Hydrodesulfurization of Iraqi Atmospheric Gasoil by Ti-Ni-Mo/γ-Al_2O_3 Prepared Catalyst

Abdul Halim Abdul Karim Mohammed
Professor
AL-Farabi University College
imahalim 2005 @yahoo.com

Hussain Kasim Hussain
Assistant Professor
Engineering College - Baghdad University
husseinqassab@yahoo.com

Tariq Mohammed Naife
Lecture
tariqaltaee@yahoo.com

ABSTRACT

This study investigates the improvement of Iraqi atmospheric gas oil characteristics which contains 1.402 wt. % sulfur content and 16.88 wt. % aromatic content supplied from Al-Dura Refinery by using hydrodesulfurization (HDS) process using Ti-Ni-Mo/γ-Al_2O_3 prepared catalyst in order to achieve low sulfur and aromatic saturation gas oil. Hydrodearomatization (HDA) occurs simultaneously with hydrodesulfurization (HDS) process. The effect of titanium on the conventional catalyst Ni-Mo/γ-Al_2O_3 was investigated by physical adsorption and catalytic activity test.Ti-Ni-Mo/γ-Al_2O_3 catalyst was prepared under vacuum impregnation condition to ensure efficient precipitation of metals within the carrier γ-Al_2O_3. The loading percentage of metals as oxide; titanium oxide 3 wt. %, nickel oxide 5 wt. % and molybdenum oxide 12 wt. %. The performance of the synthesized catalyst for removing sulfur and aromatic saturation were tested at various temperatures 275 to 350°C, LHSV 1 to $4h^{-1}$, constant pressure 40 bar and H_2/HC ratio 500 ml/ml.Results showed that the sulfur and aromatic content were reduced at all operating conditions. Maximum sulfur removal was 75.52 wt. % in gas oil on Ti-Ni-Mo/γ-Al_2O_3 at temperature 350°C, LHSV $1h^{-1}$, while minimum aromatic content achieved was 15.6 wt. % at the same conditions.

Keywords: hydrodesulfurization, hydrodearomatization, gas oil, hydrotreating catalyst.

أزالة الكبريت بالهيدروجين لزيت الغاز العراقي بواسطة الحفاز المحضر Ti-Ni-Mo/γ-Al_2O_3

عبدالحليم عبدالكريم محمد *
استاذ متمرس
*كلية الفارابي الجامعة

حسين قاسم حسين
استاذ مساعد
كلية الهندسة – جامعة بغداد

طارق محمد نايف
مدرس

الخلاصة

هذه الدراسة تحقق تحسين من خصائص زيت الغازالعراقي والذي يحتوي 1.402 ٪ نسبة وزنية من الكبريت و 16.88٪ نسبة وزنية من المركبات الاروماتية والذي تم الحصول عليه من مصفى الدورة عن طريق إدخاله لعملية ازالة الكبريت بالهيدروجين باستخدام الحفاز المحضر Ti-Ni-Mo /γ- Al_2O_3 لغرض الحصول على زيت غاز عراقي واطئ الكبريت واشباع المركبات الاروماتية ، عملية معالجة المواد الاروماتية بالهيدروجين تحدث تلقائيا مع عملية ازالة الكبريت بالهيدروجين ، تاثير اضافة التيتانيوم على الحفاز التقليدي Ni-Mo/γ- Al_2O_3 تحقق بواسطة الامتزاز الفيزياوي واختبار اداء الفعالية ، تم تحضير الحفاز تحت ضغط التحميل الفراغي لضمان كفاءة ترسيب المعادن داخل الحامل γ-Al_2O_3. نسبة تحميل اكاسيد المعادن على الحامل كانت 3 % نسبة وزنية من اوكسيد التياتنيوم و 5 % نسبة وزنية اوكسيد النيكل و 12 % نسبة وزنية من اوكسيد

المولوبدنيوم.تم اختبار اداء الحفاز المحضر لازالة الكبريت واشباع المركبات الاروماتية لمختلف درجات الحرارة من 275 – 350 م°وسرعة حجمية فراغية للسائل من 1- 4 سا $^{-1}$ ، وضغط 40 بار ونسبة H_2/HC 500مل/ مل .اظهرت النتائج أن محتوى الكبريت واشباع المركبات الاروماتية ينخفض في جميع ظروف التشغيل للحفاز المحضر. اعلى نسبة ازالة للكبريت تم الحصول عليها 75.52 % نسبة وزنية لزيت الغاز باستعمال الحفاز $Ti-Ni-Mo/\gamma-Al_2O_3$ حصلت في درجة حرارة 350م°وسرعة حجمية فراغية للسائل 1 سا $^{-1}$ ، بينما اقل قيمة للمحتوى الاروماتي 15.6 % نسبة وزنية وبنفس الظروف التشغيلية.

الكلمات الرئيسية :ازالة الكبريت بالهيدروجين ،الهدرجة الاروماتية ،زيت الغاز ،حفازات الهدرجة.

1. INTRODUCTION

The primary goal of recently decade proposed legislation in most countries in the world is to reduce the sulfur content of transportation fuels, **Babich, 2003**. Sulfur present in fuels leads to SOx air pollution generated by vehicle engines. Diesel fuel is presently used as the primary energy source for the ship, trains, trucks and some automobiles. It is in principle a more attractive fuel than gasoline since the higher compression ratios used to give higher fuel efficiencies. However, the further use of diesel will require solutions to some major environmental pollution problems, **Kabe, et al., 1999**. Hydrodesulfurization is one type of hydrotreating process which catalytically stabilizes petroleum products and/or removes objectionable elements from products or feedstocks by reacting them with hydrogen. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization (HDS). To meet environmental objectives it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins, **Gray, 1994** and **Kinya, et al., 2003.** The S-containing molecules present in petroleum or synthetic oils are generally classified into two types: non-heterocycles and heterocycles. The former comprises thiols, sulfides and disulfides. Heterocycles are mainly composed of thiophenes with one to several aromatic rings and their alkyl or aryl substituent sulfur and nitrogen compounds, which comprises maintaining a bed of a sulfided catalyst, **Liu, et al., 2009.** When hydrodesulfurization reaction is found hydrodearomatization also occurs simultaneously because aromatic compounds are always present in refinery streams, **Gabor, et al., 2007.** As environmental considerations become of greater concern, it is desirable to treat hydrocarbons such as naphthenes and middle distillate hydrocarbons to decrease the content of undesirable aromatic components, **Gachet, et al., 1984**. Noble metal catalysts, which are excellent for aromatic saturation, but will quickly get poisoned by the sulfur and nitrogen compounds that are present in typical hydrocarbon feedstocks, and lose their hydrogenation activity in a short time. Therefore, noble metal catalysts cannot be used for a one-step process for hydrodearomatizing (HDA), **Speight, 2007**. The most typical HDS catalysts consist of an MoS_2 active phase promoted by Co or Ni atoms, called ‘CoMoS’ or ‘NiMoS’ phase, both of which have been extensively researched and by porous γ-Al_2O_3 supports, **Song, 2003, Venner, 2000,** and **Girgis** and **Gates, 1991**. Noble metals have often been proposed as newly developed active phases. Improvement in the properties of γ-Al_2O_3 based supports and enhancement of the catalytic functions of CoMoS or NiMoS phase might be achieved by the use of newly developed supports or promoters such as TiO_2 or mixed oxides comprising 0.1 to 15% by weight of one or more non-noble Group VIII metals; and from 1 to 50% by weight of tungsten and/or from 1 to 20% by weight or molybdenum or chromium, parameters affecting on hydrotreating process such as passing a charge hydrocarbon feed in the presence of hydrogen into contact with catalyst, thereby effecting hydrogenation, hydrodearomatization, hydrodesulfurization and hydrodenitrogenation of charge hydrocarbon feed containing undesired aromatic components, sulfur and nitrogen, and forming a product stream of hydrocarbon containing a lesser concentration of undesired aromatic components because it affected on health of human and causes in many life problems especially the cancer diseases and respiratory system, sulfur and nitrogen. Hydrotreating is applied to a wide range of feedstocks, from naphtha to residue for reducing crude undesired compound, **Schulz, et al., 1999**. The aim of present study is to introduce and characterize a modified HDS catalyst which is suitable and applicable to HDS processes.

2. EXPERIMENTAL WORK

2.1 Feedstock

Iraqi atmospheric gas oil, supplied by Al-Dura Refinery –Baghdad, is used as the feedstock in the present investigation, the specifications of Iraqi Gas Oil are characterized in AL-Dura refinery and Labrotaries in Chemical Engineering Department - College of Engineering at the University of Baghdad. These characteristics are tabulated in **Table 1**.

2.2 Materials

2.2.1 Support

Alumina support (γ- Al_2O_3) with a spherical shape and an average diameter of 3mm was supplied by the FLUKA AG Company. The properties of γ- Al_2O_3 are tabulated in **Table 2**.

2.2-2 Chemicals

The chemicals used in this study are listed in **Table 3.**

2.2.3 Gases

2.2-3-1 Nitrogen

Nitrogen was supplied from Baghdad Company with purity 99.9 %.

2.2-3-2 Hydrogen

Hydrogen was supplied from Baghdad Company with purity 99.9 %.

3. CATALYST PREPARATION

3.1 Impregnation Apparatus

The impregnation apparatus consists of a conical flask conducted with a separating funnel, vacuum pump, electric shaker and trip to absorb the moisture and gases for efficient deposition of metal oxides into the carrier. The flask was placed upon shaker to ensure good contacting between the aqueous solution and alumina particles. The objective is to impregnate the carrier with an aqueous solution of metal salt, which was adjusted to a concentration which gives desired metal loading.

3.2 Preparation of Ti-Ni-Mo/γ-Al_2O_3Catalyst

Ti-Ni-Mo/γ-Al_2O_3 catalyst was prepared by three impregnation stages. A first impregnation solution was prepared by dissolving 19.73 g of ammonium paramolybdate and 8.72 cm^3 of ammonium hydroxide in 96.45 cm^3 of distilled water.This first impregnation solution was employed to impregnate the alumina which is calcined at 538 °C for 16 hours by pouring the solution on the 309 g alumina with continuous shaking. The prepared material was air dried for 16 hours at 120 °C. A second impregnation solution was prepared by dissolving 77.93 g of Ni $(NO_3)_2.6H_2O$ in 229.72 cm^3 of distilled water.This second impregnation solution was employed to impregnate the dried molybdenum containing material by pouring this impregnation solution in dried molybdenum with continuous shaking. Then, this material was air dried at 120 °C for 16 hours and calcined at 538 °C for 16 hours. A third impregnation solution was prepared by dissolving 80.78 cm^3 of titanium tetrachloride in 370 cm^3 of n- heptane. The third impregnation solution was employed to impregnate the calcined molybdenum and nickel containing material under substantially anhydrous conditions. After the third impregnation, the catalyst is air dried at 120°C for 16 hours and calcined at 538 °C for 16 hours, **Beuther, et al., 1976,** and **Peyman** and **Matin**, **2011**. The weights percents of titanium, molybdenum and nickel are deposited on γ-Al_2O_3 support by impregnation were determined by using atomic absorption spectrophotometer (PERKIN-ELMER 5000).The properties of the prepared catalyst are listed in **Table 4**.

3.3 Catalytic activity test

Catalytic activity studies were carried out in a continuous hydrotreating pilot plant unit located in the Petroleum Development and Research Center / Ministry of Oil (Baghdad). The hydrotreating unit designed by (VINCI technologies). The unit consists mainly of vertical tubular stainless steel reactor (17.5 mm I.D., 25.5 mm O.D. and 300 mm length) electrically heated in a two oven, temperature controller, dosing pump, gas meter and high-pressure separator **Fig. 1**. Hydrogen gas was supplied to the unit from a hydrogen cylinder. 50 g of catalyst (catalyst layer length 23 cm) was loaded into the midsection of the reactor, while the upper and lower sections were packed with ceramic balls (ceramic layer length 3.5 cm). The unit was purged with nitrogen to ensure oxygen removal from the system, the was pressure increased gradually up to 65 bars for 3h to check leaks, then the pressure was reduced to 10 bar and nitrogen was replaced by hydrogen with 99.99% purity. The static hydrogen pressure increased up to 65 bars to check the leaks again. The hydrogen pressure was reduced to 5 bars to prepare the unit for sulfiding process.

Pre-sulfiding was carried out at pressure 30 bars, temperature 310˚C, and feed flow rate 1ml/min for 12h using gas oil with 1.402 wt. % sulfur content.

The hydrotreating of gas oil was carried out at 40 bar hydrogen pressure, 1 to 4 h^{-1} LHSV, 275 to 350 ˚C reaction temperatures and hydrogen to hydrocarbon ratio 500 ml/ml. The liquid product was collected (after a stabilization period to attain a steady state) in a receiver from which samples were taken for analysis the sulfure content by X-ray fluorescence device located in the oil training institute / Baghdad.

4. RESULTS AND DISCUSSION

4.1 Surface area and Pore volume

The specific surface area determination was carried out using the BET isotherm, nitrogen adsorption and desorption isotherms were measured on Thermo Finnegan type instrument located in the Petroleum development and Research Center / Ministry of Oil. The specific surface area [SA] which is the area in m^2 of one gram of solid is calculated as in equation (1).

$$S_A = \frac{Vm}{22400} \times a_m \times N \times 10^{-20} \qquad (1)$$

Where Vm is the monolayer coverage, a_m is the area occupied by one molecule of adsorbate in the monolayer which is 0.162 nm^2 for nitrogen molecule, and N is Avogadro’s constant, 6.02 x 10^{23} molecules/mol. Results of surface area and pore volume are 225.1 m^2/g and 0.37 cm^3/g respectively.

4.2. Pore Size Distribution

Fig.2 shows the pore size distribution for Ti-Ni-Mo /γ-Al_2O_3 prepared catalyst, these characteristics were measured by Thermo Finnegan type instrument located in the Petroleum Development and Research Center / Ministry of Oil. It's obvious from the figure that there are numerous pores goes toward macro size diameter. This certainly affected the pore-size distribution change with a decrease in total pore volume.

4.3. Catalytic test

The HDS activity of the prepared catalyst was tested at hydrotreatment pilot plant.

4.3.1 Effects of Temperature and LHSV on sulfur removal

Fig.3 shows the effect of temperature and LHSV on sulfur removal on Ti-Ni-Mo /γ-Al_2O_3 prepared catalyst. The values of sulfur removal calculated by Eq. (2), **Herna** and **Yang, 2004**.

$$\text{Sulfur removal} = [(C(S)o - C(S))/C(S)o] * 100 \qquad (2)$$

Where C(S)o is initial sulfur concentration (ppm), in this study 1.402 wt. % sulfur content, and C(S) residual sulfur concentration (ppm). It can be observed from the figure that catalyst in general shows better sulfur removal than standard conventional catalysts (Co-Mo, Ni-Mo) at all the temperatures and LHSVs which is characterized by **Abdul-Halim, et al., 2015** and **Swaty, et al, 2001**. Maximum sulfur removal was 75.52 wt. % in gas oil on Ti-Ni-Mo/γ-Al_2O_3 at temperature 350˚C, LHSV $1h^{-1}$. This implies that the HDS activity of promoter's catalysts improves the HDS activity, a decrease in LHSV from 2.5 to 1 h^{-1} a better range for sulfur removal for the catalyst. Increasing the temperature generally leads to increasing in hydrotreating conversion even at higher LHSV, **Steiner** and **Blekkan, 2002**. This indicates that rate of HDS is fast enough at a higher temperature to mask the effect of an increase in LHSV. The increasing of sulfur removal at high reaction temperature may be attributed to that the unreactive sulfur compounds which most properly belong to thiophene derivatives become activated enough to react with hydrogen.Thus, the upper-temperature value is limited by the undesirable side reactions such as hydrocracking reactions which are expected to occur at high temperature. As the LHSV increases sulfur conversion slightly decreases, which means that the film diffusion has no effect on the reaction kinetics. The decrease in LHSV means that lesser quantity of gas oil contacting the same quantity of catalyst per time, while increasing in LHSV provides for a greater quantity of gas oil through the reaction per unit of time, **Segawa** and **Satoh, 1999**.

4.3.2 Effects of Temperature and LHSV on aromatic content

Aromatic test was done in AL-Dura refinery by using Agilent Technologies Instrument (7890 A, GC system, Wasson – ECE instrumentations). Hydrogenation of aromatics may occur simultaneously in HDS process. **Fig. 4** shows the aromatic content of the hydrotreated product. The figure indicates that the aromatic content decrease with increasing reaction temperature and decreasing of LHSV. The increase of reaction temperature leads to increase the rate of hydrogenation of aromatic and decrease the equilibrium constant, as mentioned by **Girgis** and **Gates, 1991,** while the LHSV decreasing leads to increasing the contact time. Also, as temperature increases, the aromatic compounds are decomposed into smaller one which can more easily diffuse into the catalyst macro and mesopores and reach the inner active sites where the desulfurization reaction mainly occurs. The maximum aromatic reduction is achieved between (300 – 350 °C) because of the interrelation between thermodynamic equilibrium and reaction rates and also for a given pressure, the optimum temperature is a function of the types of aromatic compounds in the feed and space velocity, **Peyman** and **Matin, 2011**.

5. CONCLUSIONS

1. Titanium is a good additive that increases the activity of the catalyst for sulfure removal from gas oil.

2. Sulfur removal from gas oil is highly dependent on the reaction temperature and LHSV variation within the range of studied operation.

3. The aromatic compounds of the hydrodesulfurized products decrease with increasing the reaction temperature and decreasing of LHSV, while the saturated compounds increase with temperature increasing and LHSV decreasing.

NOMENCLATURE

a_m = area occupied by one molecule for N_2 ,Eq.1
C(S)o = intial sulfur concentration (ppm) , Eq.2
C(S) = residual sulfur concentration in liquid product (ppm) , Eq.2
V_m = Monolayer volume, Eq.1
N = Avogadro’s constant 6.02 x 10^{23} molecules / mol., Eq.1
r'_p = Pore radius, A°

V_P = Pore Volume , A°

ABBREVIATIONS

HAD = Hydrodearomatization
HDS = Hydrodesulfurization
LHSV = Liquid hourly space velocity
SA = Surface area

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Table 1. Properties of atmospheric gas oil.

Specification	Value
Specific gravity at 15.6 ˚C/15.6˚C	0.8289
API gravity	37.6
Viscosity / 40 ˚C ,C.st	6.62
Sulfur content ,wt. %	1.402
Aromatic content ,wt. %	18.66
Flash point, ˚C	82
Pour point, ˚C	-9
Diesel index	63
Aniline point, ˚C	71.5
Cetane Number	57
Colour, ASTM	0.5

Table 2. Properties of /γ-Al_2O_3.

Surface Area, m^2/g	280
Pore Volume, cm^3/g	0.365
Porosity	0.45
Bulk density, g/cm^3	1.06
Crushing strength, Kg	18
Loss in attrition, wt. %	1.6

Table 3. Chemical component used.

No.	Compound	Purity	Company
1.	Titanium tetrachloride	99%	BDH
2.	Ammonium paramolybdate	99%	HOPKIN & WILLIAMS
3.	Ammonium hydroxide	99%	Fluka
4.	Nickel nitrate hexahydrate	99%	AAG
5.	n-Heptane	99%	Riedel-DE HAENAG

Table 4. Properties of prepared catalyst.

NO.	Property	Ti Ni Mo /γ-Al_2O_3
1	NiO ,wt.%	5
2	MoO ,wt.%	12
3	TiO, wt.%	3
4	Surface Area, m^2/g	225.1
5	Pore Volume, Cm^3/g	0.38
6	Porosity	0.33
7	Bulk density, g/Cm^3	1.71
8	Crushing strength, Kg	14
9	Loss in attrition, wt.%	1.45

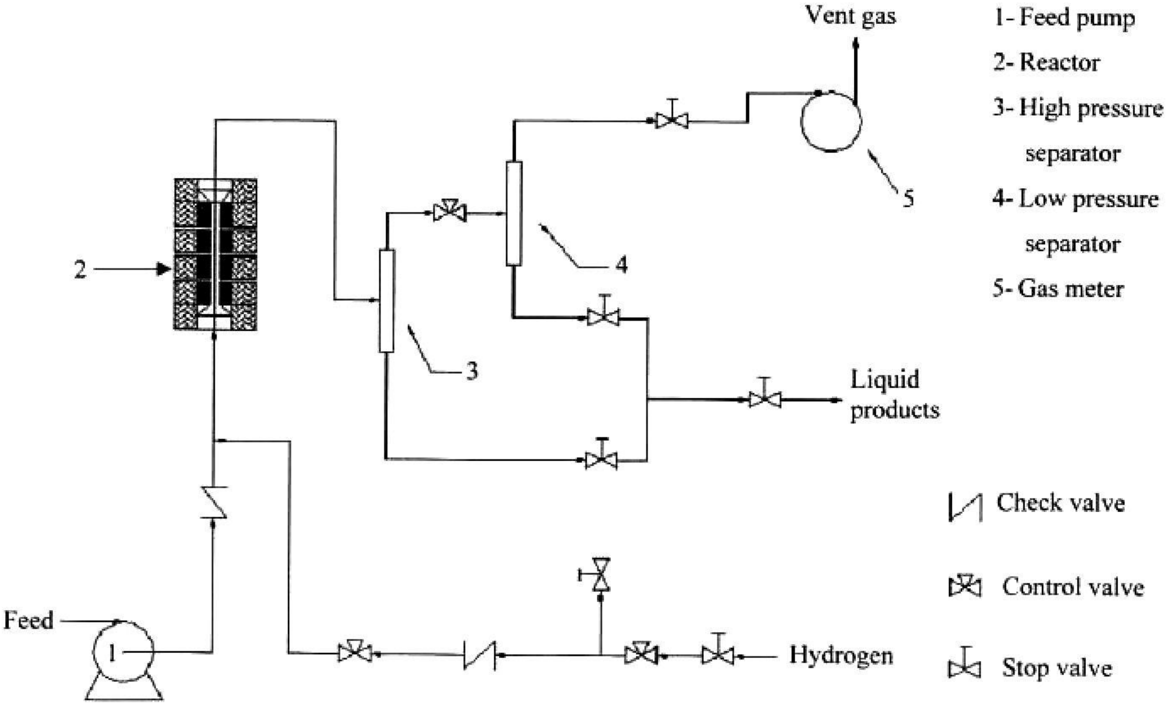

Figure 1. Schematic diagram of the hydrodesulfurization unit.

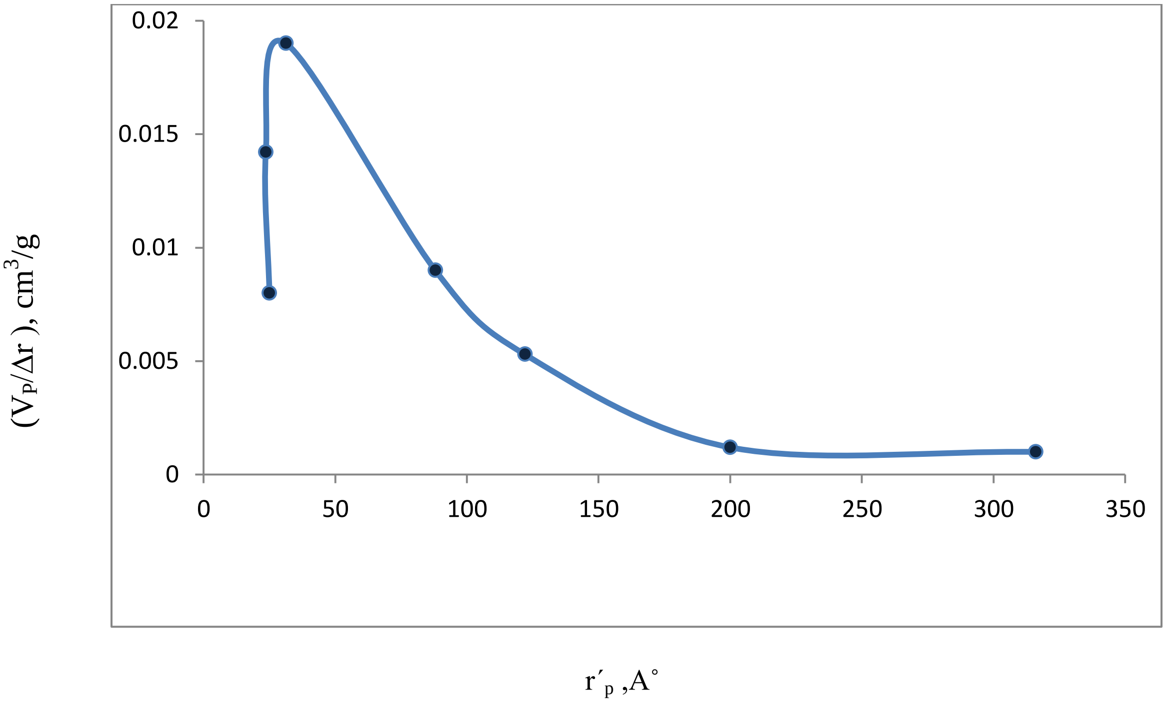

Figure 2. Pore size distribution of Ti-Ni -Mo/ γ-Al_2O_3 catalyst.

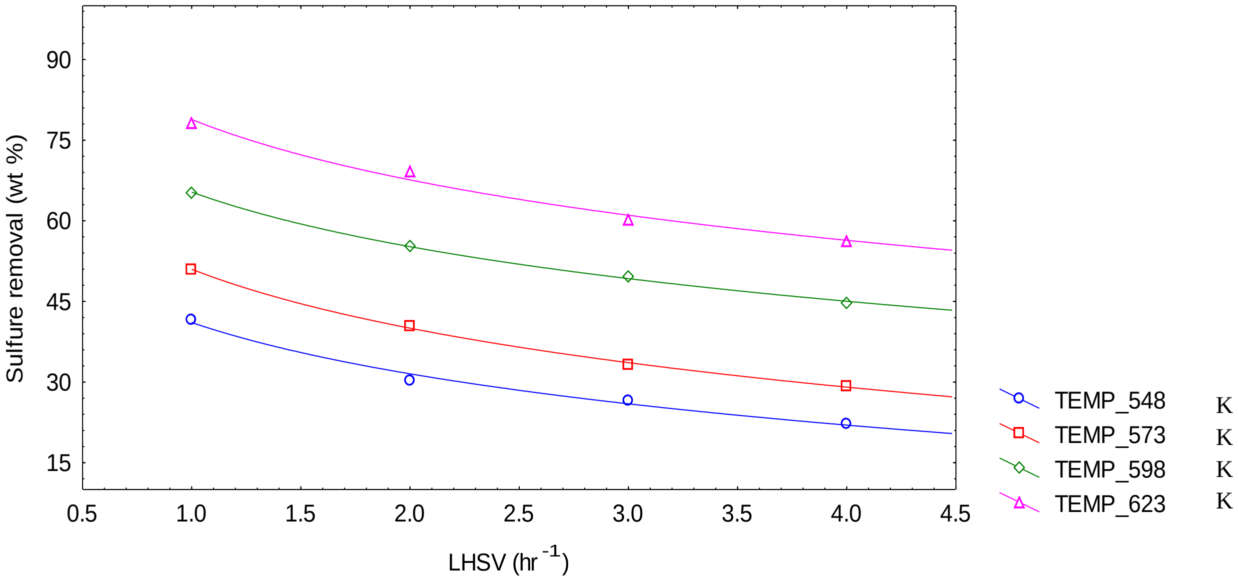

Figure 3. Effect of LHSV on the sulfur removal of hydrotreated product for Ti Ni Mo/γ-Al_2O_3 catalyst.

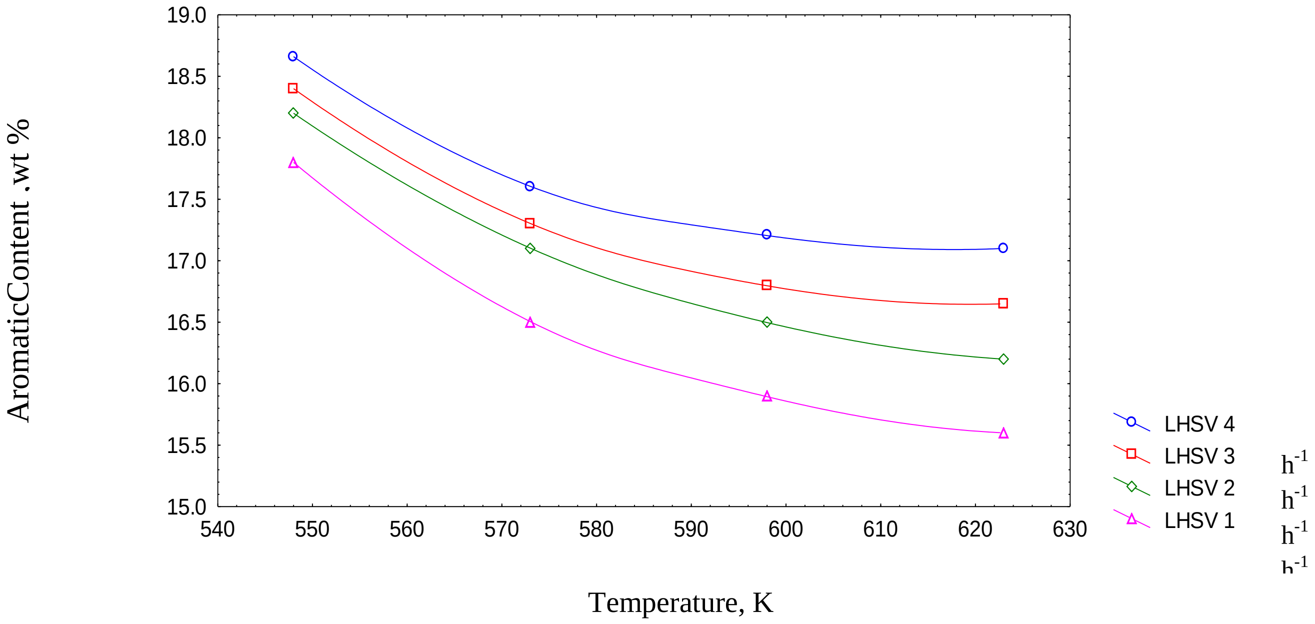

Figure 4. Effect of temperature on aromatic content of atmospheric gas oil for Ti Ni Mo/ γ-Al_2O_3catalyst.