# THE EFFECT OF ASPHALTENES REMOVAL ON THE KINETICS OF IRAQI REDUCED CRUDE OIL HYDROTREATING

**Abdul-Halim A-K Mohammed, and Ammar S. Abbas**
Chemical Engineering Department – College of Engineering - University of Baghdad - Iraq

## ABSTRACT

*Iraqi reduced crude oil (45 % Vol. of the original Basrah crude oil) was solvent deasphaltened at specific conditions using pentane fraction (53 % wt.* $n\text{-}C_5$*) as the precipitant. Both the original and deasphaltened reduced crude oil was hydrotreated in a trickle bed reactor with commercial* $Co\text{-}Mo/\gamma\text{-}Al_2O_3$ *catalyst. Reaction temperature varied from 598 to 698 K over a liquid hourly space velocity ranging from 0.9 to 3.3* $h^{-1}$*. Hydrogen pressure was kept constant throughout all the experiments at 4.4 MPa with hydrogen to oil ratio about 300 Nl/l. Kinetic analysis showed that the desulfurization followed a second order kinetics while the vanadium removal followed a first order kinetics. Activation energies were 94.17 and 104.56 kJ/mole for desulfurization and 28.07 and 31.88 kJ/mole for vanadium removal from the original reduced crude oil and the deasphaltened oil respectively.*

## INTRODUCTION

The technology of petroleum refining is developing accompanying the changes in the amount and the type of crude oils available as well as the changes in consumption of certain products and the changing environmental protection restrictions. Thus catalytic hydrodesulfurization (HDS) of residual oils may be employed to prepare feedstock for catalytic cracking units in order to maximize light distillates yield with minimum catalyst contamination to produce low sulfur feedstock for coke production. And to prepare low sulfur fuel oil meeting the demand of local authority pollution regulations.

Hydrodesulfurization is a catalytic process whereby crude oil fraction (or product), as the feedstock is passed with hydrogen, over or through a catalyst bed at elevated temperature and pressure (1). The basic chemical concept of the process is to convert the organic sulfur in the feedstock to hydrogen sulfide.

In a series of desulfurization tests, analysis of the various fractions obtain by liquid chromatographic separation showed that the asphaltenes were the most difficult to desulfurize (2). Although they were converted to lower-boiling materials, their molecular weight distribution and sulfur concentration were unchanged by hydroprocessing (3,4). Flinn *et al.* (5) noted that the desulfurization rate increased four-fold when Kuwait vacuum residue was removed of about 20 % of the residue as asphaltenes. The reaction rate constant for the desulfurization of deasphaltened Khafji crude oil (1.5 wt % asphaltenes) was approximately twice that for Khafji crude oil (4.3 wt % asphaltenes). The fact that the removal of the relatively small amount of asphaltenes causes such a change in reactivity indicates perhaps that asphaltenes may increase pore diffusion resistance or may be so strongly adsorbed on the catalyst that they hinder the reactions of the oil and resins (2).

Many studies have been made to determine the reaction order for residue desulfurization with respect to sulfur concentration. In published studies of the apparent kinetics of residue hydrodesulfurization, one of three approaches has generally been taken:

1. The reactions can be described in terms of simple first order expressions. Frye and Mosby (6) showed that the desulfurization of three compounds found in cycle oil feedstock followed a first order model, the kinetics of hydrodesulfurization of distillates (7), Kirkuk reduced crude (8), Bai-Hasan reduced crude (9) and another reduced crudes (10,11) are first order rates.
2. The reactions can be described by use of two simultaneous first order expressions. One expression for easy-to-remove sulfur and a separate expression for difficult-to-

remove sulfur. Arey *et al.*(12) fitted kinetics data for heavy vacuum gas oils, atmospheric residues, a vacuum residue and a deasphaltened residue according to this model. The same analysis was approached by the work of Flinn *et al.* (5) several years before.

3. The reactions can be described using a second order treatment. Beuther and Schmid (13) found the HDS of a Kuwait residue over two types of catalysts is obey to this model. Scamangas *et al.* (14) and Mohammed *et al.* (8) show that the HDS of high sulfur atmospheric residue fitted to be second order reaction.

## EXPERIMENTAL

### Feedstock

Iraqi reduced crude oil (about 45 % Vol. of the original crude oil) and the deasphaltened reduced crude oil (95.5 wt. % of the original reduced crude oil) were used as feedstock. Their chemical and physical properties are given in Table (1).

Table (1) Properties of the range and deasphaltened Iraqi reduced crude oil

| Property | Reduced crude | Deasphaltened |
|---|---|---|
| Sp. Gr. (15.6/15.6°C) | 0.9497 | 0.9390 |
| API | 17.5 | 19.2 |
| Sulfur (wt. %) | 3.25 | 2.85 |
| Nickel (wt. ppm) | 11 | 4 |
| Vanadium (wt. ppm) | 42 | 26 |
| CCr (wt %) | 8.5 | 4.6 |

### Catalyst

Cobalt-molybdenum supported over γ-alumina was used as a hydrotreatment catalyst. Catalyst properties are given in Table (2).

Table (2) Properties of commercial catalyst Kf.3E124 Co-Mo/γ-$Al_2O_3$

| | | | |
|---|---|---|---|
| $MoO_3$ | 12.0 wt% | $Al_2O_3$ | Balance |
| CoO | 4.00 wt% | Form | Extrude |
| $Ni_2O$ | 0.06 wt% | Normal size | 2-5 mm |
| Fe | 0.03 wt% | Surface area | 280 $m^2/g$ |
| $SO_4$ | 1.50 wt% | Pore volume | 0.55 $cm^3/g$ |

### Catalyst presulfiding

Catalyst presulfiding was accomplished by a solution of 0.6 % Vol. of $CS_2$ in a commercial gas oil. The first 4 hours of activation was carried out at 2.2 MPa and 473 K with LHSV of 4 $h^{-1}$ and no hydrogen flow. After that, the conditions are changed to 573 K, LHSV of 1 $h^{-1}$ and hydrogen to oil ratio of 200 Nl/l for a constant pressure of 2.2 MPa over a period of 16 h.

### Hydrotreating experiments

The HDS runs were preformed in a pilot plant continuous high-pressure unit employing an up-flow cocurrent.

The reactor is stainless steel, and heat resisting steel with dimensions of 650 mm length 20 mm in diameter. The reactor was jacketed with 4 separately heat controlled block shells in order to ascertain isothermal operation.

The reactor products were cooled in a condenser-cooler and separated from hydrogen unreacted and $H_2S$ and the hydrocarbon gases by passing into a high and low-pressure separators. The gases were then vented to the exterior through a gas flow meter. The unit was supplied with a high pressure-dosing pump to introduce the feedstock into the unit.

The reaction conditions employed are temperatures of 598 to 698 K, pressure of 4.2 to 4.4 MPa, liquid hourly space velocity (LHSV) of 0.9 to 3.3 $h^{-1}$ and hydrocarbon oil ratio of 300 Nl/l.

Products were collected only after steady-state operation was establish and initial operating products were discarded.

The reactor was packed with about 60 $cm^3$ of the commercial Co-Mo-Alumina type catalyst (after drying at 393 K for 2 h) between two layers of inert material (glass beads with 4 mm diameter).

### Test method

The sulfur content of reduced crude oil, deasphaltened oil and the hydrotreated products were determined by quartz tube method (IP 63/55). Analysis of vanadium content of feedstock and hydrotreated products was achieved by using the PYE UNICAM SP-9-atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

### The effect of temperature and LHSV on the Hetroatoms removal

The hydrodesulfurization of residue oils in a fixed catalyst bed reactor is a complex process and many process variables affect the extent of hetroatoms removal. Temperature, pressure, LHSV and hydrogen to oil volumetric ratio are the main process variables. Throughout this study the hydrogen, pressure and hydrogen to oil ratio were kept at 4.4 MPa and 300 Nl/l, respectively. HDS experiments were carried out in the temperature range 598 to 698 K over liquid hourly space velocities ranging from 0.9 to 3.3 $hr^{-1}$.

For BRC and DAO, the removal of hetroatoms (sulfur and vanadium) increases with increasing temperature, and decreases LHSV as shown in Figs. (1-4). These results are in well agreement with other studies on the HDS of several residues $^{(1,8,14,15)}$.

The increasing sulfur removal at higher reaction temperature may be attributed to several reasons:

1. At high reaction temperature the unreactive sulfur compounds which most probably belong to the thiophene derivatives $^{(16)}$, become activated enough to react with hydrogen.
2. The large molecule asphaltenes are decomposed into smaller molecules, which can more easily diffuse into the catalyst micropores and reach the inner active sites where the desulfurization reaction occurs, and
3. Increases of oil diffusivity through the catalyst micropores due to decreases in the viscosity.

Higher temperature level limited by the undesirable side reactions such as hydrocracking and thermal cracking reactions.

As space velocity decreased, desulfurization increased because of the contact time increases between hydrogen and sulfur compounds, which increases the rate of desulfurization.

Metals removal or demetalization reactions occurring simultaneously with the desulfurization reaction. As shown in Figs. (3 and 4), the extent of vanadium removal, for both of BRC and DAO largely depends on LHSV and temperature employed. And it could be noticed that the effect of LHSV on vanadium removal was significant in the temperature region above 623 K. This was due to increasing in destructive of large molecules especially asphaltenes which is carry the major portion of metals of the residue oil $^{(1,17)}$.

Sulfur as well as vanadium removal was slightly higher for DAO than that obtained for the full BRC at the same operating conditions as shown in Figs. (1-4). For example when the feedstock was DAO about 73 % sulfur and 65 % vanadium removal at condition of temperature of 698 K and LHSV of 1.0 $h^{-1}$, while 68 % sulfur, and 62 % vanadium was removed when approximately same conditions employed for the original BRC. At higher temperature the percentage removal of hetroatoms of BRC tend to approach of that for DAO, this gave a quite evidence to that destructive and hydrotreating of asphaltenes for BRC is not so difficult.

## Kinetics of the hydrotreating process

Kinetic studies for data obtained from laboratory unit or pilot-plant scale usually play an important role in modeling and scale up designs for new hydrodesulfurization units.

## Kinetics of desulfurization

Data obtained from the pilot-plant unit for the desulfurization of the BRC and DAO were analyzed by the available kinetics models. The governing equation for the HDS reactor performance when the desulfurization reaction supposed to be first-order, may be expressed as$^{(18)}$:

$$\ln\left(\frac{C_{S_{in}}}{C_{S_{out}}}\right) = \frac{k}{LHSV} \qquad (1)$$

and when the reaction supposed to be second-order, as:

$$\frac{1}{C_{S_{out}}} - \frac{1}{C_{S_{in}}} = \frac{k}{LHSV} \qquad (2)$$

It is distinct that, in the absence of backmixing and holdup or incomplete catalyst wetting effects. A log-log plot of $\ln(C_{Sin}/C_{Sout})$ and $(1/C_{Sout}-1/C_{Sin})$ vs. (1/LHSV) should be straight line with a slope of unity. Furthermore, at constant LHVS, the conversion should be independent on catalyst bed length.

If the holdup effect is important but the backmixing is insignificant, then the holdup model of Henry and Gilbert (19) when the desulfurization governs the first-order reaction, it can be expressed as:

$$\ln\left(\frac{C_{S_{in}}}{C_{S_{out}}}\right)=\frac{k\ L^{\beta}}{(LVSH)^{1-\beta}} \qquad (3)$$

It can be seen from equation (3) that a log-log plot of $\ln(C_{Sin}/C_{sout})$ vs. 1/LHSV should yield as straight line with a slope equal to $(1-\beta)$. Different values of $\beta$ have been reported (20,21). Henry and Gilbert took $\beta = 1/3$.

A similar effect of LHVS and catalyst bed length on conversion is obtained in the absence of back mixing was also predicted on the basis of catalyst wetting model of Mears (22) (Mears took $\gamma$=0.32).

$$\ln\left(\frac{C_{S_{in}}}{C_{S_{out}}}\right)=\frac{k\ L^{\gamma}}{(LHSV)^{1-\gamma}} \qquad (4)$$

A log-log plot of $\ln(C_{Sin}/C_{Sout})$ vs. 1/LHSV should yield a straight line with slop equal to $(1-\gamma)$.

Equation (3) is valid in Reynolds number range 10 to 600 (19) and equation (4) is valid at lower Reynolds number. Mears (22) reported that incomplete catalyst wetting has been observed at Reynolds number of 55. At very low Reynolds number, equation (4) may be more valid than equation (3).

Data correlated with first and second order kinetics equation assuming ideal plug flow and those models including the effects of fluid flow.

Results show that hydrodesulfurization data have a deviation from ideal first order kinetics model as showing in Figs (5 and 6). According to the hold-up model of Henry and Gilbert (equation 3) and the incomplete catalyst wetting model of Mears (equation 4), Figs. (7 and 8) show a plot of log $\ln(C_{si}/C_{So})$ vs. log (1/LHSV) for BRC and DAO respectively, a straight lines yielded with slope equal to $(1-\beta)$. The value of $\beta$ varied from 0.47 to 0.52 for BRC and from 0.48 to 0.57 for DAO compared to a value of 0.33 used by Henry and Gilbert (19) and 0.32 used by Mears (22). The value of $\beta$ seems to depend on the type of feedstock and is most probably higher than zero and less than one (19).

Second order kinetic model used to fit data obtained. Plotting $(1/C_{So}-1/C_{Si})$ vs. 1/LHSV gives straight lines cut through the origin with slopes equal to desulfurization rate constants as shown in Figs. (9 and 10). The values of rate constants were ranging from 0.27 $(h.wt.\%)^{-1}$ at 598K to 4.22 $(h.wt.\%)^{-1}$ at 698 K for BRC and from 0.32 $(h.wt.\%)^{-1}$ at 598 K to 6.36 $(h.wt.\%)^{-1}$ at 698 K for DAO which are an indication to the large effect of temperature on the rate constants. This means that increasing the HDS temperature will result in faster desulfurization reactions and quicker equilibrium conditions will be attained.

The values of the desulfurization rate constants, for BRC and DAO, calculated above are listed in Table (3). The rate constants of the desulfurization reactions are higher for the DAO than that obtained for the original BRC for all temperature range studied.

## Kinetics of Demetalization

The vanadium removal for each BRC and DAO appeared to obey the ideal first order kinetics equation with negligible deviations from plug flow.

Plots of $\ln(C_{Vin}/C_{vout})$ vs. 1/LHSV at different temperatures for BRC and DAO are shown in Figs. (11 and 12) respectively. The straight lines with slopes equal to the rate constant. The rate constant values calculated from these slopes are found in Table (3).

The values of the rate constants calculated for vanadium removal were ranging from 0.67 $h^{-1}$ at 598 K to 1.81 $h^{-1}$ at 698 K and from 0.7 $h^{-1}$ at 598 K to 1.74 $h^{-1}$ at 698 K for BRC and DAO respectively.

The rate constant appears to increase with increasing temperature and especially in the high temperature region (above 648 K) where the rate constants show a slight increase. This might be explained in view of the easily asphaltenes conversion at such temperatures.

A comparison rate constants for demetalization of BRC and DAO, show that the rate constants for DAO are slightly higher than that for BRC, which gives a quite evidence for easily asphaltenes conversion.

## Thermodynamics of the hydrotreating process

The activation energy for the desulfurization reactions was calculated by using the Arrhenius equation, which satisfies the relationship between rate constant and the reaction temperature (16,23).

$$k = A\exp\left(-\frac{E_a^*}{RT}\right) \qquad (5)$$

a plot of ln k vs. (1/T) gives a straight line with a slope equal to $-E_a^*/R$ from which the activation energy was calculated.

The activation enthalpy and entropy for the hydrodesulfurization reactions were calculated by using the following equation, which was obtained from the absolute rate theory (23).

$$k = \frac{KK_bT}{h}\exp\left(\frac{\Delta S_a^*}{R}\right)\exp\left(\frac{-\Delta H_a^*}{RT}\right) \qquad (6)$$

A plot of ln (k/T) vs. (1/T) gives a straight line with a slope equal to $-\Delta H_a^*/R$ and intercept of this line equal to $\ln(K K_b/h)+\Delta S_a^*/R$, then the activation enthalpy and entropy can be calculated (Figs. 13-16). The results of these calculations are showing in Table (3).

Table (3) Calculated Rate Constant, Apparent Activation Energy, Enthalpy and Entropy of Activation for the HDS.

| | | Sulfur | | Vanadium | |
|---|---|---|---|---|---|
| | | BRC | DAO | BRC | DAO |
| | | Rate Constant (h.wt.%)$^{-1}$ | | Rate Constant h$^{-1}$ | |
| Temperature (K) | 598 | 0.27 | 0.32 | 0.67 | 0.70 |
| | 623 | 0.44 | 0.54 | 0.79 | 0.84 |
| | 648 | 0.72 | 0.99 | 0.95 | 1.05 |
| | 673 | 1.70 | 2.72 | 1.26 | 1.38 |
| | 698 | 4.22 | 6.36 | 1.81 | 1.74 |
| Thermodynamic Properties | | | | | |
| $E_a^*$ (kJ/mole) | | 94.17 | 104.56 | 28.07 | 31.88 |
| $\Delta H_a^*$ (kJ/mole) | | 88.64 | 109.89 | 28.43 | 26.47 |
| $\Delta S_a^*$ (J/mole.K) | | -130.2 | -94.11 | -222.40 | -225.06 |

The values of activation energy for both of BRC and DAO are acceptable with the activation energy of Greece atmospheric residue hydrodesulfurization of 121 kJ/mole (24), apparent activation energy of Kuwait residue 27 kCal/mole (113 kJ/mole) (13), apparent activation energy of Khafji residue 27.5 kCal/mole (115 kJ/mole) (19) and in the range of activation energies for Bai-Hassan reduced crude and its deasphaltened oil (8). Also Nomora (18) found that the apparent activation energies were 80-120 kJ/mole at 365-430 °C.

The activation energies for vanadium removal obtained from this study are in a good agreement with the results published for Bai-Hassan reduced crude and its deasphaltened oil (8).

## CONCLUSIONS

1. The effect of temperature on sulfur removal is more significant than LHSV variations, however vanadium removal seemed to be more influenced by LHSV variations compared to sulfur removal.
2. Kinetic analysis shows that the desulfurization reactions of the original BRC and DAO during the hydrodesulfurization process follow second-order kinetics. While the demetalization reactions follow a first order kinetics for both the original BRC and DAO.
3. Activation energies for desulfurization are 94.17 and 104.56 kJ/mole and for demetallization 28.07 and 31.88 kJ/mole for BRC and DAO respectively.

## NOTATION

| | | |
|---|---|---|
| A | Frequency factor | h$^{-1}$ |
| BRC | Basrah Reduced Crude Oil | |
| C | Concentration, weight percent | wt. % |
| CCR | Conradson Carbon Residue | wt. % |
| DAO | Deasphaltened Reduced Crude | |
| E | Energy | kJ/mole |
| H | Enthalpy | kJ/mole |
| h | Plank's constant | 6.6262x10$^{-24}$ J/s |
| K | Transmission coefficient | |
| $K_B$ | Boltzmann constant | 1.3806x10$^{-23}$ J/K |
| k | reaction rate constant | |
| L | Length of catalyst bed | m |
| LHSV | Liquid hourly space velocity | m$^3$liquid/h.m$^3$cat. |
| R | Universal gas constant | 8.314 kJ/kmole.K |
| S | Entropy | KJ//kmole.K |

| | | |
|---|---|---|
| S | Sulfur Concentration | Wt. % |
| T | Temperature | K |

Greek Letters

| | |
|---|---|
| β | Empirical constant in equation (3) |
| γ | Empirical constant in equation (4) |
| Δ | Change |

Subscripts

| | |
|---|---|
| a | Apparent |
| In | Inlet |
| Out | Outlet |
| S | Sulfur |
| V | Vanadium |

Superscripts

| | |
|---|---|
| * | Activation |

## REFERENCES

1. Speight J. G., "*The Desulfurization of Heavy Oils and Residua*", (1981).
2. Crynes B. L., "*Chemical Reaction as a Means of Separation Sulfur Removal*", (1977).
3. Papayannakos N. and Marangozis J., Chem. Eng. Sci., 39 (6), 1051 (1984).
4. Al-Mayah A. K., M.Sc. Thesis, Baghdad University (1983).
5. Flinn R. A., Benther H. and Schmid B. K., Petroleum Refiner, 40 (4), 139 (1961).
6. Frye C. G. and MosbyJ. F., Chem. Eng. Progr., 63 (9), 66 (1967).
7. Chu C. I. and Wang I., I&EC Proc. Des. Dev., 21 (2), 338 (1981).
8. Mohammed A-H. A-K. and Hankish K., J. Petrol. Res., 4 (2), 37 (1985).
9. Abbas A. A., Mohammed A-H. A-K., Ahmed A. B. A. and Abbas K., Fuel Science and Technology Int. L., 8 (7), 307 (1990).
10. Parskos J. A., Frayer J. A. and Shah Y. T., I&EC Proc. Des. Dev., 14, 315 (1975).
11. Montagna A. A. and Shah Y. T., I&EC Proc. Des. Dev., 14, 479 (1975).
12. Arey W. F. Jr., Blackwell N. E. and Reichle A. D., Seventh World Petroleum Congress, (1968), 4, 167.
13. Benther H. and Schmid B. K., 6th World Petrol. Congress, June (1963), Section III, Paper 20.
14. Scamangas A., Papayannakos N. and Marangozis J., Chem. Eng. Sci., 37 (12), 1810 (1982).
15. Richardson J. T., "*Principles of Catalyst Development*", (1989).
16. Weisser O. and Landa S., "*Sulphide Catalysts, their Properties and Application*", (1973).
17. Corbett L. W., ACS Preper. Dev. Pet. Chem., 12 (2), A83 (1967).
18. Nomura H., Sekido Y. and Ohguchi Y., (Nippon Oil Co. Ltd.), J. Jap. Petrol. Int., 22 (5), 296 (1979).
19. Henry H. C. and Gilbert J. B., I&EC Proc. Des. Dev., 12 (3), 328 (1973).
20. Hochman J. M., Efforn E., I&EC Fund., 8, 63 (1969).
21. Mohunta D. M. and Laddha G. S., Chem. Eng. Sci., 20, 1069 (1956).
22. Mears D. E. and Hulburt H. M., Chem. React. Eng., ACS Monograph Series, 123, 218 (1974).
23. Bond G. C., "*Heterogeneous Catalysts*", (1974).
24. Scamangas A., Papayannakos N. and Marangozis J., (Chem. Process Eng. Lab. Natal. Tech., Univ., Athens Greece), Congress Miditerr in Quim (Actas), 2nd Ed. (1981), F.O.I.M. Barcelona, Spain.

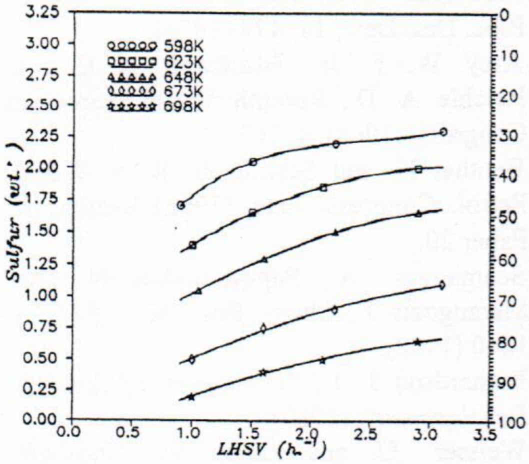

Fig. (1) The effect of LHSV and temperature on the sulfur removal from Basrah reduced crude oil

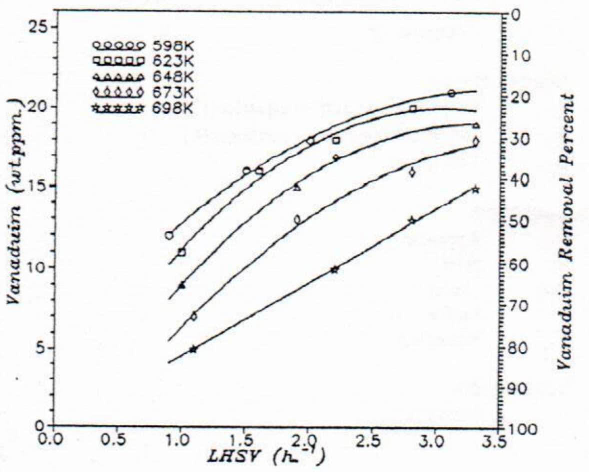

Fig. (4) The effect of LHSV and temperature on the vanadium removal from deasphaltened oil.

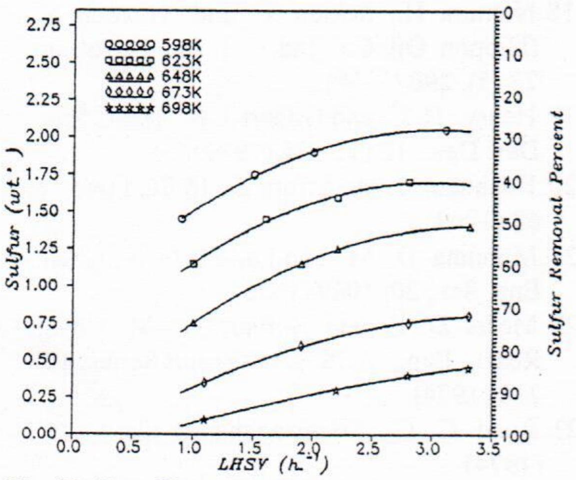

Fig. (2) The effect of LHSV and temperature on the sulfur removal from the deasphaltened oil.

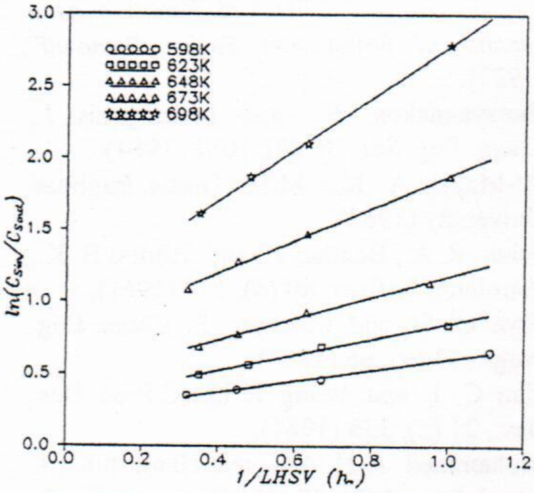

Fig. (5) First order kinetic model for hydrodesulfurization of Basrah reduced crude oil.

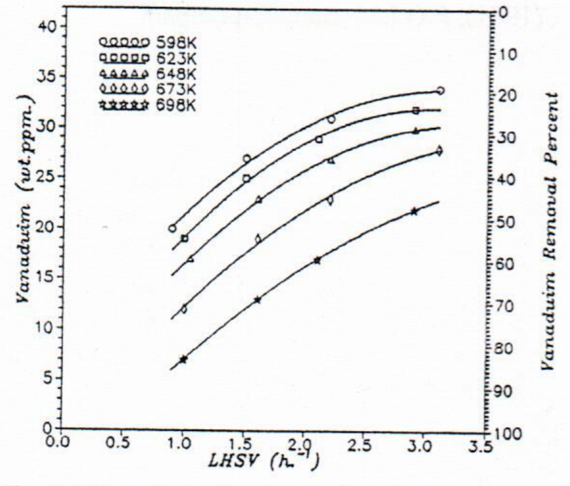

Fig. (3) The effect of LHSV and temperature on the vanadium removal from Basrah reduced crude oil.

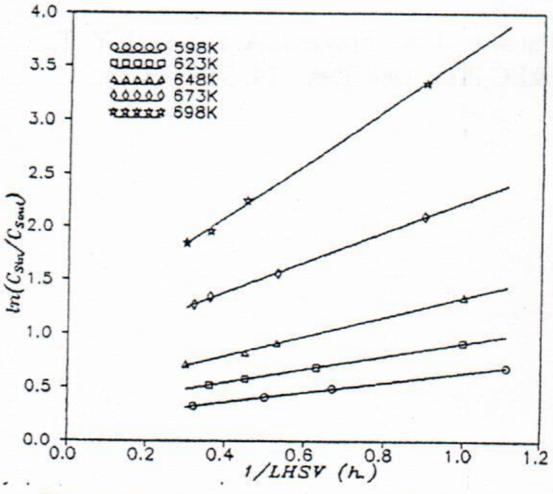

Fig. (6) First order kinetic model for hydrodesulfurization of deasphaltened oil.

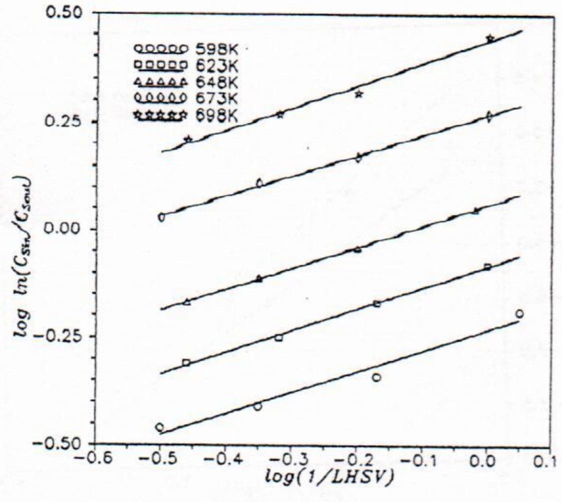

Fig. (7) log-log plot of $\ln(C_{Sin}/C_{Sout})$ versus 1/LHSV for Basrah reduced crude oil.

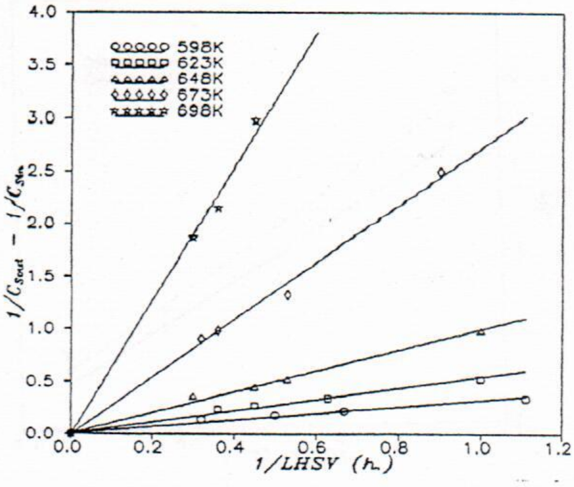

Fig. (10) Second order kinetic model for hydrodesulfurization of deasphaltened oil.

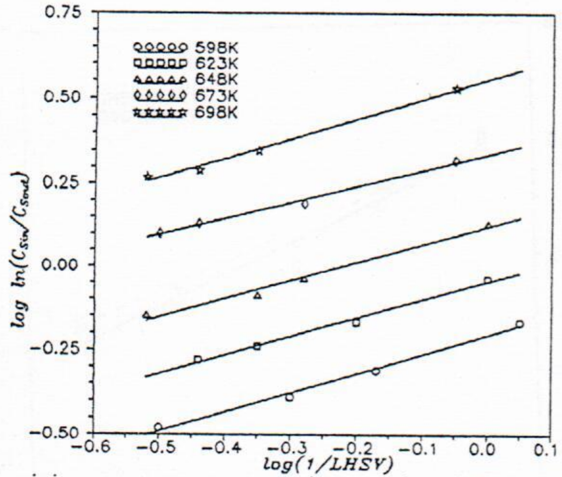

Fig. (8) log-log plot of $\ln(C_{Sin}/C_{Sout})$ versus 1/LHSV for the deasphaltened oil.

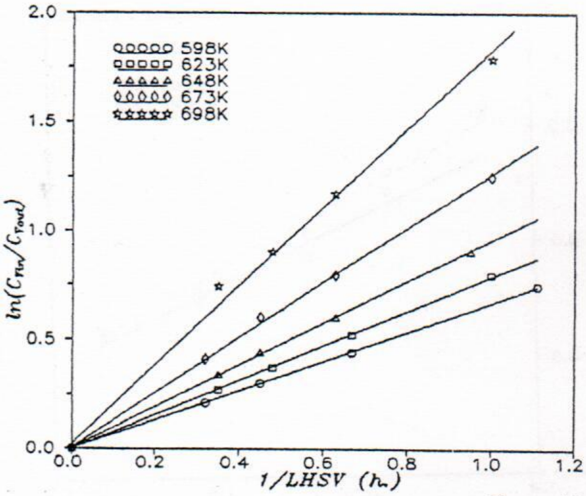

Fig. (11) First order kinetic model for vanadium removal from Basrah reduced crude oil.

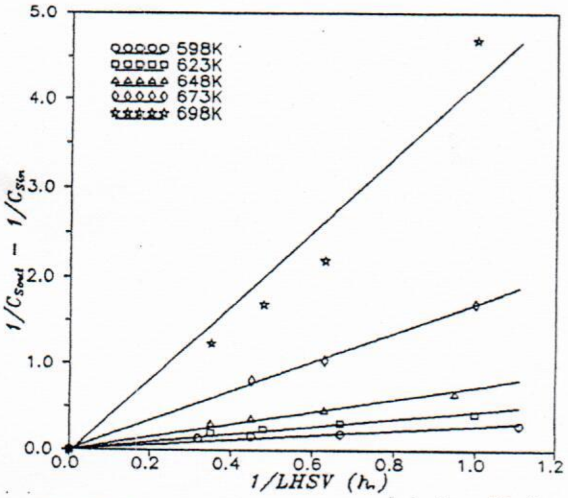

Fig. (9) Second order kinetic model for hydrodesulfurization of Basrah reduced crud oil.

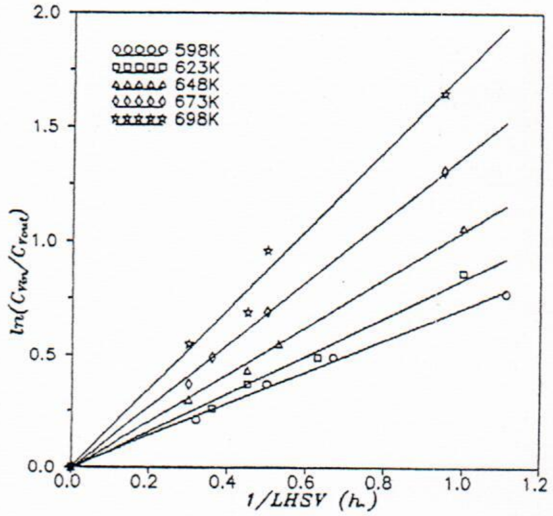

Fig. (12) First order kinetic model for vanadium removal from the deasphaltened oil.

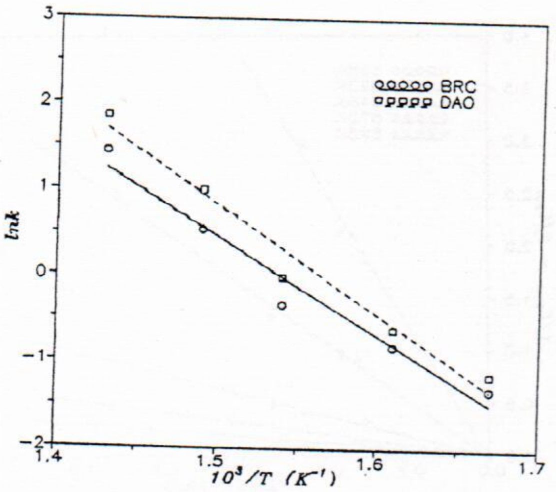

Fig. (13) lnk versus 1/T second order kinetic model for dehydrosulphurization.

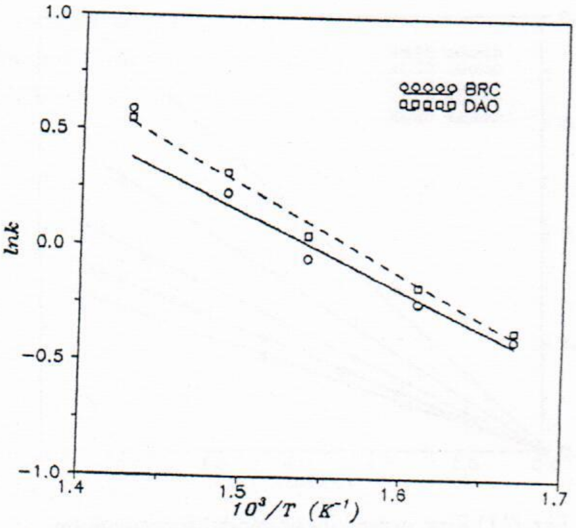

Fig. (14) lnk versus 1/T of first order kinetic model for vanadiunm removal.

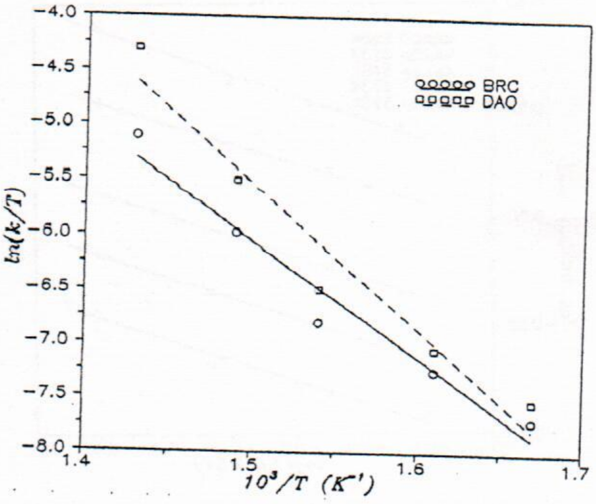

Fig. (15) ln(k/T) versus 1/T of second order kinetic model for hydrodesulfurization

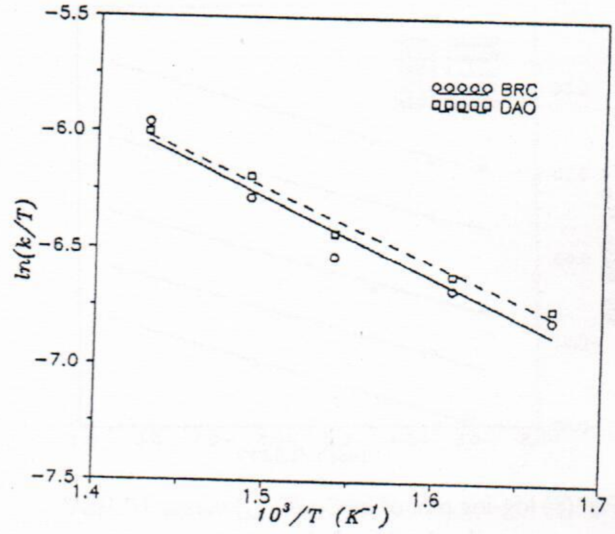

Fig. (16) ln(k/T) versus 1/T of first order kinetic model for vanadium removal.