

## HYDROTREATING OF SHARKI BAGHDAD RESIDUE

Abdul-Halim A.-K. Mohammed, Khalid Keza'al, and Karim Henekish

Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

### ABSTRACT

*Sharki Baghdad residue (+623K) was deasphalted using pure n-heptane at solvent reflux temperature. The deasphalted residue was hydrotreated on presulfided commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at specified conditions in a laboratory trickle bed reactor. The hydrotreating temperature varied from 573 to 723 K over liquid hourly space velocity (LHSV) ranging from 1.0 to 2.5 hr<sup>-1</sup>, pressure and hydrogen to residue ratio were kept constant at 6.1 Mpa and 300 L/L, respectively. The results indicate that the desulfurization (DS) and demetallization (DM) reactions increased with increasing hydrotreating temperature and decreasing LHSV and the vanadium removal is higher than other metals removal. The CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst gives higher DS activity than the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and vice versa for DM activity.*

### INTRODUCTION

The catalytic hydrotreating process is one of the preferred methods employed to lower the sulfur and metals content of residue and to improve the quality of feedstocks of most refining process<sup>(1,3)</sup>. During the hydrotreating, the hydrodesulfurization reaction involves the cleavage of C-S bond according to an incompletely understood mechanism<sup>(4)</sup>. The various sulfur compounds reacts with different rates according to their reactivity. The stability of sulfur compounds decrease in series: Thiophenes > Thiophanes > Sulfides > Mercaptanes<sup>(5)</sup>. It is generally recognized that the ease of DS is dependent upon the type of compounds and lower-boiling fractions are desulfurized more easily than the higher boiling fractions. The difficulty of sulfur removal increased in the following order: Paraffins < Naphthenes < Aromatics. This means that the sulfur compounds of similar molecular weight will undergo DS with different rates<sup>(6, 7)</sup>. Hydrotreating of petroleum fraction has revealed the presence of DM reaction take place in parallel with DS reaction. The organometallic compounds react with hydrogen on the catalyst and yield solid deposits of metal sulfides on the catalyst<sup>(8)</sup>. Compared with distillate hydrotreating, the hydrotreating of petroleum residue is more difficult, because the residue contains high molecular weight of sulfur and metal compounds and large quantities of asphaltenes whose characteristics are not sufficiently known<sup>(9,10)</sup>. On the other hand the hydrotreating of residue requires severe conditions of temperature, pressure and high

hydrogen consumption rate. This paper deals with investigation of the effect of hydrotreating temperature and LHSV on the hydrotreating process of Sharki Baghdad residue.

### EXPERIMENTAL WORK

#### Feed Stock

Sharki Baghdad residue (Sh. B. R.) was obtained from distillation of Sharki Baghdad crude oil in a laboratory distillation unit using 16 sieve tray Oldershow column. The properties of Sh. B. R. are shown in Table (1).

#### Asphaltenes Removal

Asphaltenes precipitated from Sh. B. R. were carried out using 5 parts of n-heptane (by vol.) to 1 part of residue (by wt.). the mixing was achieved by bubbling with nitrogen for 4 hour at solvent reflux temperature. The asphaltenes were filtered from the slurry after mixing step. The mixture of solvent and deasphalted residue (DAR) was introduced to a stripping stage in order to remove the solvent from DAR. The percentage of asphaltenes precipitated by heptane is 6.9 and the properties of DAR are shown in Table (2).

#### Catalysts

Commercial cobalt molybdenum and nickel molybdenum supported over  $\gamma$ -Aluminum oxide (CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalysts were obtained from Ketjenfme Company

(Netherlands). The chemical and physical properties of catalyst are tabulated in Table (3).

### Presulfiding of the Catalyst

The presulfiding process was used to convert the calcined catalyst into active state. The fresh catalyst was charged to the hydrotreating reactor after drying at 383 K for 2 hours. Catalyst presulfiding was accomplished by a solution of 0.6 Vol. % of CS<sub>2</sub> in 1 % sulfur gas oil. The first 4 hours of activation was carried out at 2.1 MPa and 477 K with LHSV of 4hr<sup>-1</sup>. The next step in the catalyst activation took 16 hours with the following conditions; temperature of 573 K, LHSV of 1 hr<sup>-1</sup>, pressure of 2.1 MPa and hydrogen to oil ratio of 200 L/L.

### Hydrotreating Experiments

The hydrotreating was carried out in a continuous high pressure laboratory unit shown Fig. 1. The preliminary preheated feedstock is pumped upward into reactor after being mixed with dried hydrogen. The reactor heaters is in the form of four separated heat-controlled block shells. The reactor products are separated from gases by the pressure separator and cooler. The gases are then vented to the exterior. For both CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, the temperature range varied from 573 to 723 K over LHSV ranging from 1 to 2.5 hr<sup>-1</sup>. The pressure and hydrogen to feed ratio were kept constant at 6.1 MPa and 300 L/L respectively.

### Test Methods

The specific gravity, pour point, Conradson carbon residue, asphaltenes content of the Sh. B. R. and DAR. were determined according to ASTM standard test methods. Sulfur contents of both feedstock and hydrotreated products were determined using standard test methods (IP 63/55). The metal contents of Sh. B. R., DAR. and hydrotreated products were determined using Atomic Absorption Spectrophotometer.

## RESULTS AND DISCUSSION

The results of sulfur and metals removal from heptane deasphalted residue using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Figs. (2-5). These figures show that the DS and DM reaction increases with increasing the hydrotreating temperature and decreasing LHSV.

This is may be due to the fact that at high temperature, some asphaltenes are decomposed to smaller molecules, which can be more easily diffuse to the catalyst micropores and reaches the active sites where the DS and DM reaction mainly occur. Furthermore, at high temperature, the unreactive sulfur compounds which probably belong to thiophene derivatives become activated enough to react with hydrogen. But the upper temperature level is limited by the undesirable side reaction such as cracking reaction.

At the same time the DS and DM reaction are function of contact time (inverse of LHSV) between the reacted residue and catalyst. Therefore, increasing LHSV will shorten the contact time leading to decrease in the extent of sulfur and metals removal as shown in Figs. (2-5). However, the desired degree of DS and DM can be achieved by employing compromise combination of temperature and LHSV.

The differences in the extent of removal of nickel, iron and vanadium are shown in Figs. (6-11) using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> respectively. It could be seen that the vanadium removal is higher than the other metals at 573 K and all the working range of LHSV. This is in agreement with the results of several investigators concerned with the behavior of iron, nickel and vanadium compounds during hydrotreating of different petroleum residue<sup>(11,13)</sup>. Shah *et al*<sup>(14)</sup> have inferred that the vanadium is more easily removed than nickel because vanadium presents in porphyrins combines firmly with oxygen. This oxygen forms a strong link with the surface of the catalyst, thereby making removal of vanadium from residue easier than nickel. At high hydrotreating temperature the other types of reaction such as cracking may be affected on the behavior of vanadium removal.

Figures (2-11) also indicate that the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibits a higher DS activity than the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst while the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts gives high DM activity. This is in agreement with the result obtained by Agudo *et al*<sup>(15)</sup> and disagreement with the results of Bonysieres<sup>(16)</sup>. The difference between the results of this work and Bonysieres may be due to the uses of individual sulfur compound by Bonysieres. On the other hand, Bonysieres used a narrow range of reacting temperature of 501 to 539°K. Furthermore, Gillian Bial<sup>(17)</sup> stressed that the higher or lower activity of catalysts can be changed according to the reaction temperature employed.

## CONCLUSIONS

1. The sulfur and metals removal is highly dependent on temperature and LHSV. The DS and DM increase with increasing the hydrotreating temperature and decreasing the LHSV.
2. The removal of vanadium is higher than the removal of nickel and iron.
3. The  $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$  catalyst exhibits a higher DS activity than the  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$  catalyst and vice versa for DM in the operating conditions of this investigation.

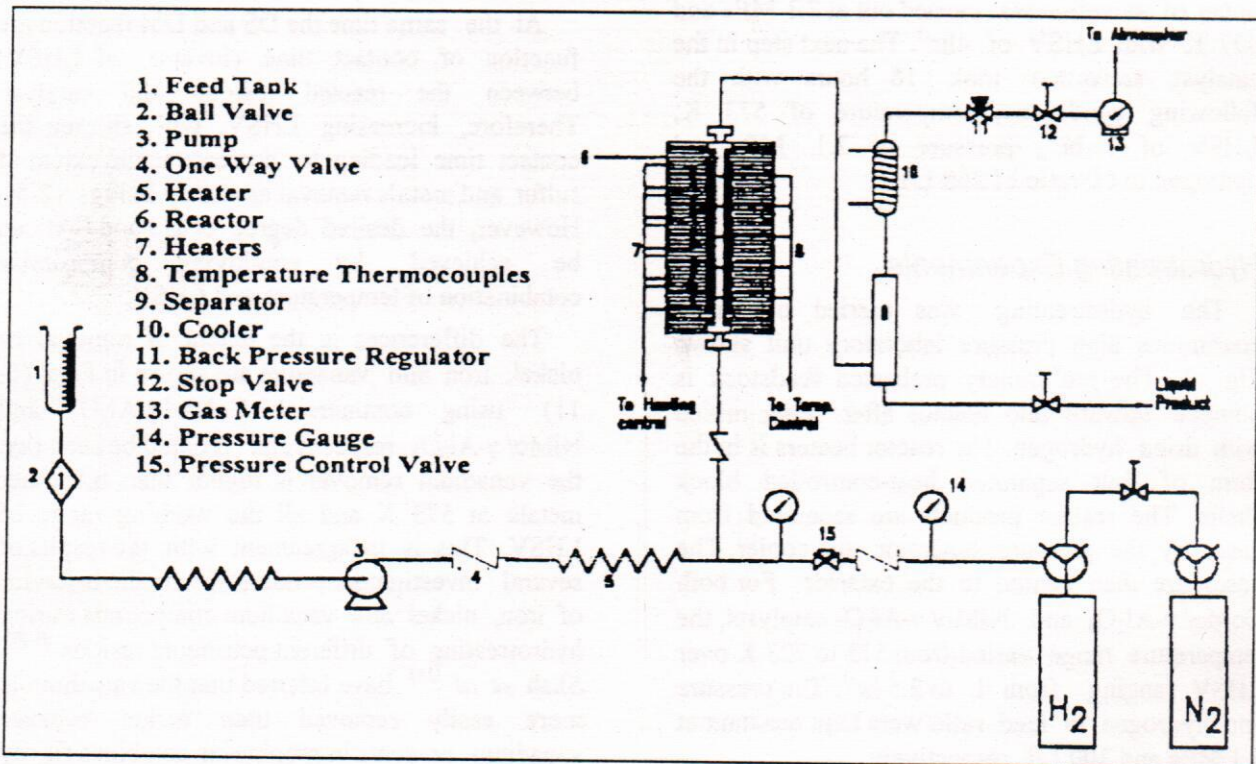


Fig.(1) Flow diagram of laboratory hydrotreating system

Table (1) Properties of Sharki Baghdad residue and deasphalted residue

Properties	Sharki Baghdad Residue	Deasphalted Residue
Specific gravity at 15.6/15.6 °C	1.0100	0.9930
Degree API gravity	8.59	10.99
Sulfur content, wt %	6.48	5.20
<b>Metal content, ppm</b>		
Ni	35.3	32.4
Fe	22.74	22.41
V	155.53	110.25
Asphaltenes content by heptane, wt%	16.08	-
Pour point, K	279	294
CCR, wt %	23.24	-
Ash content, wt %	0.165	0.14

Table (2) Chemical and physical properties of commercial catalyst

	$\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$	$\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$
$\text{MoO}_3$ , wt %	12	15
$\text{CoO}$ , wt %	4	-
$\text{NiO}$ , wt %	-	3
$\text{Na}_2\text{O}$ , wt %	0.06	0.06
$\text{Fe}$ , wt %	0.03	0.06
$\text{SO}_4$ , wt %	1.50	1.50
$\text{Al}_2\text{O}_3$ , wt %	Balance	Balance
Form	Extrudate	Quadruloble
Normal size, mm	2.5	2.5
Average length, mm	5	5
Surface area, $\text{cm}^2/\text{g}$	280	285
Pore volume, $\text{m}^3/\text{g}$	0.55	0.53
Bulk density, $\text{kg}/\text{m}^3$	680	620
Crushing strength,	19.9	20.1
Atrition, wt %	2	1.5

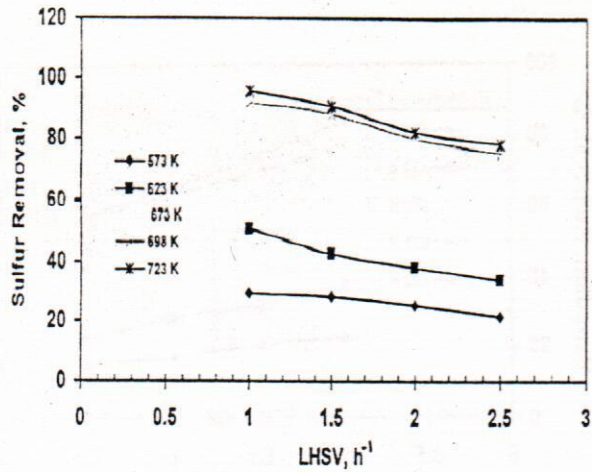


Fig. (2) Effect of hydrotreating temperature and LHSV on the sulfur removal using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

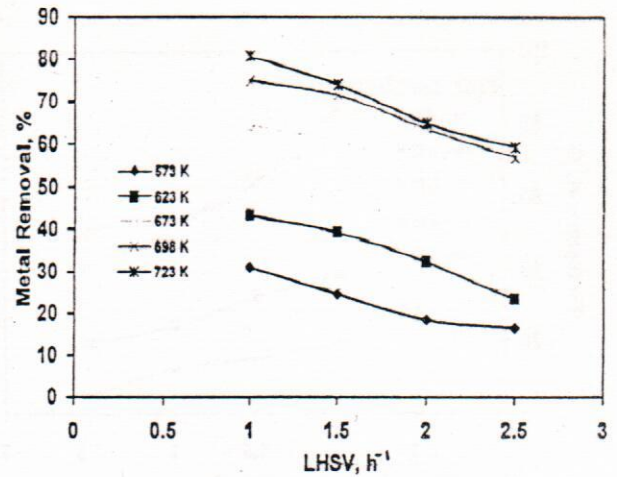


Fig. (5) Effect of hydrotreating temperature and LHSV on the total metals removal using commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

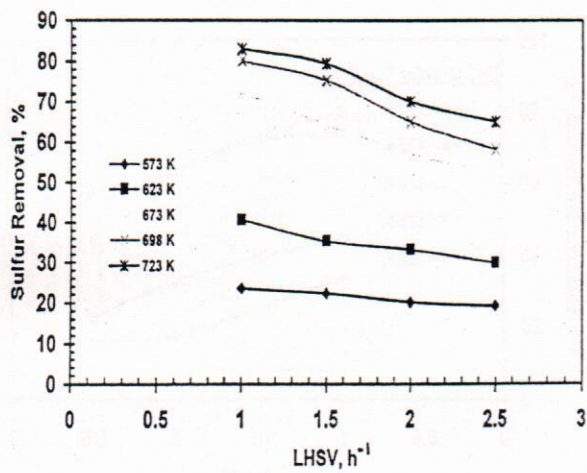


Fig. (3) Effect of hydrotreating temperature and LHSV on the sulfur removal using commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

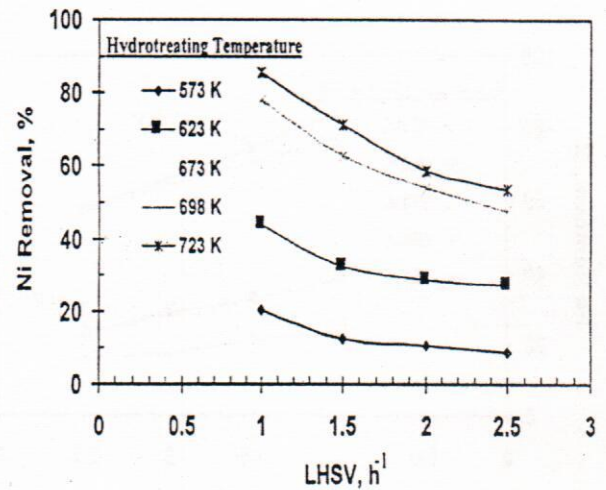


Fig. (6) Effect of hydrotreating temperature and LHSV on the nickel removal using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

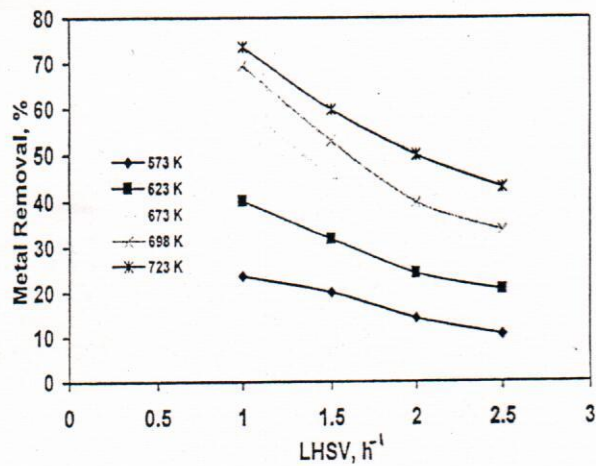


Fig. (4) Effect of hydrotreating temperature and LHSV on the total metals removal using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

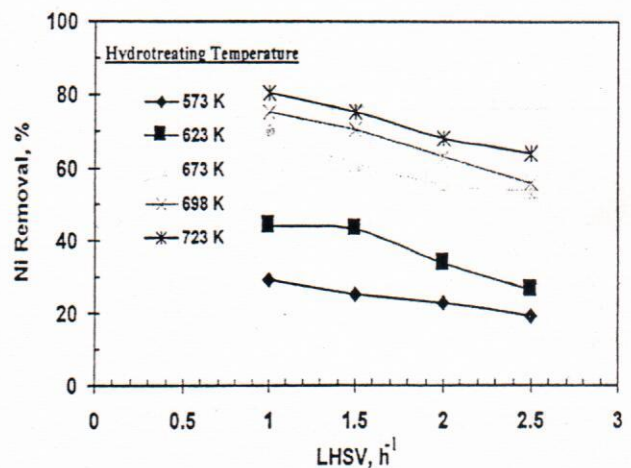


Fig. (7) Effect of hydrotreating temperature and LHSV on the nickel removal using commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

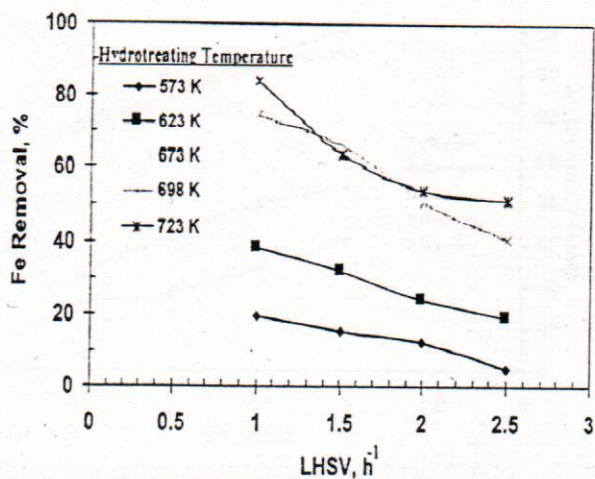


Fig. (8) Effect of hydrotreating temperature and LHSV on the iron removal using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

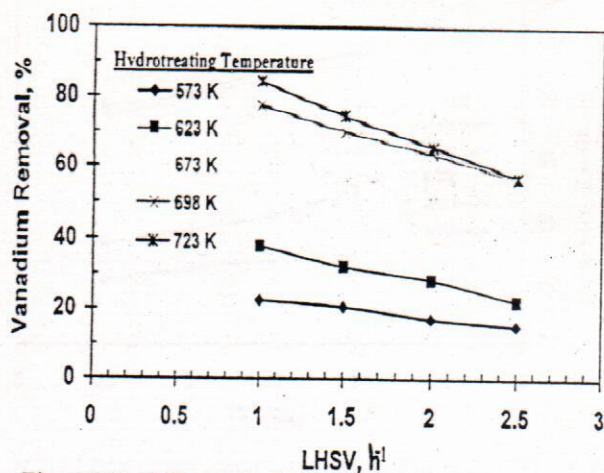


Fig. (10) Effect of hydrotreating temperature and LHSV on the vanadium removal using commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

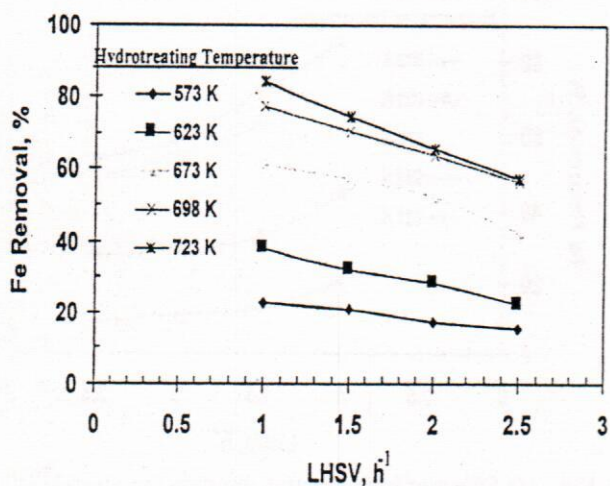


Fig. (9) Effect of hydrotreating temperature and LHSV on the iron removal using commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

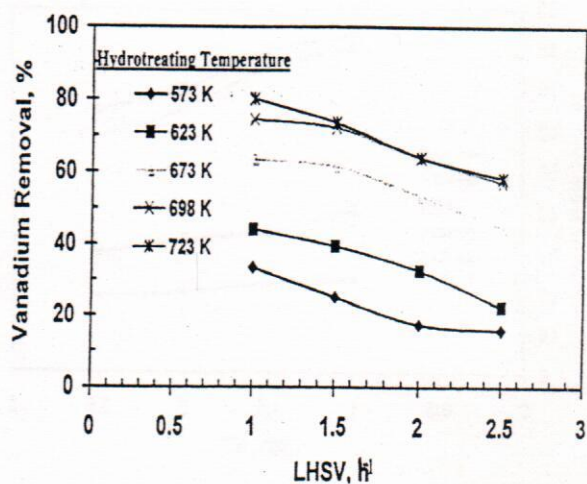


Fig. (11) Effect of hydrotreating temperature and LHSV on the vanadium removal using commercial NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst