DEASPHALTENING AND HYDRODESULFURIZATION OF BASRAH VACUUM RESIDUE

Abdul-Halim A-K Mohammed, and Hussain K. Hussain
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

ABSTRACT

Vacuum residue of Basrah crude oil above 773 K with specific gravity 1.0170 and 4.87 wt.% sulfur, was treated with commercial pentane and hexane fractions provided from Al-Taji Gas Company for preparing deasphaltened oil (DAO) suitable for hydrodesulfurization process. Solvent deasphaltening was examined with mixing time 0.25-4 h and solvent ratio 4-15 ml:g at different temperatures. The asphaltenes yield was decreased with increasing mixing time and increased with increasing solvent to oil ratio.

Hexane deasphaltened oil (94.82 wt.% of origin Basrah vacuum residue) was hydrotreated on presulfided commercial Co-Mo/γ-Al$_2$O$_3$ catalyst at specified operating conditions in a trickel bed reactor. The hydrotreating process applied at a range of temperatures varied from 623 K to 698 K, liquid hourly space velocity from 0.7 to 2.2 h^{-1}, H$_2$ / oil ratio about 300 l/l and pressure 4 MPa. The results of hydrotreating process indicate high sulfur and metal removal with decreasing LHSV as well as high temperature applied. The kinetic of desulfurization and demetalization reactions followed 2nd and 1st order reactions, respectively.

INTRODUCTION

Vacuum residues contain a fraction "asphaltenes" which has a particularly strong influence on the rate of HDS, and removal of 20% of asphaltenes from the residues allows a several-fold increase in space velocity, while maintaining a comparable desulfurization level. Furthermore, the number of catalyst poisons and deactivators in the asphaltenes fraction is so large that the removal of the asphaltenes substantially improves the life of HDS catalyst [1]. Therefore, the deasphaltening process with low boiling liquid hydrocarbons for the vacuum residue before the hydrotreating process is very important, because the most sulfur and metals could be removed with the precipitated asphaltenes[2]. In order to obtain an acceptable level of sulfur and metals in the residue. The hydrotreating process could be used for deasphaltened vacuum residue. The process is accomplished by the catalytic reaction of hydrogen with the organic sulfur compounds at high pressure and temperature to give hydrogen sulfide, which easily is separated from oil or liquid hydrocarbon products. In addition, HDS upgrades the resids, because the accompanying hydrocracking reaction produced light distillates [3, 4].

EXPERIMENTAL WORK

Asphalt Feedstock

Vacuum residue of Basrah crude oil above 773 K distilled from Basrah crude oil with specific gravity 1.0170 and 4.87% sulfur provided from Dura refinery, was used as starting feedstock for preparing feed for the HDS process, asphalt was treated by commercial hexane fraction.The original residue and HDS feedstock properties tabulated in Tables (1and 2).

Petroleum Solvent

Commercial Pentane and hexane fractions were the low-boiling petroleum solvent used for asphaltenes separation from the feedstock. These solvents obtained from Al-Taji Gas Company. Solvent chromatographic analysis showed in Table (3).

Deasphaltening Unit

The deasphalting unit consists of three main stages as follows:

Mixing stage

The vacuum residue was mixed with solvent in 2-neck glass flask with a solvent ratio range 4-15 ml: 1g.

The flask set on a magnetic stirrer and the mixing proceed by 12.5 mm magnetic bar for 0.25-4 hr. High efficiency condenser connected

with upper neck of the flask for solvent recovery, this condenser already cooled by circulating alcohol chiller at temperature of 256 K, the other neck fitted with the thermometer. The mixing was examined at a range of 293-309.5 K for pentane fraction and 293-339 K for hexane fraction, where 309.5 K and 339 K was the solvent reflux temperature for pentane and hexane fractions respectively.

Filtration and drying

The asphalt-solvent mixture was introduced to the filtration process, where Buchner funnel (250 mm I.D) connected to the filtration flask fitted with filter paper for medium filtration speed. The filtration flask connected to a vacuum system includes a trap, condenser, and cooling machine. For removing of the remaining precipitate inside the mixing flask, washing solvent (pentane or hexane) were added and then filtrated. Then the filter paper placed for 10-20 min in a hot electrical furnace 383K to evaporate the solvent associated with the precipitated asphaltenes for about 10 to 20 min. The dried filter paper then weighted to evaluate the percentage of asphaltenes yield.

Solvent recovery stage

The DAO-solvent mixture obtained from filtration stage introduced to a stripping stage in order to remove the solvent from the deasphaltened oil.

Hydrodesulfurization Unit

The desulfurization of deasphaltened oil was done in hydrotreating pilot plant continuous high-pressure unit located in Al-Basil Company. The unit consists of feed pump, reactor, high-pressure separator, and cooler.

The reactor used is a stainless steel with 19 mm inside diameter, 800 mm length and 3 mm wall thickness. The reactor supplied with 4 heaters (150-mm length for each) with 2 insulators (100-mm length). It was packed with 90 ml of commercial Co-Mo /γ-Al$_2$O$_3$ catalyst between two layers of inert glass balls. Catalyst presulfiding was made by passing commercial gas oil containing 0.6 vol.% Cs$_2$ through the catalyst bed. Firstly the catalyst treated for 3 h, at temperature 473 K, LHSV of 4 h^{-1}, pressure 2.2 MPa and no hydrogen flow. Then the operating conditions were changed to 573 K, LHSV of 1 h^{-1}, pressure

2.2 MPa, H$_2$/oil 200 l/l and duration of experiment 16 hours. After that, the HDS runs employed at various reaction temperatures (623-698 K) with various LHSV (0.7-2.2 h). The gas flow was measured by gas meter.

The DAO was pumped co-current up-flow inside the reactor by high pressure-dosing pump (30-600 ml/h). The feed was preheated and mixed with H$_2$ gas and entering the reactor. The reactor products were cooled in a condenser-cooler and separated from unreacted hydrogen, H$_2$S and hydrocarbon gases by passing into high and low-pressure separators.

Products at various reaction conditions were collected only after steady-state operation obtained and products before were discarded.

Distillation of Hydrodesulfurization Products

The hydrotreating product was distilled at laboratory vacuum distillation for low boiling fractions separation. A 250 ml of the HDS product putted in a 500 ml distillation flask, supplied with a heating mantle of 2.4 kW. A voltage regulator was connected with the heating mantle for controlling the amount of heating supplied. Vertical high efficiency condenser was connected with the distillation flask, where a thermometer (623 K) fitted to measure the temperature of the vapors. Circulating Cooling machine was supplied a cooled water with temperature 293 K to a double shell receiver and though it to the condenser. The collecting flask was connected with the receiver, and a triple connector was attached with vacumm system and vacumm controller used for preventing vacuum pump damage. This trap was connected with a vacuum pump through one way valve, and connected with a vacuum controller (Büch 165) from the another side. The vacuum distillation proceeds under 3 mm. Hg and a maximum vacuum temperature 593 K. This temperature equal to 803 K under atmospheric pressure.

Tests for The Feedstock and Products

Density and specific gravity

The density and the specific gravity of the feedstock, deasphaltened oil were determined by (ASTM D-287).

Viscosity

The viscosity of the feedstock, and deasphaltened oil were determined by capillary U-tube viscometer according to (ASTM D-446).

Sulfur content

The sulfur content of the feedstock determined by x-ray fluorescence (ASTM D-2622) in Al-Dura Refinery and by quartz tube method (IP 63/55), while the deasphaltened oil and the hydrotreated product determined by quartz tube method.

Carbon residue

The carbon residue of asphalt and deasphaltened oil were determined by ASTM D-189 and IP 13/66.

RESULTS AND DISCUSSION

Solvent Deaphaltening of Basrah Vacuum Residue

Effect of Temperature

The effect of temperature on asphaltenes yield was studied at various temperatures and solvent ratio 10:1 using commercial pentane and hexane fractions. The results of Figures 1-4 show that increasing in temperature results in decreasing in asphaltenes yield, because of increasing solubility of oil medium (oil + resins) with increasing the temperature, and due to the stripping of some of the unit sheets in the asphaltene molecule.The lowest asphaltenes yield was obtained at solvent reflux temperature.

Effect of Mixing Time

The effect of mixing time on the asphaltenes yield was studied with constant solvent to oil ratio 10:1 at different temperatures, with mixing time 0.25-4 hr. Figures 1 and 2 and show that the increasing in mixing time results decreasing asphaltenes yield. This is due to decreasing resins accompanying with the precipitated asphaltenes that lead to extracting the most of resins into the DAO with increasing mixing time.

Effect of solvent to oil ratio

The effect of solvent to oil ratio was studied at different temperatures with mixing time 1 hr. and solvent ratio 4-15 ml:1g.

Figures 3 and 4 show that the increasing solvent to oil ratio, results in increasing of asphaltene yield due to the degradation of asphaltene molecules with increasing solvent added, that could lead to the creation of activated centers on both the remaining asphaltenes and the freed sheets, thus leading to an overall reduction average number of layer and increased yield of asphaltenes [5].

Effect of Solvent Composition

The solvent composition appeared an active influence on decreasing the asphaltenes yield with increasing solvent chain length, as shown in Figures 1- 4 , due to the increasing the oily materials adsorbed on the precipitated asphaltenes with decreasing solvent chain length.

Effect of asphaltenes yield on hetroatoms removal

Variation of the asphaltenes yield had an effective influence on sulfur and metals removal because these hetroatoms concentrated in asphaltenes particles and the separation of them produced DAO with low hetroatoms.Figures 5&6 show the effect of asphaltenes yield on sulfur removel increasing sulfur removal. Figures 7-10 show the effect of asphaltenes yield on the metals removal. It was appeared that increasing asphaltenes yield results in high metals removal. The results indicated that deasphaltening process was more selective towards metals removal than sulfur removal.

The Deasphaltened Oil Hydrotreating

Effect of temperature and LHSV on the hetroatoms removal

Figure 11 shows the relationship between LHSV and sulfur removal at different temperatures. Desulfurization decreased with increasing LHSV. However, increasing the reaction temperature can offset detrimental effect of increasing LHSV.

The maximum percentage of sulfur removal was 77% at 698 K and 0.7 h^{-1} from the deasphaltened oil. Figure 12 shows the effect of LHSV and reaction temperature upon vanadium removal. It should be noted that in the low temperature region, the removal of vanadium was low. However, as the temperature increased and LHSV decreased he vanadium removal was increased. This due to the increasing of the rate of adsorption metals containing molecules or catalyst surface. It well established that the vanadium present in porphyrin combines strongly

with oxygen, this oxygen forms a strong link with the surface of the catalyst, there by making removal of vanadium from the oil easier at high temperatures. The maximum percentage of vanadium removal was 95%.

Kinetics of Hydrodesulfurization

The kinetics of HDS for the deasphaltened oil by hexane was studied. Attempts were made to correlate the data with the first and second order kinetics. In the case of 1st order kinetic reaction, the data obtained correlated with kinetic equation for ideal situation, where back mixing and holdup or incomplete catalyst wetting effects is negligible. Fig.13 shows a plot of $\ln(Cs_{in}/Cs_{out})$ vs. 1/LHSV for ideal first order reaction at different temperatures. The result of these figures indicates that there is a deviation from 1st order reaction. Second order kinetic model applied for the data of HDS. Plotting $(1/Cs_{in}-1/Cs_{out})$ vs. 1/LHSV gives straight lines from the origin at different temperatures and with slopes equal to HDS rate constants as shown in Fig. 14. The desulfurization rate constants varied from 0.299 h^{-1} at 623 K and 0.586 h^{-1} at 698 K . The results indicated that the desulfurization rate constant increased with increasing reaction temperature.

Kinetics of Vanadium Removal Reaction

The data obtained from vanadium removal of Basrah deasphaltened vacuum residue correlated with the 2nd order kinetic . Fig. 15 shows the plotting of $(1/Cs_{in}-1/Cs_{out})$ vs. 1/LHSV. The result shows that the 2nd order reaction was not agreed with the data obtained for the vanadium removal. The vanadium data appeared to follow 1st order reaction. the data correlated with the 1st order kinetic Fig. 16 shows the plotting of $\ln(Cs_{in}/Cs_{out})$ vs. 1/LHSV and the data gives a straight lines through the origin at different temperatures with slopes equal to the reaction rate constants. The values of the rate constants for vanadium removal were from 1.667 h^{-1}. At 623 K to 2.812 h^{-1} at 698 K. The rate constants were increased with increasing the temperature and especially in the high temperature region (above 648 K). This might be explained in view of the increasing asphaltenes decomposition at high temperatures.

REFERNCES

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3. Speeight, J. G" ،.The Desulfurization of Heavy Oils and Residua", (1981).
4. Crynes, B. L" ،.Chemical Reaction as a Means of Separation Sulfur Removal", (1977).
5. Mustafa, M. F., Hussain H., Rita, L., Hisham, I. and Suha, S., Fuel Science & Technology International, 4 (3), 257 (1986).

Table (1) The properties of Basrah vacuum residue

Property	Unit	Data
Boiling Range	°C	500 plus
Specific Gravity at 15.6/15.6 °C	-	1.0170
API	-	7.6
CCR	wt. %	20.36
Sulfur	wt. %	4.87 (by X-ray fluorescence)
Kinematic Viscosity at 100 °C	cSt	595.3
Flash Point	°C	310
Ash	wt. %	.0304
Vanadium	wt. ppm	268.12
Nickel	wt. ppm	9.43
Penetration	-	265
Softening Point	°C	40

Table (2) The properties of deasphaltened Basrah vacuum reside

Property	Unit	Data
Specific Gravity at 15.6/15.6 °C	-	1.005
API	-	9.10
CCR	wt. %	16.86
Sulfur	wt. %	4.0 (by quartz tube method)
Ash	wt. %	.012
Vanadium	wt. ppm	240
Nickel	wt. ppm	5.34

Table (3) Solvent chromatographic analysis

Compositions (vol.%)	Pentane Fraction	Hexane Fraction
n-Pentane	95.00	2.9
i-Pentane	2.300	-
n-Hexane	1.200	49.7
i-Hexane	-	27.2
M-C-P	-	13.9
n-Heptane	1.5	-

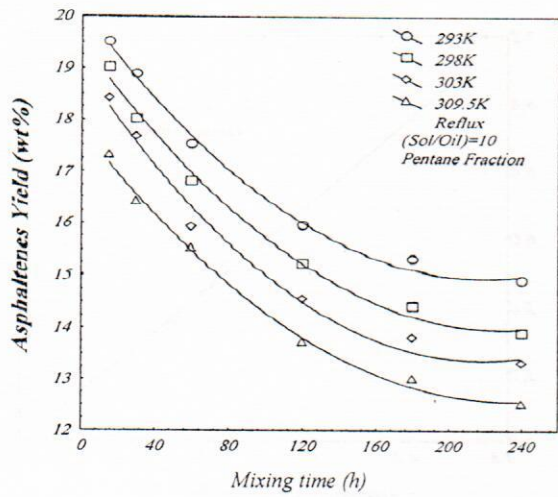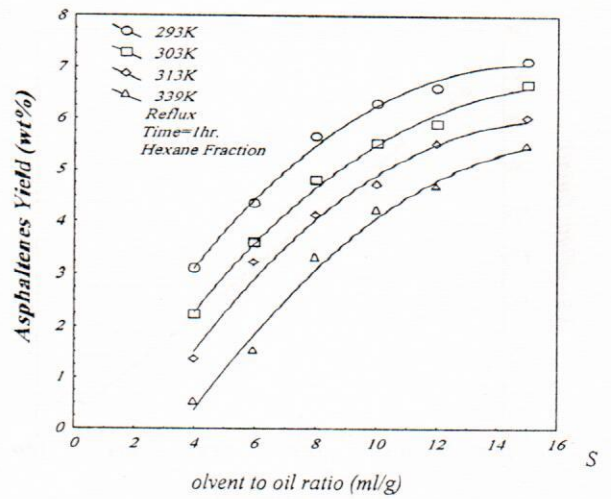Fig. (1) Effect of mixing time on the asphaltenes yield at various temperatures.

Fig. (2) Effect of mixing time on the asphaltenes yield at various temperatures

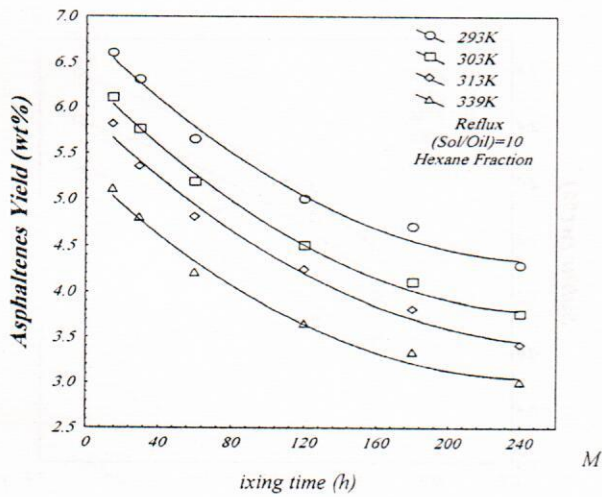Fig. (3) Asphaltenes yield vs. solvent to oil ratio at various temperatures

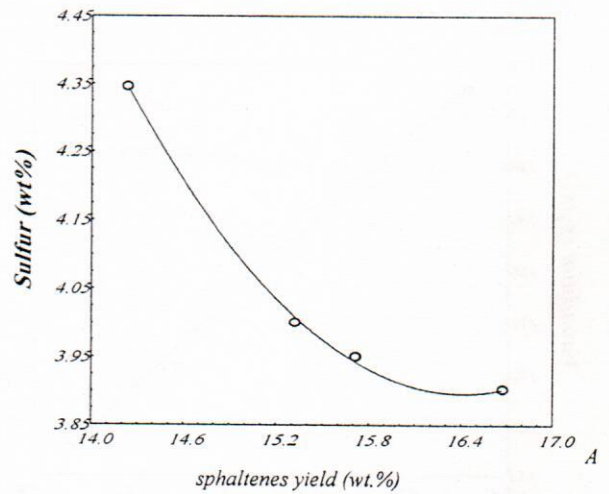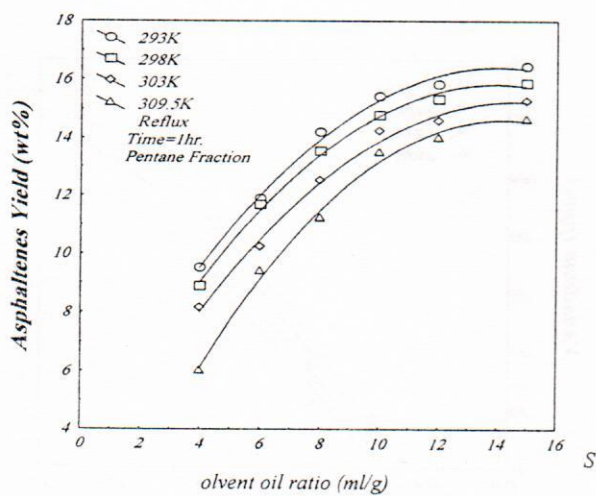Fig. (4) Asphaltenes yield vs. solvent to oil ratio at various temperatures.

Fig. (5) Asphaltenes yield vs. sulfur concentration in pentane fraction deasphaltened vacuum residue
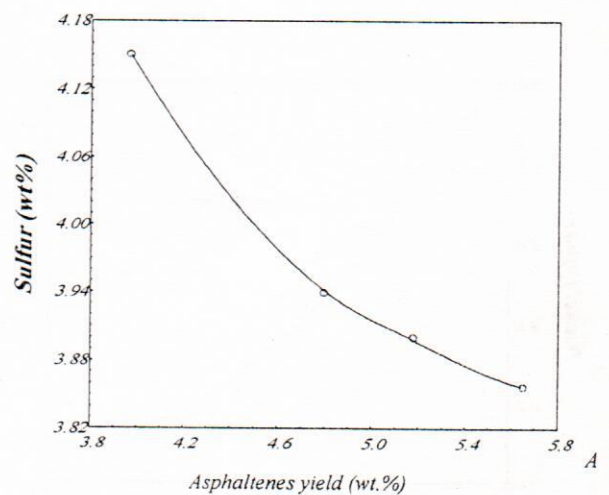
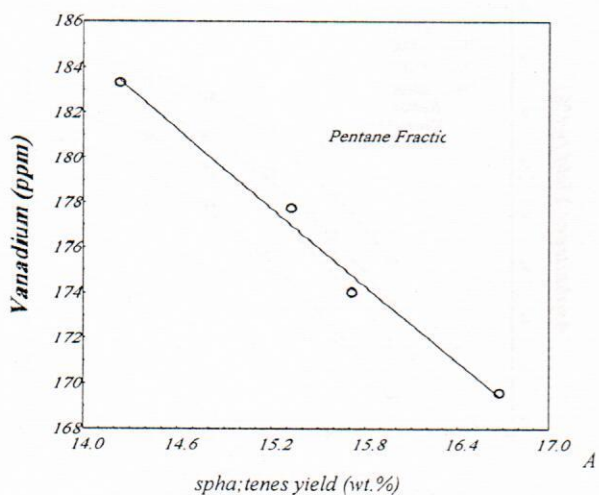Fig. (6) Asphaltenes yield vs. sulfur concentration in hexane fraction deasphaltened vacuum residue

Fig. (7) Vanadium content in deasphaltened vacuum residue vs. asphaltenes yield
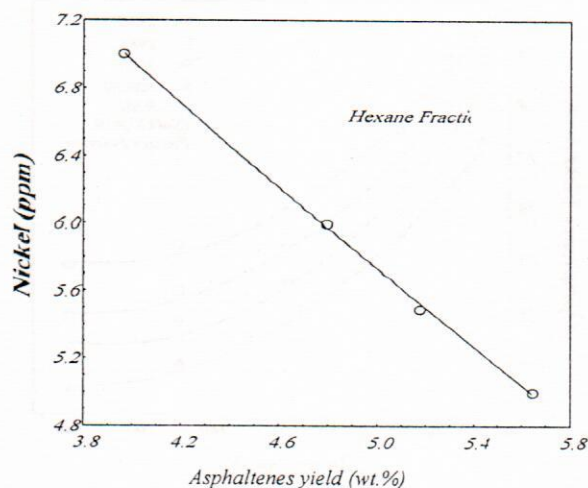
Fig. (8) Vanadium content in deasphaltened vacuum residue vs. asphaltenes yield.

Fig. (9) Nickel content in deasphaltened vacuum residue vs. asphaltenes yield.

Fig. (10) Nickel content in deasphaltened vacuum residue vs. asphaltenes yield.
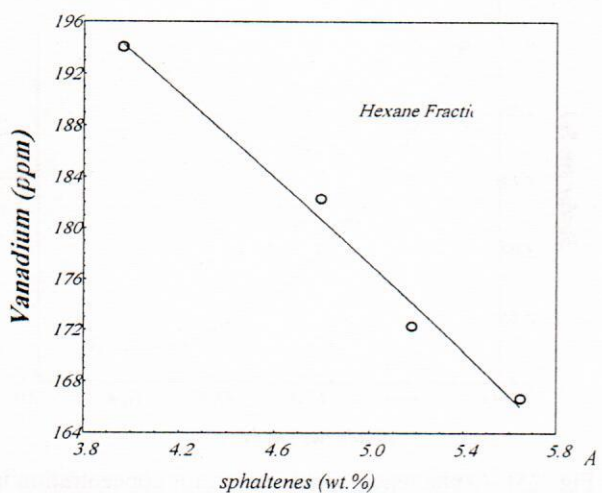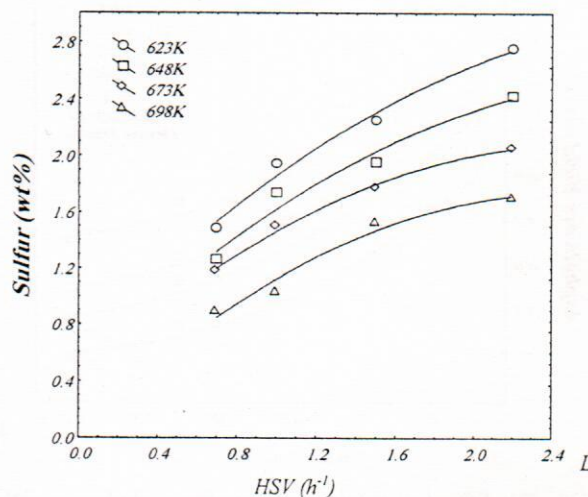
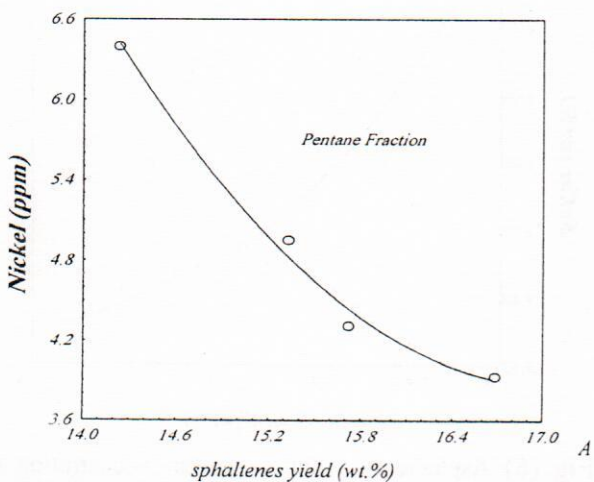**Fig. (11)** Effect of LHSV and temperature on the sulfur removal from the deasphaltened vacuum residue.
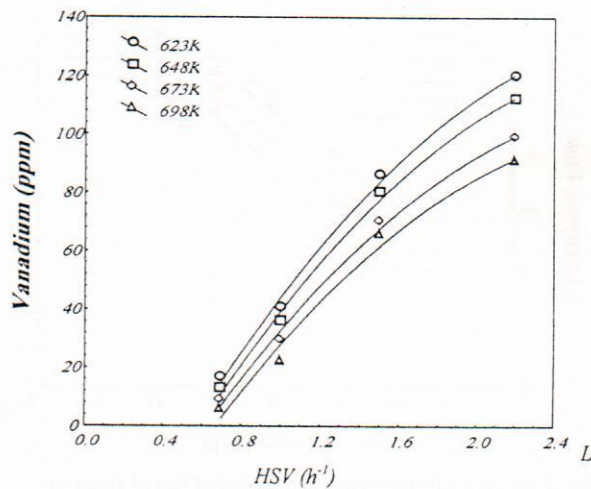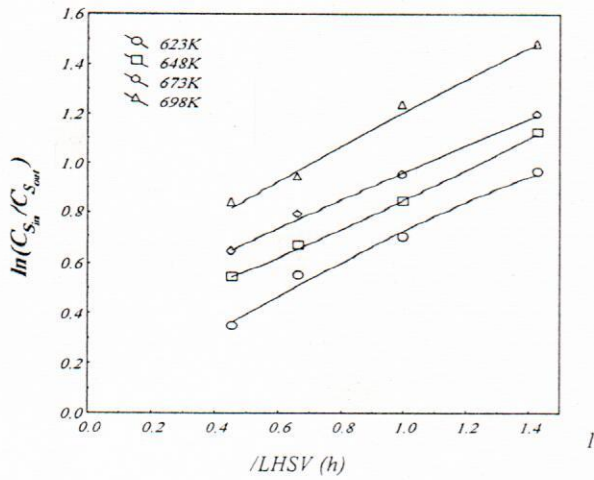
Fig. (12) Effect of LHSV and temperature on the vanadium removal from the deasphaltened vacuum residue.

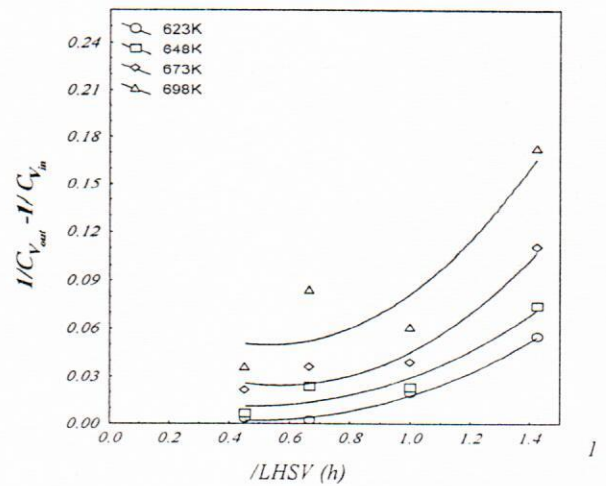Fig. (13) First order model for hydrodesulfurization of deasphaltened vacuum residue.

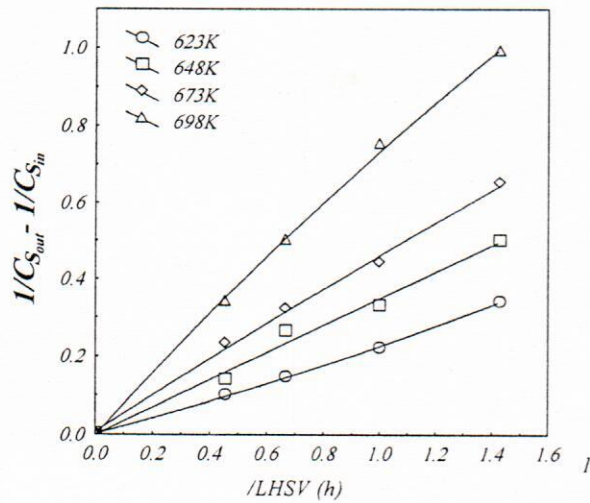Fig. (15) Second order model for vanadium removal from deasphaltened vacuum residue.

Fig. (14) Second order model for hydrodesulfurization of deasphaltened vacuum residue.
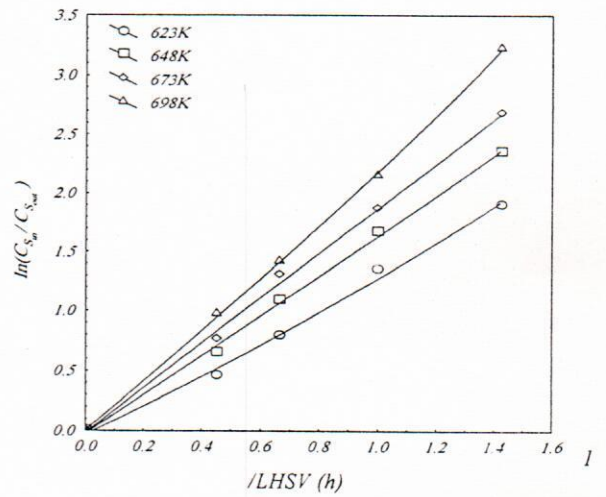

Fig. (16) First order model for vanadium removal from deasphaltened vacuum residue.