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RESEARCH ARTICLE

EFFECTS OF OPERATING VARIABLES ON CATALYTIC HYDROTREATING OF HEAVY GAS OIL: EXPERIMENTAL AND KINETIC STUDIES

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ABSTRACT

Experimental study to evaluate the effect of hydrotreating CoMo/ γ -Al₂O₃ catalyst for upgrading heavy gas oil (HGO). Hydro desulfurization (HDS) and hydro dearomatization (HDA) activities were conducted in a continuous flow micro trickle-bed reactor at the temperatures, pressures, liquid hourly space velocity (LHSV) and hydrogen-to-feed ratio of; 3500-4500C, 40-75 bar, 0.5-1.0 h⁻¹, and 400 LL-1 respectively. This work identifies and measures the key parameters in hydro desulfurization, and at conversion levels above 95 and 90 %, respectively. The experimental results fitted with the Power Law model yielded reaction orders of the first order reaction for HDS and HAD, and activation energies of 31.4 and 36.9 kJ/Mol respectively.

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INTRODUCTION

Hydrotreating catalysts are playing an important part in the modern refinery to make clean fuel (SK and SK, 2003; Hanafi and Mmdouh, 2011). Nevertheless, it is a great challenge for the conventional hydrotreating catalyst to create ultra-low sulfur and low aromatic diesel (Song and Ma, 2003). Therefore, it is imperative to grow more active and more selective hydrotreating catalyst for hydro desulfurization (HDS) and hydro dearomatization (HDA) (Ma *et al.*, 2010; Hanafy and Doheim, 2000). The increasing need for engine fuels has stimulated the oil refinery industry to look for the possibility of processing heavy crude oil. One of the problems related to this possibility is that the aforementioned oil contains a substantial amount of organic sulfur compounds as well as other undesired compounds, which must be ruled out during the procedure. Their elimination is fundamental because they are toxic for both the catalysts used in the oil processing and the environment (Beškoskia *et al.*, 2008). The reactions such as hydro desulfurization (HDS) and (HDA) of refinery streams are carried out with catalysts consisting of Mo promoted with Ni or Co or W, all in the sulfide state (Dominguez-Crespoa *et al.*, 2008). The industrial hydro treatment of petroleum and is ordinarily achieved by using γ -Al₂O₃ as support; and although other kinds of supports have been proposed (Ancheyta *et al.*, 2005) to achieve production

cost, mechanical resistance and deactivation continue to be better with alumina (Song, 2003). Catalytic hydrotreating (HDT) is one of the most significant stages in the processing of crude oil distillates for fuels and petrochemical feedstock. Depending on their origin, HDT feed stocks contain moderately large concentrations of hetero atoms, which are doled out over the whole boiling range and they generally increase with increasing in their boiling points. In the refining industry, HDT reactions are often classified according to the severity of the operation. Under relatively mild operating conditions, the primary aim is to saturate the feed molecules and/or to remove the undesirable hetero atoms from the oil without significantly changing either the boiling point range or the molecular size distribution. At the other extreme (i.e. Hydro cracking), the primary purpose is to maximize the conversion of a heavy feed to desirable lower boiling-range fractions (Ancheyta *et al.*, 2005).

The functions of middle distillates HDT include predominantly the desulfurization of kerosene, diesel fuel and jet fuel, and its application is developed to fit various needs, including the processing of heavier feeds and the production of high-performance lubricants (Song, 2003; Riad and Mikhail, 2012). In addition, hydrogenation of high-boiling cracking products has become increasingly important where hydro desulfurization (HDS) and saturation of aromatic compounds improve product quality. The reacting conditions of the HDS process vary with the case of crude oil; whereas light oils are easy to desulfurize, the asphaltene and metals which are set

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up in heavy-oil fractions in large quantities shorten catalyst life and reach of heavy oils very difficult (Gawel *et al.*, 2005).

New diesel specifications are being presented around the Earth. The acceptable limits of sulfur content diesel fuel have been slimmed down drastically from 2000 to 500 in many countries due to recent environmental regulations (Europe: from 0.2± 0.3 to 0.05 wt%; Japan: from 0.2 to 0.05 wt%; US from 0.3±0.5 to 0.05 wt%; Mexico from 0.5 to 0.05 wt%) (Ancheyta-JuaÁreza, 1999). In this work, the hydrotreating activity was evaluated on heavy gas oil under conditions close to those used commercially in the refinery using a micro trickle-reactor operating in down-flow-mode. Several kinetic studies documented in the literature on the hydrotreating reactions using real feedstocks have mostly utilized the power law model (Boahene *et al.*, 2013; Bej *et al.*, 2006) to determine significant kinetic parameters. It is well known that in hydrotreating heavy gas oil adsorption of reactant species, such as sulfur and aromatics on the catalytic active sites is known to be the rate-determining step in the response procedure. The aim of the present study was to identify and evaluate the key parameters in hydro desulfurization and hydro dearomatization at high conversion levels (up to 90 %), and as well to conduct kinetic studies using the Power Law model to find the effects of process variables on the rate of HDS and HDA reactions on the heterogeneous CoMo/Al₂O₃ hydrotreating catalyst.

MATERIALS AND METHODS

Feedstock

Heavy gas oil (HGO) obtained from Suez Oil Processing Company was used as a feedstock in our experiments. The feedstock was characterized by 0.9356 g/ml specific density, 21839 ppm sulfur content and 72 wt% total aromatics contents.

Catalyst preparation

Catalyst samples were prepared by impregnation of commercial γ -Al₂O₃ supports with aqueous solutions of ammonium heptamolybdate through incipient-wetness impregnation method. After impregnation; the moist paste was preliminary dried in an oven at 120°C over night and then calcined in a muffle furnace at 450 °C for 4 h. The loadings of MoO₃ and CoO for prepared catalyst were kept constant at 12 and 3 wt%, respectively. The prepared hydrotreating catalyst CoMo/ γ -Al₂O₃ (100 ml catalyst volume, surface area 134 m²/g, pore volume 0.21 ml/g, CoO 4.0 wt%, and MoO₃ 12 wt%) was used in all experiments. The catalyst was presulfiding in situ prior to starting hydrotreating runs.

Catalyst Reactivity

The hydrotreating experiments were performed in a fixed bed reactor (cata-test unit) in the down-flow mode. Its length, internal and external diameter are 500, 19 and 27 mm respectively. A detailed schematic diagram of the cata-test unit is described elsewhere (El Kady *et al.*, 2010). The catalyst was presulfided by injecting sulfidation solution containing 2 wt% DMDS in straight-run atmospheric gas oil under the

following conditions: 50 bar hydrogen pressure, 350°C temperature, 400 L/L hydrogen to feed ratio, 1.5 h⁻¹ LHSV for 12 h before injection the feedstock. The experimental run conditions for the hydrotreating experiments were indicating in Table (1).

Table 1. Experimental runs operating conditions

Process parameter	Temperature effects	Pressure effects	LHSV effects
Temperature (°C)	350,375,400,425, 450	375	375
Pressure (bar)	55	40, 55, 70	55
LHSV (h ⁻¹)	0.5	0.5	0.5, 0.75, 1.0
Hydrogen-to-oil ratio (LL ⁻¹)	400	400	400

Analysis

The liquid products were collected and stripped with nitrogen for removing the dissolved ammonia and hydrogen sulfide. The treated liquid samples were analyzed for total sulfur and aromatic contents according to ASTM D-4294 and ASTM D-2549, respectively.

RESULTS AND DISCUSSION

Influence of the Reactor Design on Catalyst Distribution

All the runs were carried out in a dynamic system on a fixed bed reactor. The axial dispersion of a catalyst is minimized, if L / DP is greater than 350, where L is the length of the reactor and DP is the mean diameter of the catalyst particles. In the present study since L / DP (L = 50 cm, DP = 1.2 mm) was 417, which can be taken for granted that there was no significant axial dispersion or back mixing. The wall flow chances of being trifling and a uniform liquid distribution are very honest, if diet / DP is greater than 18 (= the external diameter of reactor tube) (Herskovitz and Smith, 1978). In the present study dt / dp was 23. Hence, it can be assumed that the liquid distribution was very good with no adverse channeling effects (van Klinken and van Dongen, 1980). Under the experimental conditions described above, in the presence of hydrogen, the reaction happens in the vapor phase and the reaction mixture is vaporized completed at the intake of the catalyst bed, which was attributed to passing over the catalyst bed with inert particles in the top and rear of its zone. Also, the catalyst was diluted with low surface area Al₂O₃ in a ratio of 1. Of late, closer attention has been compensated to the deep desulfurization of heavy gas oil and diesel fuel. Since in the near future their sulfur content must be limited to 0.05 wt % to meet the regulation for environmental security.

Effect of reaction temperature

The temperature is commonly regarded as the most comfortable and the most effective parameter to control the hydrotreating reactions (Ferdous *et al.*, 2006). In parliamentary law to examine the consequence of temperature on the sulfur reduction (HDS) and aromatic hydrogenation (HDA) activities, experiments were performed at temperature ranges of 350 to 375 apiece, while pressure, LHSV and hydrogen-to-gas, oil ratio was held constant at 55 bar, 0.5 h⁻¹, and

400 L/ L, respectively. In Figure (1), the product quality shown the classical behavior when the temperature is increased from 350 to 375 °C, that is a continuous increase in sulfur removal. This may be due to the equilibrium limitation occurs at higher reaction temperatures for the reversible HDS reaction (Steiner and Blekkan 2002; Stanislaus *et al.*, 2010). The data reveal that the reaction temperature has the major effect and contributes significantly among the response of HDS activity with respect to the total pressure. The results of Figure (1) also, Discovered that a maximum predicted HDS activity was attained. Indeed, the enhancement of HDS activity up to 99% is reached as the temperature increased up to 450°C at an operating hydrogen pressure in the range of 55 bars.

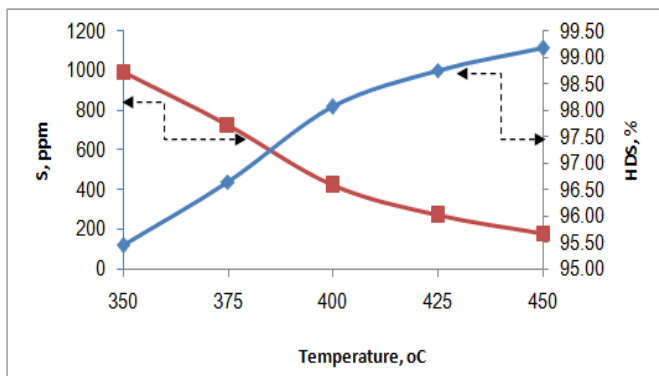


Figure 1. Effect of reactor temperature on total sulfur content of hydro treated HGO and its removal (HDS)

This can be attributed to the effect that a certain rise in the reaction temperature favored the desulfurization of non-refractory sulfur compounds and saturate some of aromatic hydrocarbons. However, these sulfur compounds mainly desulfurized via the direct desulfurization (DDS) pathway, for which the CoMo-S catalyst has the highest HDS activity. Therefore, the enhancement of the HDS activity of the catalyst was observed under high reaction temperature. In contrast, the decreasing temperature suppressed the conversion of sulfur compounds to H₂S.

Effect of reaction pressure

The effect of pressure on product quality was examined between 40 and 70 bar for the feedstock. Figure (2a) shows the effect of the reaction pressure on sulfur content at temperature ranges of 350° to 450°C with constant LHSV of 0.5 h⁻¹, and ratio of hydrogen-to-oil ratio = 400 L L⁻¹. The data for the feedstock show that the growth in reactor pressure, improved product quality (Kim and Choi, 1987). The effect of pressure on HDS for catalyst is applied in Figure (2b). It can be noted from the figure that the rate of HDS reaction is faster during the pressure range from 40 to 55 bars. It implies that the CoMo-S catalyst shows a value of HDS activity as 91.4 wt% at 40 bars, then increases to 96.7 wt% at 55 bars (at 375oC). The figure also revealed that a maximum predicted HDS activity was attained. However, very high pressures reduce the activity of the catalyst, owing to the adhesion of carbon to its surface (El Kady *et al.*, 2010; Vogelaar *et al.*, 2003). The hydrogen pressure has a much smaller impact on the effectiveness of

HDS activity, even if the increase of pressure as high as 55-70 bars, which will make a moderate decrease from 450 ppm-wt to 130 ppm-wt in residual sulfur. One other potential cause for the phenomenon of data indicated in Fig.2 could be the extra reduction of active Co-Mo-S sites on the catalyst surfaces, which is responsible for direct desulfurization (DDS). This might give the explanation for the low HDS activity effect at higher hydrogen pressure (Fig.2) in all the temperature ranges and hydrogen pressure (from 55 to 70 bars). Desulfurized via the DDS pathway, for which the Co-Mo-S catalyst has the highest HDS activity.

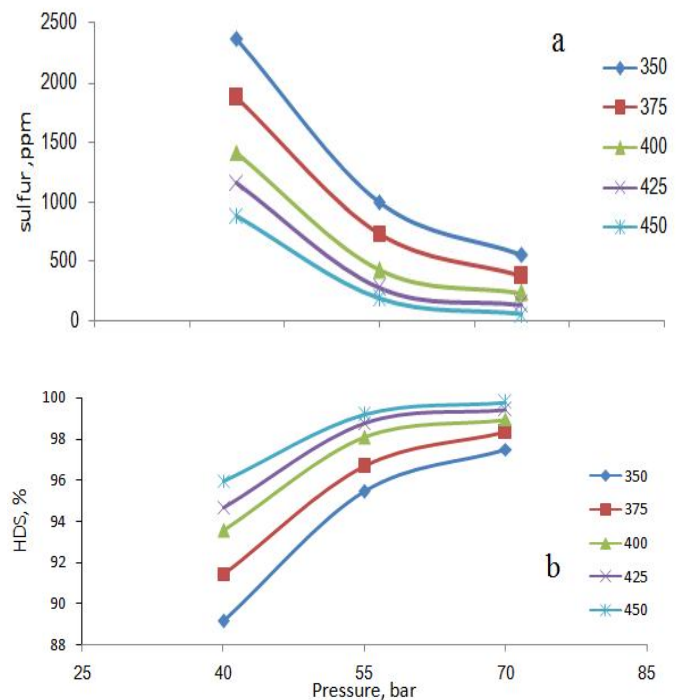


Figure 2. Effect of hydrogen pressure on total sulfur content (a) and sulfur reduction (HDS) (b) of HGO under variables reaction temperature

Effect of space velocity

The effect of space velocity on product sulfur content was studied between 0.5 –1.0 h⁻¹ for the HVG feedstock. Figure (3) shows the effect of LHSV of sulfur at 55 bars and 350-450°C at a constant ratio of hydrogen-to-oil ratio 400 L L⁻¹. The data show that the decrease in LHSV resulted in improved product quality. The sulfur content of the hydro treated product is approximately proportional to the LHSV and hence the contact time. Therefore, the heavier the HDT feedstock the lower the LHSV required. The changes in LHSV can have a slight significant effect on the HDS activity.

Effect of Operating Conditions on Product Aromatic Content

Most of the environmental legislation in the world has focused on the concentration of aromatic in gas oil. Aromatic saturation in hydrotreating (HDT) process begins with the partial saturation of multiple-ring aromatics. Monoaromatics are significantly more difficult to saturate. With low-severity

processing, the monoaromatics content may actually increase as the maturing compounds are saturated.

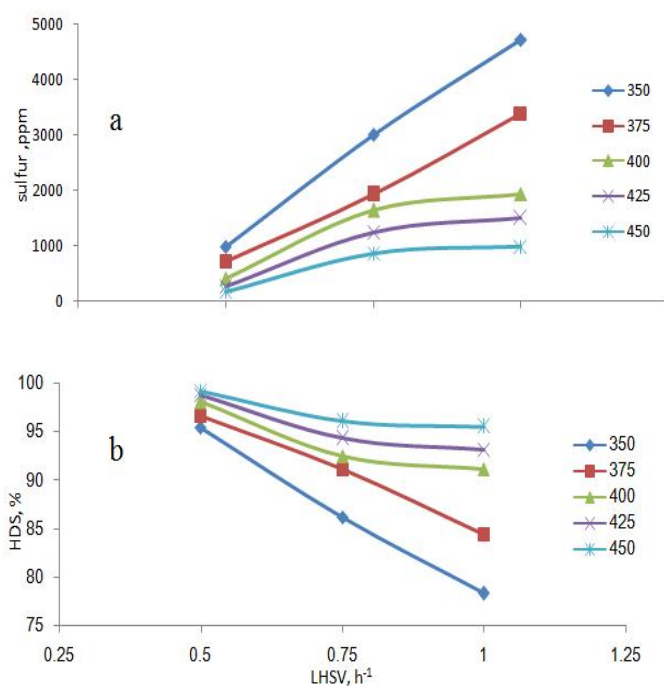


Figure 3. Effect of LHSV on total sulfur content (a) and sulfur reduction (HDS) (b) of HGO under variables reaction temperature

Despite the saturation of aromatic generally increases the cetane index of a particular feedstock; the relative improvements variable (Rodríguez and Ancheyta, 2004; Jarullah *et al.*, 2011; Choudhary, 2007). The data of Figure (4) indicate that the product aromatic contents were decreased as reaction temperature increased up to 375 °C, and then increased as the temperature rose from 375 °C to 450 °C, 10 to 40 wt. %, respectively. The product aromatic content shown the classical behavior when temperature increases in the range of 350- 450 that decrease in total aromatic. It means that the reversibility of the aromatic saturation reaction was observed at higher temperatures (i.e. 450 °C at 55 bars), and reached 40 wt. %. The best aromatic conversion was obtained by the mild severe combination of temperatures, 350 ° and 375 °C and 0.5 h⁻¹ LHSV, and the reduction in aromatic was from 72 to 15 and 10 wt. % of these conditions, respectively.

Literature information (Lylykangas *et al.*, 2002) on kinetic studies of aromatic hydrogenation in industrial feedstocks such as crude and synthetic middle distillates is relatively scarce, probably due to the complexity of the reactions. The reverse reaction was, nevertheless, not taken into account in this approach. The conversion of aromatic to naphthenes is a reversible reaction and affects a chemical equilibrium which is temperature dependent. Thus, the data shown in Figure (4) show that the aromatic contents of the liquid products decreases with increasing reaction, up to 375 °C, but then increases as the temperature is further raised from 375 °C to 450 °C, that is, the aromatic contents pass through a minimum (Ibrahim and A'reff, 2009). On the other hand, high aromatic content in gas oil is suspected to contribute to undesired

emissions in exhaust gases from diesel engines (Maiboom *et al.*, 2008). In HDT process the aromatic saturation requires high severity (Chowdhury *et al.*, 2002). The growth in reactor pressure at 55 bar, reactor temperature up to 375 °C and a decrease in liquid hourly space velocity at constant hydrogen to feed ratio at Flow rate, 400 L L⁻¹ lead to increase the hydrogenation of aromatic as shown in Figures (4-6). As exemplified in Figure (4), the consequence of temperature on the aromatic saturation of the CoMo/Al₂O₃ catalyst, the hydrogenation of aromatic gradually increases when the temperature is raised from 350 to 375 °C, and then starts to decrease with further increase of temperature. This is because, AHYD is kinetically and thermo-dynamically controlled: in the kinetically controlled region (up to 375 °C), an increase in temperature increases the rate of forward reaction (hydrogenation), resulting in a higher hydrogenation of aromatic.

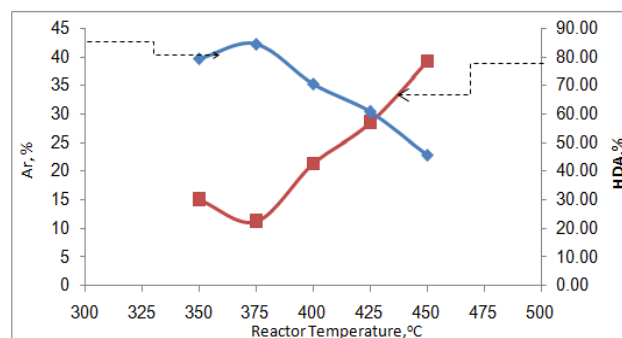


Figure 4. Effect of reactor temperature on (a) aromatic content of hydro treated HGO and (b) its removal (HDA) at different temperature

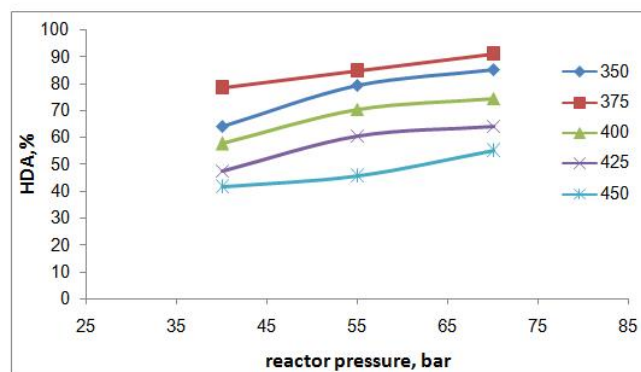


Figure 5. Effect of reactor pressure on hydridearomatization (HDA) of hydrotreated HGO at different temperature

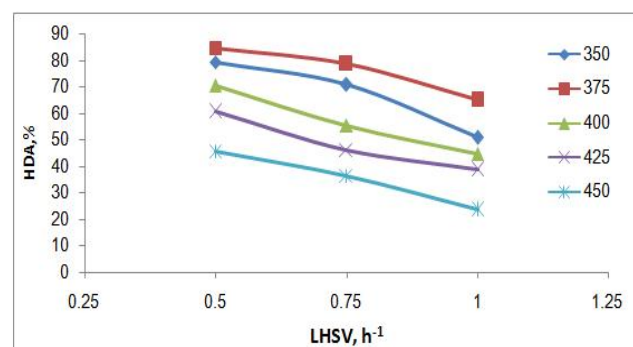


Figure 6. Effect of LHSV on hydridearomatization (HDA) of hydrotreated HGO at different temperature

At higher temperatures, thermodynamic effects dominate, hence contributing to a shift in equilibrium in favor of the reverse reaction (dehydrogenation), which results in more aromatic being produced by the hydro treated products and AHYD passing through a minimum (Owusu-Boakye *et al.*, 2005). The HDA activity strongly depended on the total pressure Figure (5). With increasing the total pressure from 40 to 70 bars, the HDA degree increased from 41.53 to 85.42 using CoMo/Al₂O₃ catalyst at different temperature. The effect of LHSV on HDA is given in Figure (6). From Figure (6), it is observed that HDA degree increased by decreasing LHSV due to increase in reaction time. For example, the HDA degree increased from 23.47 to 84.58 wt.% for CoMo/Al₂O₃ with decrease in LHSV from 1.0 to 0.5 h⁻¹ at different temperature.

Overall Gas Oil HDS and HDA Kinetics

Data available in the literature on kinetic parameters evaluation and modeling for hydro desulfurization and hydro dearomatization reactions are normally derived using the Power Law and Langmuir-Hinshelwood models (Boahene *et al.*, 2013; Bej *et al.*, 2006). The kinetics for sulfur removal from gas oil is complex and depends on the distribution of sulfur compounds and degree of conversion. Although the kinetics of HDS of some model sulfur compounds have been reported in the literature (Rodríguez and Ancheyta, 2004). This is likely referable to the complexity of the reactions caused by the compartment of a great mixture of sulfur compounds with different reactivities (Mapiour *et al.* 2010). For industrial feedstocks, the structural differences between the sulfur containing molecules make it impractical to make a complex rate equation to describe the HDS kinetics, thus, the present work uses conventional power law kinetic expression. Data from both HDS and HDA studies fitted a first order reaction model quite satisfactorily, in accord with the results of others who have used a similar feedstock and the reactor (Shaban S.A., 2005; Boahene *et al.*, 2013). And so, the following rate equations can be applied for calculating rate constants:

$$\ln \frac{S_f}{S_p} = \frac{k_s}{LHSV}$$

$$\ln \frac{A_f}{A_p} = \frac{k_A}{LHSV}$$

Where SF; sulfur content in the feedstock, AF; total aromatic content in the feedstock, Sp; sulfur content in the product, Ap; total aromatic content in the product, LHSV; liquid hourly space velocity (Mohamed *et al.*, 2013). Values of apparent rate constants k_s and k_A were evaluated from experimental data by plotting $\ln S_f / S_p$ or $\ln A_f / A_p$ against $(LHSV)^{-1}$ at five different temperatures for the investigated catalyst (Figures 7,8). The figures proved that the observational data are easily fitted to the first order model and the results indicate that the kinetics of desulfurization and dearomatization of gas oil can be described well with the first-order equation (Deraz *et al.*, 2010). Hence, the rate constants for different temperatures were calculated. Correlation coefficients larger than 0.96 were obtained, as can be seen in Figures (9,10). These results agree with those reported in the literature (Mapiour *et al.*, 2010), in contrast to the close to the first order behavior typically

observed in individual model compound studies (Mapiour *et al.*, 2010). The HDS, HDA reactions order increases and the activation energy diminish with the quantity of HGO. This is because the most reactive molecules of the feedstock disappear first and the remaining compounds, which are more difficult to remove, have a lower kinetic constant and will be less reactive as the HDS, HDA proceeds and the sulfur, aromatic concentration decrease Figure (7,8). The activation energies (EA) for HDS and HDA were calculated by plotting the inverse of absolute temperatures against the logarithm of kinetic constants according to the Arrhenius equation.

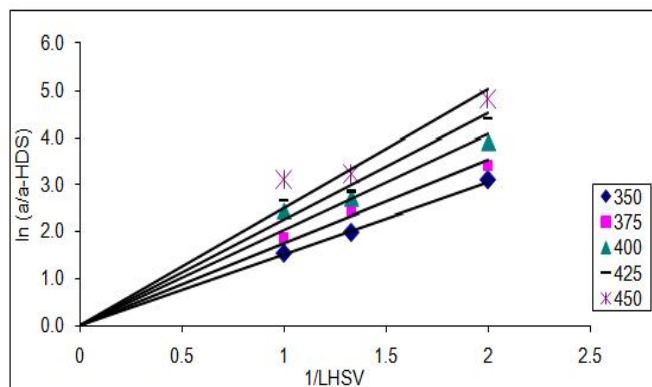


Figure 7. First Order Plot of Hydro desulfurization (HDS) at different temperature

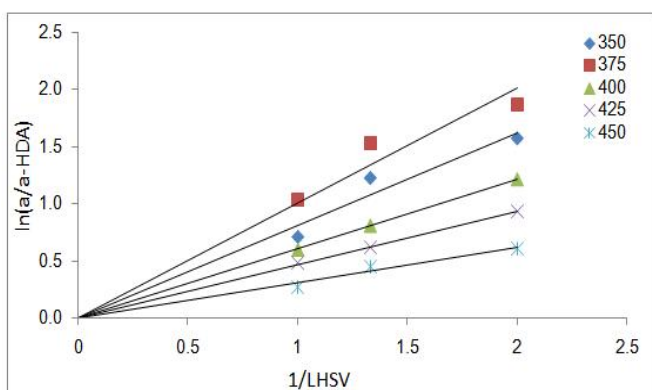


Figure 8. First Order Plot of Hydro dearomatization (HDA) at different temperature

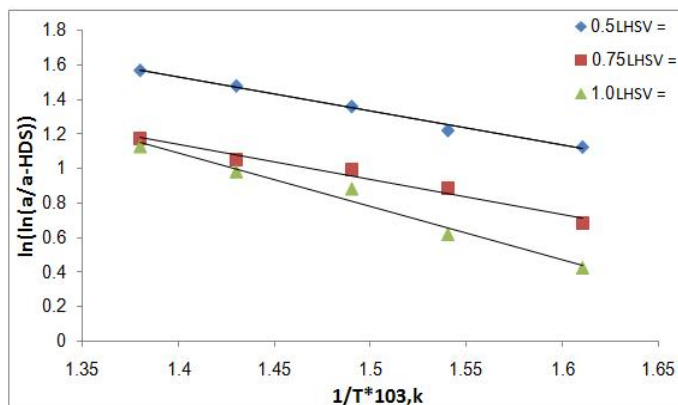


Figure 9. Arrhenius Plot of Hydro desulfurization (HDS) at different temperature

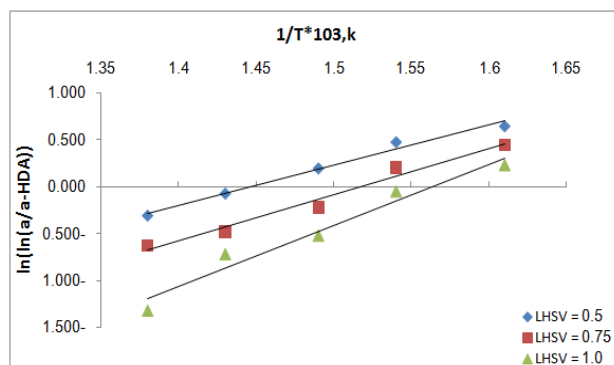


Figure 10. Arrhenius Plot of Hydro dearomatization (HDA) at different temperature

Activation energies of 31.43 kJ mol⁻¹ for HDS and 36.89 kJ mol⁻¹ for HDA were obtained over the sulfide CoMo/Al₂O₃ at best conditions Tables (2,3) (El Kady *et al.*, 2010 ; Mapiour *et al.*, 2010).

Table 2. The apparent activation energies (EA) for HDS

LHSV, h ⁻¹	Ea, k cal	Ea, k jole
0.5	3.97	17.00
0.75	4.03	17.26
1.0	6.23	26.65

Table 3. The apparent activation energies (EA) for HDA

LHSV, h ⁻¹	Ea, k cal	Ea, k jole
0.5	8.62	36.89
0.75	9.89	42.34
1.0	13.07	55.92

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Conclusion

Heavy gas oil hydrotreating overcome λ -Al₂O₃ catalyst was considerably influenced by operating temperatures, pressure, and liquid hourly space velocity. HDT of the feedstock to produce low-sulfur liquid products could be achieved by varying any one of these process parameters studied. The data showed that in general, product quality was improved as the reaction temperature and pressure increased or space velocity decreased. It means that sulfur and aromatic were upgraded. However, aromatic were always greater for HGO. The HDS and HDA activation energies decreased with the quantity of HGO in the range 26.65 – 17.00 and 55.92 - 36.89 KJ/ Mol, respectively. The desulfurization and the dearomatization process of gas oil is fitted with different temperature. The results are shown that the orders of the reaction are approximately equal to 1 and the correlation coefficients are above 0.98. The results show that the kinetics of desulfurization of gas oil can be described well with the first-order equation. The importance for studying the impact of HGO product quality when in HDT reaction arises from the need for efficient design and simulation of units and a better understanding of catalyst behavior and the effect of the process

conditions. This also allows a better insight into the behavior of an existing reactor.

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