower molecular weight hydrocarbons. Indeed, hydrotreating capacity has been growing steadily (at about 6% per year since 1976) and represents today nearly 50% of the total refining capacity [1]. The increasing application of hydrotreating can be ascribed to: i-The ever decreasing availability of light,sweet crudes and thus the increasing fraction of heavy ,high sulfur crudes that must be processed.ii-The trend to increase upgrading of feedstock's for improvement of downstream processing such as catalytic reforming and catalytic cracking [2].

The hydrodesulphurization (HDS) of petroleum fractions has long been an integral part of refining operation. HDS is practiced in every modern refinery (3). The technology of the HDS process is well established, and petroleum stocks of every conceivable molecular weight range can be treated to remove sulfur. Thus, it is not surprising that an extensive knowledge of HDS has been acquired along with the development of the process over the last few decades. However, most of the available information pertaining to the HDS process has been obtained with the lighter and more easily desulfurized petroleum fractions, but it is, to some degree to the HDS of the heavier feedstocks such as the heavy oils, vacuum gas oil and residua. On the other hand, the processing of the heavy oils and residua present several problems that are not found with distillates processing and which require process modification to meet the special requirements that are necessary for heavy feedstock desulfurization [3].

Hydrodesulphurization of heavy oils to meet rapidly increasing low sulfur fuel market is one of the major technical and economic challenges facing the refining industry during this decade. One route to low sulfur oil production is vacuum gas oil (VGO) desulfurization. Atmospheric distillation tower residuum is first fractionated in vacuum distillation tower to vacuum gas oil and residuum. The sulfur content of the vacuum gas oil then significantly reduced by the means of catalytic HDS. This process has the advantage of being relatively inexpensive. Feed stock to this process may include virgin and visbreaker vacuum gas oil, thermal and catalytic cycle oils and coker gas oil[4,5].

Several classes of reactions occur simultaneously in HDS process which include hydrodenitrogenation (HDN), hydrodeoxygenation(HDO), hyrdocracking and hydrogenation [6].

The present work deals with the effect of temperature and LHSV on the HDS of vacuum gas oil using trickle bed reactor,

Experimental Work

The feedstock used in the present work is a VGO of Kirkuk crude oil with boiling range 611-833 K.

It was prepared by blending the fractions: light VGO (611-650 K),medium VGO (650-690 K), heavy VGO (690-727 K) and very heavy VGO (727-833 K) with volume percentages 13.67, 21.67, 27.00 and 37,66, respectively. The properties of the VGO used in this investigation are given in Table 1.

The sulfur content of the feedstock and the hydrotreated products was determined according to bomb method (ASTM: D 129-64). The group's composition of VGO and the hydrotreated products were determined by liquid solid chromatography using silica gel as the adsorbent. The chromatographic column has about 25 mm in. diameter, packed to a height of 500 mm with silica gel and made of glass. About 2 g of sample was introduced into the column each time. The column is shown in Figure 1. The saturated fraction eluted from column by 150 ml of n-hexane, then the aromatic fraction eluted by 200 ml of benzene. Finally, the polar aromatic fraction eluted with 150 ml of methanol-benzene mixture (20/80 by volume).Table 2 shows the sulfur content, aromatic and saturated fractions distribution in feedstock fraction.

The catalyst used was a commercial cobalt-molybdenum on alumina (Co-Mo-alumina) type and its properties are shown in Table 3.

120 ml of the fresh catalyst was first dried for two hours and then placed inside the HDS trickle bed reactor. The catalyst was surrounded by two beds of inert material at top and bottom of the reactor of 135 mm height each. The catalyst was presulfided to promote its activity by passing a solution of 0.6% of carbon disulfide in commercial gas oil over it. This activation process was carried out in two stages. The first stage was at pressure of 2.1 MPa, temperature of 477 K and liquid hourly space velocity of 4 1/h for 4 hours with no hydrogen flow. The second stage was at pressure of 2.1 MPa, temperature of 573 K and LHSV of 1 1/h for 16 hours and hydrogen to oil ratio of 200 l/l.

The HDS runs were performed in a laboratory continuous high pressure unit employing an up-flow cocurrent trickle bed reactor. Figure 2 shows the flow diagram of the HDS unit. The reactor was made of 316 stainless steel, having 20 mm in. diameter and 650 mm height. It was jacketed with five separately heat-controlled block shells in order to keep a certain isothermal operation. The reactor effluent was cooled in a condenser-cooler and the liquid products were separated from unreacted hydrogen gas, hydrogen sulfide and the hydrocarbon gases in a high and low pressure separators. The gases were vented to the exterior through gas flow meter. A high pressure dosing pump was used to introduce the feedstock to the reactor. A calibrated micrometer was fitted to the pump to estimate the feedstock flow rate. The hydrogen gas was fed to the reactor from a hydrogen cylinder through a heated high pressure line. The hydrogen gas flow rate was estimated by electrical gas inlet flow sensor using standard calibrations with the electrical pulses.

The HDS experiments of the VGO were carried out with: temperature range of 583-643 K, LHSV ranging from 1.5 to 3.75 1/h, hydrogen pressure was kept constant at 3.5 MPa and hydrogen to feed ratio was approximately 250 l/l. When the steady-state operation was established, the products were collected.

The hydrodesulfurized product was fractionated by a laboratory distillation unit. The unit consisted mainly of round bottom flask, distillation column, still head distillate recievers, reflux condenser and vacuum system. The flow diagram of the unit is shown in Fig. 3. The distillation unit was operated at atmospheric pressure up to a distillation temperature of 611 K. The distillation unit system was, then, connected to a vacuum pump through a vapor trap to continue the distillation at a vacuum pressure as low as 0.5 mm Hg. A magnetic valve connected to the reflux timer was used to obtain the desired reflux ratio. The reflux ratio was 3:1 for distillation temperature up to 611 K and 1:1 for the remainder fractions.

The specific gravity, flash point, kinematic viscosity and carbon residue of the feedstock and the products were measured by using IP 120/64, IP 15/57, IP 319/75 and IP 3/66, respectively.

Table 1 Properties of feedstock

Specification	value
Sp.gr.at 60/60 F	0.911
API	23.858
Viscosity at 323 K, cS	11.563
373 K, cS	2.784
Pour point, K	302
Flash point, K	465
Anline point, K	325
CCR, wt%	0.58
Sulfur content, wt%	2.5

Table 2 Sulfur, aromatics and saturated fraction distribution in feed stock

Fractions	Sulfur, wt%	Aromatics, wt%	Saturated, wt%
LVGO (611-560 K)	2.38	16	83
MVGO (650-690 K)	2.4	24	76
HVGO (690-727 K)	2.5	34	66
Very HVGO (727-833 K)	2.6	50	5

Table 3 The catalyst properties

Chemical properties	Value wt%
MoO_3	15.0
CoO	3.0
SiO_2	1.1
Na_2O	0.07
Fe	0.04
SO_2	2.0
Al_2O_3	balance
Physical properties	**Value**
Form	Extrudate
Surface area, m^2/g,	180
Pore volume, cm^3/g	0.5
Bulk density, g/cm^3	0.67
Mean particle diameter, mm	1.8
Mean particle length, mm	4

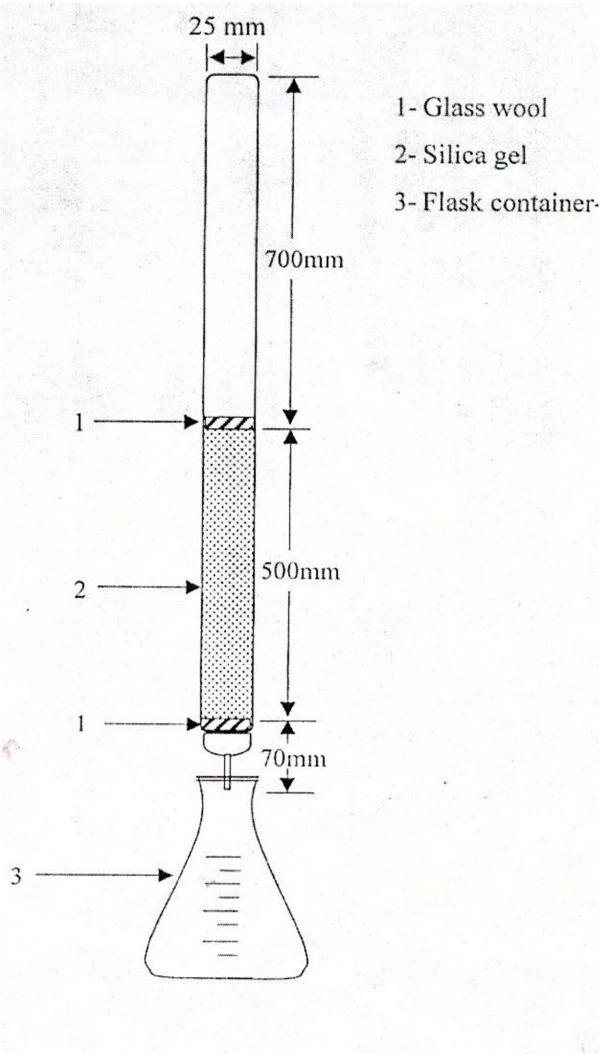


Fig. (1) Solid liquid chromatographic column

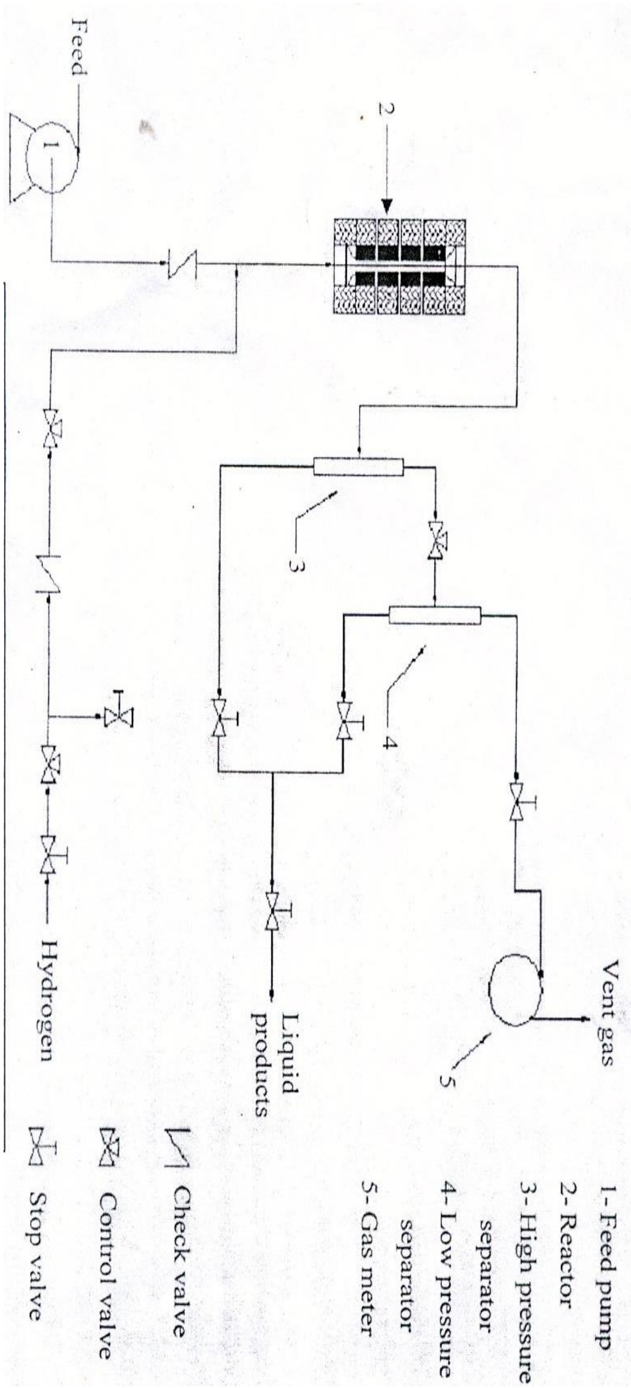


Fig. 2 Floe diagram of laboratory hydrodesulphurization unit

Results and Discussion

The HDS of VGO in a fixed catalyst bed reactor is a complex process and many variables affect the extent of sulfur removel .The main variables are temperature , pressure, LHSV and hydrogen to oil volumetric ratio. Through the present study , the hydrogen pressure and the hydrogen to oil ratio were kept constant.

At constant LHSV , the sulfur content of hydrodesulfurized products decreased (Figure 4) as the reaction temperature increased ,hence , the sulfur removal increased (Figure 5) . Whereas at constant temperature, the sulfur content increased as the LHSV increased as shown in Figure 6 . The results are in agreement with other studies for the HDS (7-10). The icreasing sulfur removal at high reaction temperature may be attributed to several reasons. Firstly, the unreactive sulfur compounds which most properly belong to thiophene derivatives become activated enough to react with hydrogen and secondly, the aromatic compounds are decomposed to smaller molecules which can more easily diffuse into the catalyst micro and mesopores and reach the inner active sites where the desulfurization reaction mainly occur(9).Thus ,the upper temperature value is limited by the undesirable side reactions such as hydrocracking and thermal cracking reactions which are expected to occur at high temperature.

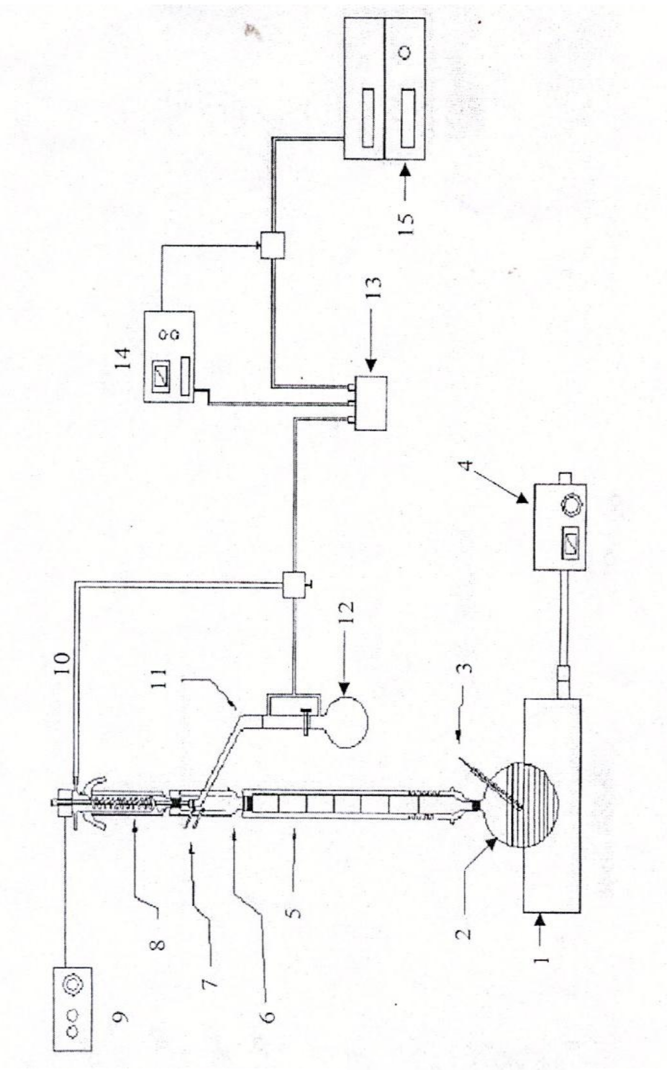
The contact time between the reacting fluid and catalyst decreased when increasing the LHSV and this led to the sulfur removel decrease with icreasing LHSV.

The distribution of sulfur content in the hydrodesulfurized fractions, LVGO, MVGO, HVGO and very heavy VGO at 643 K is shown in Fig. 7.This figure shows that the sulfur content of any fraction decreased with decreasing LHSV.

Figures 8 and 9 show that the decreasing percentage of aromatic compounds and the increasing percentage of saturated compounds in the hydrodesulfurized proudct both increase with icreasing reaction temperature and decreasing of LHSV.This is due to the increase of the rate of hydrogenation of aromatics and the increase of the contact time as mentioned by Girgis(6).

The effect of hydrotreating temperature and LHSV on aniline point of the hydrotreated products are shown in Figures 10 and 11. The aniline point increases with temperature increase and LHSV decrease due to the increase of the rate of hydrogenation reaction.

The viscosity, flash point, density and carbon residue decrease with increasing temperature and reaction time as shown in Figures 12-19. The decrease in these properties is due to the increase in the rate of hydrogenation and hydrocracking reactions.



1- Heating mantle
2- Round bottom
3- Thermometer
4- Voltage regulator
5- Column
6- Divider
7- Thermometers
8- Reflux condenser
9- Timer
10 Vacuum line
11-Receiver
12-Product flask
13-Trap
14-Vacuum pressure control
15-Vacuum pump

Fig. 3: Laboratory Distillation Unit

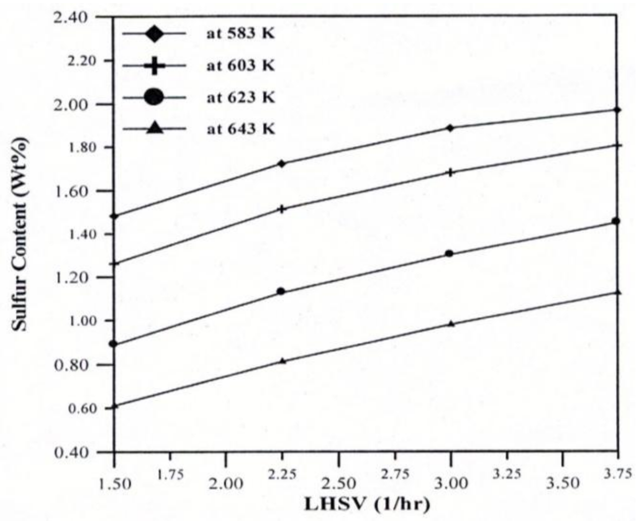


Fig. 4 Effect of LHSV on the sulfur content of the hydrotreated product.

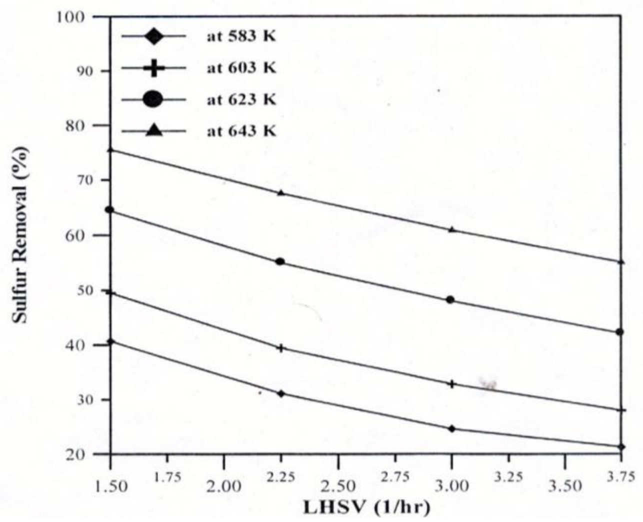


Fig. 5: Effect of LHSV on the sulfur removal of the hydrotreated product.

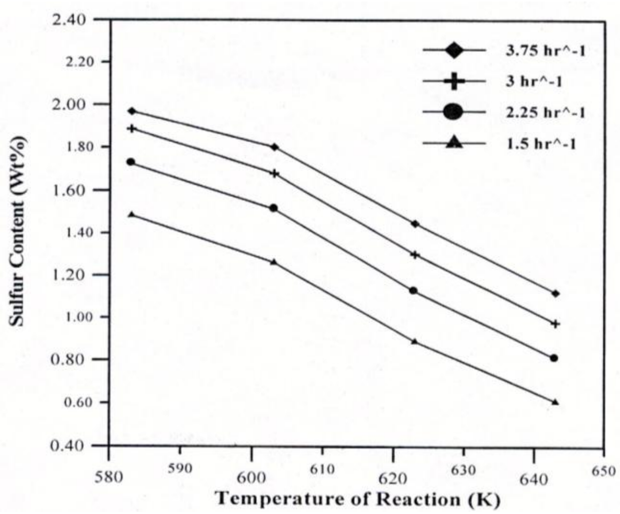
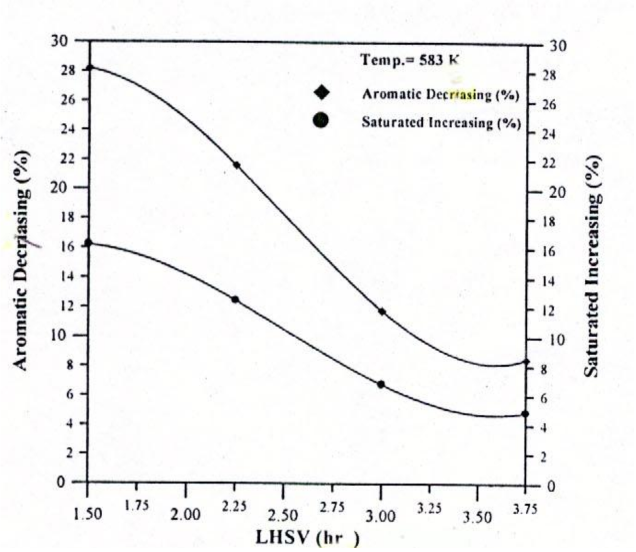


Fig. 6: Effect of Temperature on the sulfur content of the hydrotreated product.



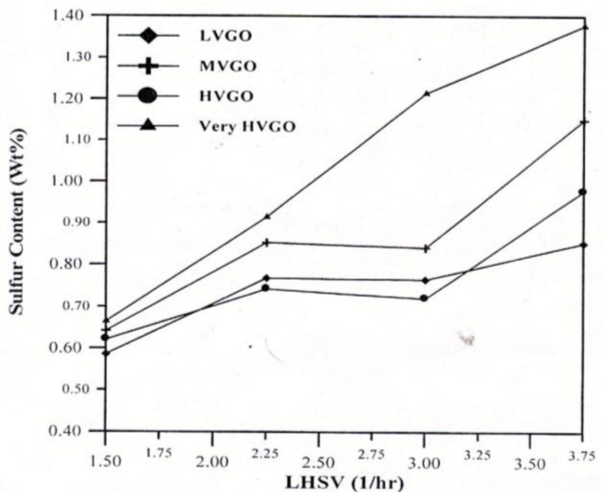
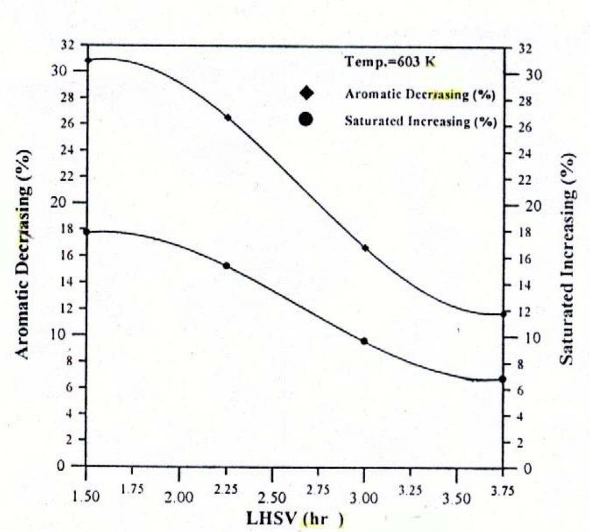


Fig. 7: Distribution of Sulfur in hydrotreated friction at 643° K



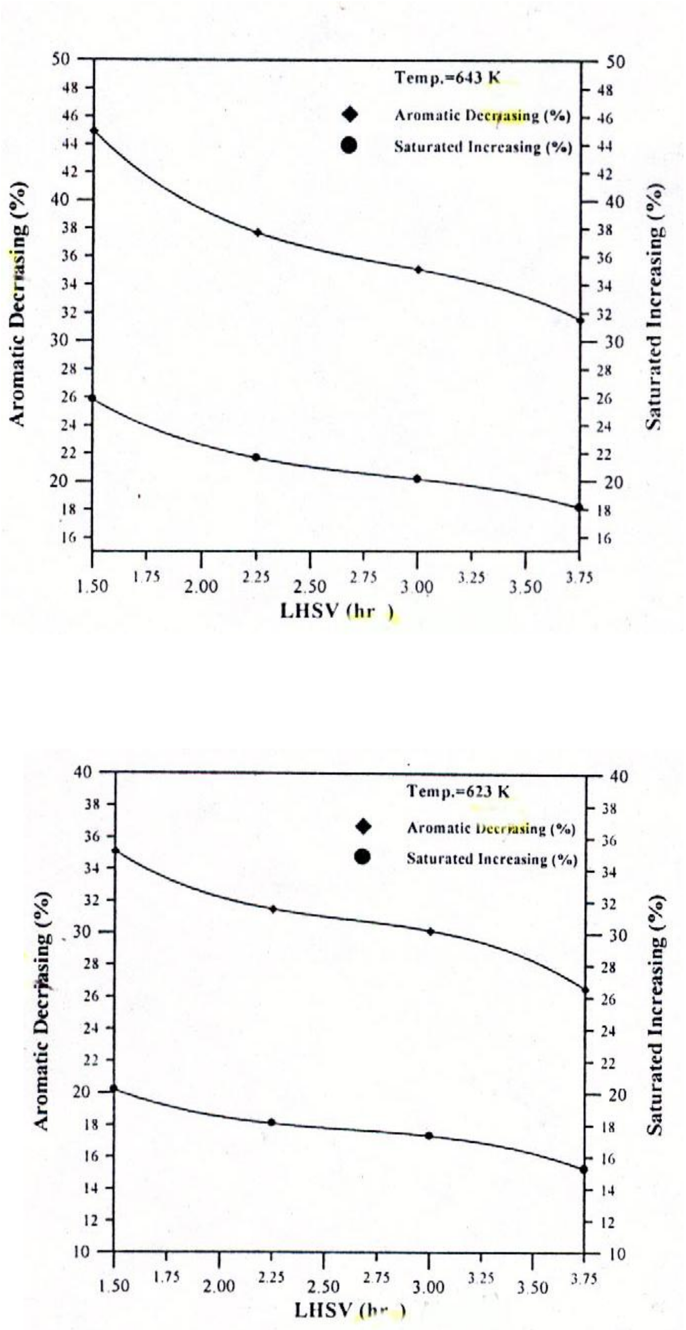
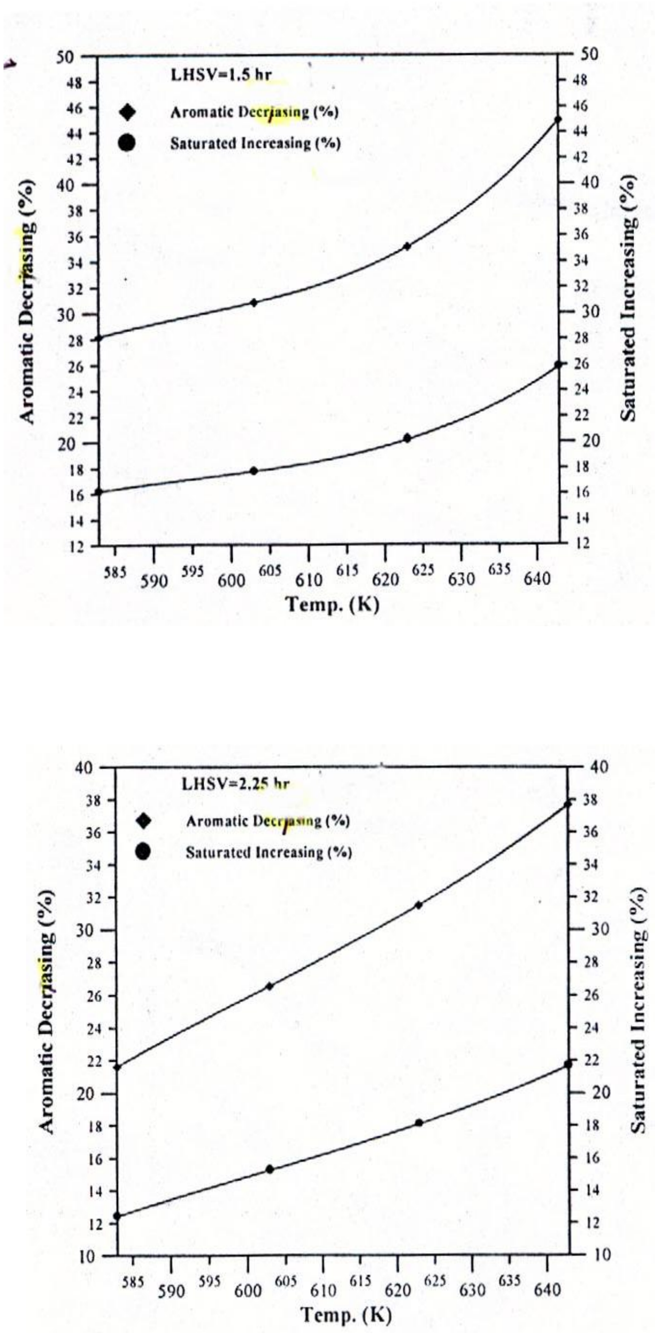
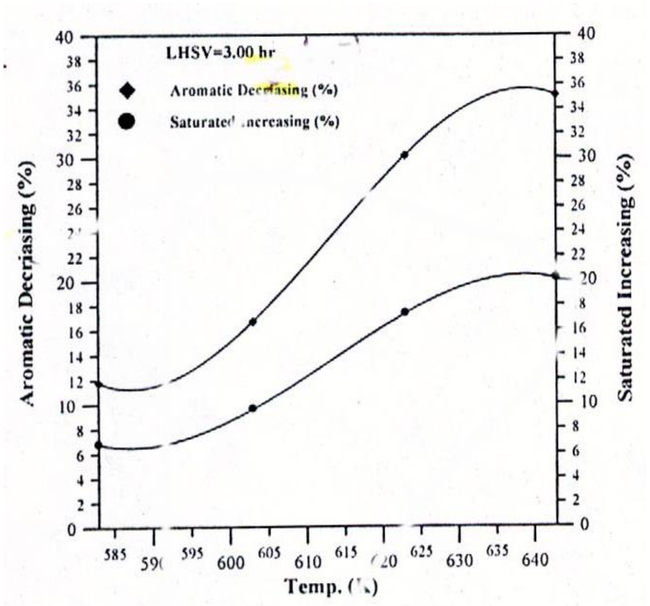


Fig. 8: Effect of LHSV on the aromatic and saturated content of hydrotreated product





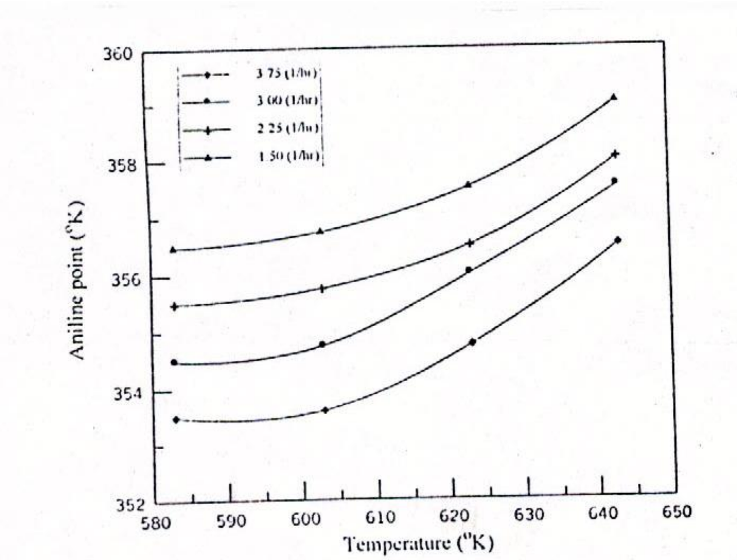


Fig.10: Effect of hydrotreating on aniline point of the hydrotreated product.

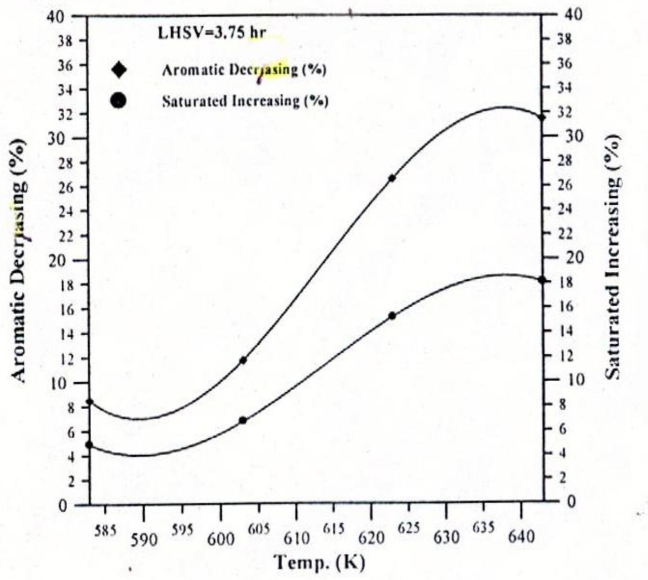


Fig. 9: Effect of temperature on the aromatic and saturated content of hydrotreated product.

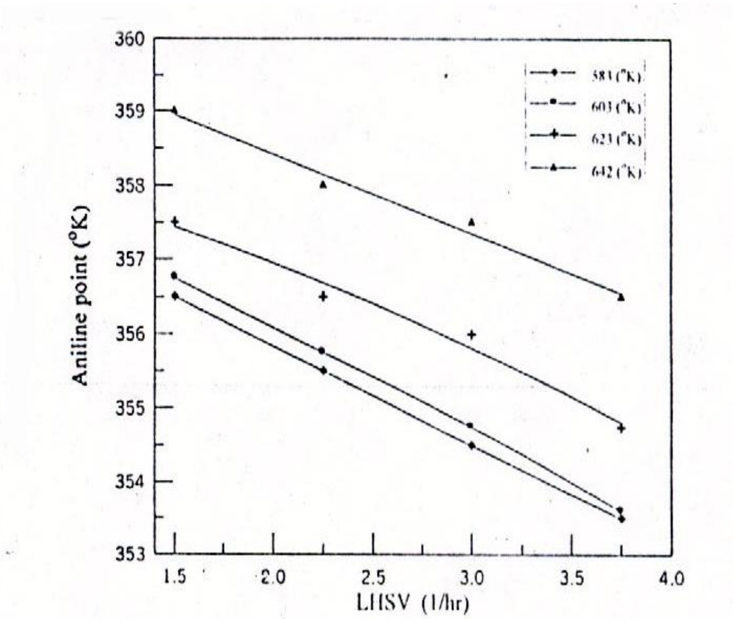


Fig.11:fect of LHSV on aniline point hydrotreated product

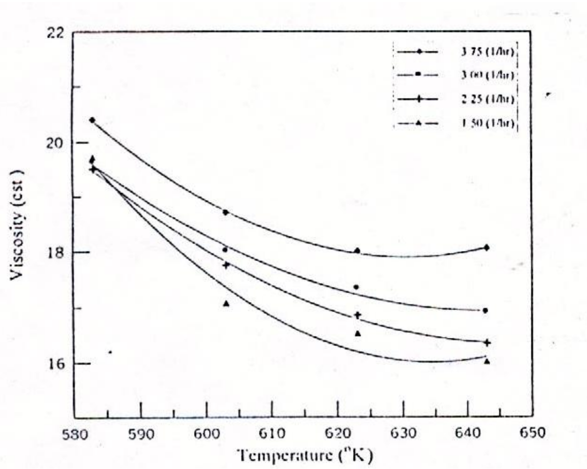


Fig.12: Effect of hydrotreating on viscosity of the hydrotreated product.

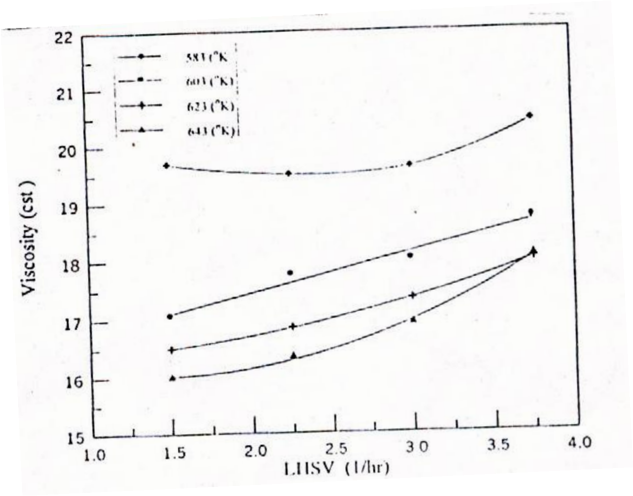


Fig.13: Effect of LHSV on the viscosity of hydrotreated product

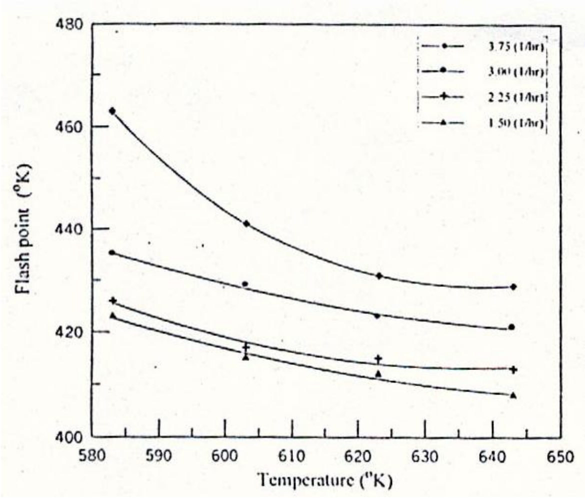


Fig.14: Effect of hydrotreating on the flash point of the hydrotreated product

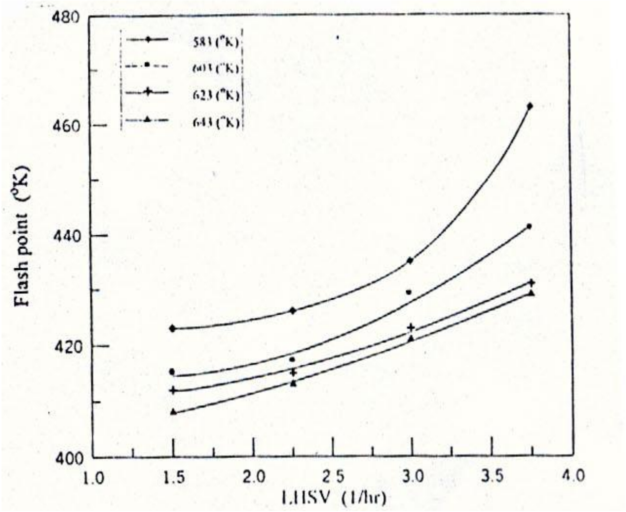


Fig.15: Effect of LHSV on the flash point of the hydrotreated product

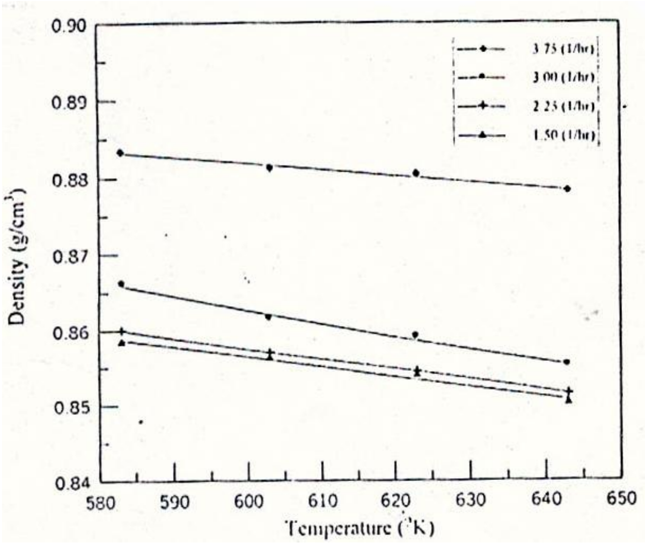


Fig.16: Effect of hydrotreating temperature on the density of the hydrotreated product

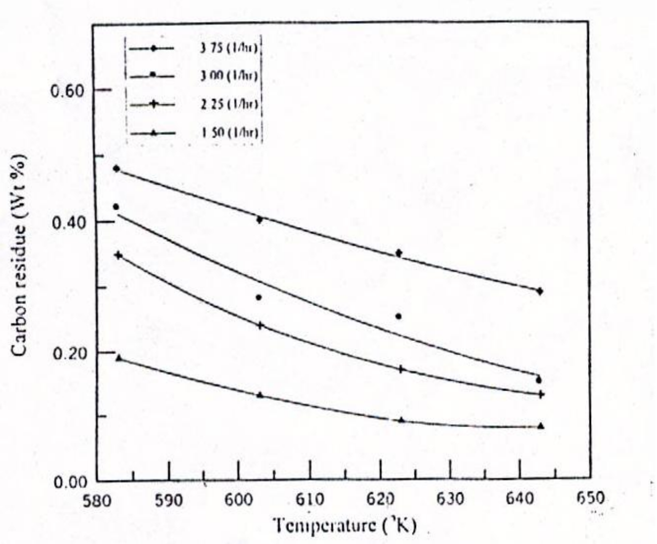


Fig.18: Effect of hydrotreating on the carbon residue of the hydrotreated product

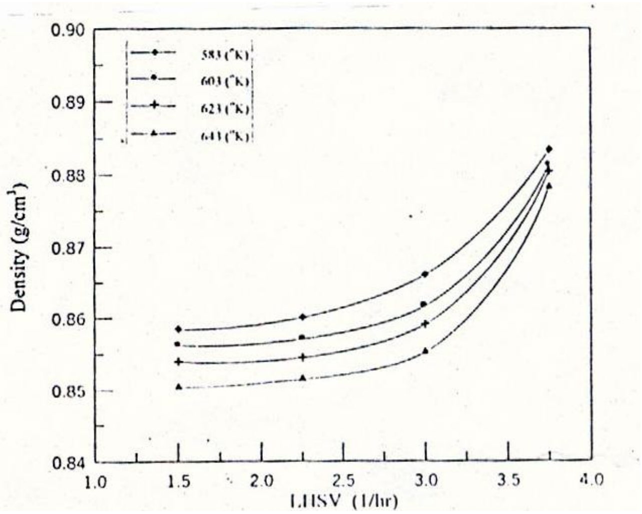


Fig.17: Effect of LHSV on the density of the hydrotreated product

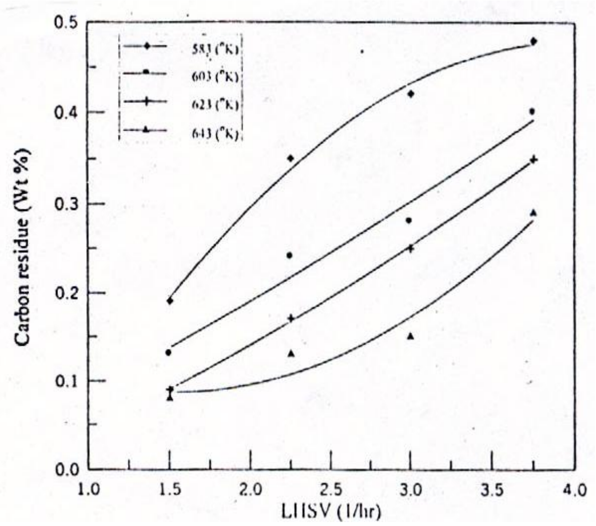


Fig.16: Effect of LHSV on the carbon residue of the hydrotreating product.

CONCLUSIONS

1. Sulfur removal from vacuum gas oil produced in Baiji refinery is highly dependent on reaction temperature and LHSV variation within the range of studied operation.
2. The aromatic compounds of the hydrodesulfurized products decrease with icreasing the reaction temperature and decreasing of LHSV, while the saturated compounds increase with temperature increasing and LHSV decreasing.
3. The viscosity of hydrodesulfurized products decrease with reaction temperature and space time (1/LHSV) increasing ,while, the aniline point increases with temperature increasing and LHSV decreasing

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