PARAMETRIC STUDY OF HYDRODESULFURIZATION AND HYDRODEAROMATIZATION OF GASOIL IN HYDROTREATING PROCESS OVER CoMo-S CATALYST USING A PILOT PLANT INTEGRAL REACTOR

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Abstract. Hydrodesulfurization (HDS) and Hydrodearomatization (HDA) of a real Straight Run Gas Oil (SRGO) were investigated over CoMo-S sulfide catalyst in a high-pressure fixed-bed integral reactor. The effect of the key process parameters on the quality of product was studied by varying the temperature (200-370°C), pressure (20 to 50 bar) and space velocity (1 to 4.7h⁻¹). Experimental results revealed that HDS,% activity improved up to 81% when the temperature was increased up to 370°C but reduced to 60% with increase of space velocity up to 4.7 h⁻¹. It has been also found that the rate of HDA, % activity enhanced up to 40.6% by increasing pressure up to 50 bar. The Cetane index underwent an increase of 1-3 degrees and gravity increased by 1-1.7 °API. The implication of these results on refining industry is that mild hydrotreating of diesel fuels using the single-stage technology will not enable local refineries to produce diesel fuel meeting the current specifications (<15 ppmwt) except with severe/deep once-through desulfurization or two-stage once- through desulfurization with or without splitting the first reactor effluent.

Keywords: Diesel fuel; hydrodesulfurization; hydrodearomatization; CoMo-S/ Al₂O₃ catalyst

Abstrak. Penyahsulfuranhidro (dirujuk sebagai HDS) dan penyaharomatikanhidro (dirujuk sebagai HDA) bagi Minyak Mentah Ringan telah dijalankan menggunakan pemangkin sulfida CoMo-S di dalam reaktor integral mangkin padat bertekanan tinggi. Kesan daripada parameter-parameter proses utama terhadap kualiti produk telah dikaji dengan mempelbagaikan suhu (200-370°C), tekanan (20 ke 50 bar) dan halaju ruang (1 hingga 4.7 h⁻¹). Keputusan eksperimen menunjukkan, % aktiviti HDS dipertingkatkan sehingga 81% apabila suhu dinaikkan sehingga 370°C tetapi berkurang sehingga 60% dengan pertambahan halaju ruang sehingga 4.7 h⁻¹. Selain itu, keputusan juga menunjukkan bahawa kadar % aktiviti HDA dipertingkatkan sehingga 40.6% apabila tekanan dinaikkan hingga mencecah 50 bar. Indeks setana menunjukkan peningkatan

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sebanyak 1-3 darjah dan graviti bertambah sehingga 1-1.7° API. Implikasi keputusan-keputusan ini terhadap industri penapisan adalah rawatan hidro sederhana terhadap bahan api diesel menggunakan teknologi tahap tunggal tidak memungkinkan loji penapisan tempatan menghasilkan bahan api yang memenuhi spesifikasi semasa (<15 ppmwt) kecuali dengan penyahsulfuran sekali lalu yang mendalam/kuat atau penyahsulfuran sekali lalu dua tahap dengan atau tanpa menumpahkan efluen reaktor pertama.

1.0   INTRODUCTION

The Environmental Protection Agency (EPA) has proposed new guidelines to limit sulfur in diesel fuels from low sulfur diesel (LSD) of 500 ppmwt to ultra low sulfur diesel (ULSD) of less than 15 ppm in 2010. Other legislations proposed by worldwide fuel character are introducing limitations on aromatic content in diesel fuels to less than 20 % in the near future [1]. Indeed, reduction of aromatics in diesel fuels contributes to the decrease of exhaust gas emissions, mainly hydrocarbons (HC) and particulate matter (PM) and improve the Cetane Index (CI). Therefore, it is expected that ultra deep Hydrodearomatization and hydrodesulphurization of gas oils may be considered necessary in order to satisfy the market and environmental requirements [2, 3].

The main key to achieve ultra-deep desulfurization is the removal of refractory sulfur aromatics compounds. However, these hindered compounds are remaining in the diesel fuel after the sulfur reduction to 500-ppm wt level by conventional hydrodesulfurization process because of the inhibiting effects of co-existing polyaromatics and nitrogen compounds [4] in the feed as well as H$_2$S in the product [5]. However, any of these could make it more difficult for the refineries to achieve less than the 15-ppmwt (ULSD) sulfur specification with the currently employed catalysts and use of typical operating conditions. In this respect, many aspects such as the catalysts, process variables, and the quality of feedstock could play a major role on the shift from normal desulfurization (LSD) to ultra deep desulfurization-dearomatization (ULSAD) of diesel feeds [6-9]. Hence, the shift from LSD to ULSD with low aromatics content is a very convoluted technical issue.

Nevertheless, it is most favorable to attain the new fuel specifications by taking into consideration both catalyst and process issues [10]. However, ultra deep

Hydrodesulfurization (HDS) and Hydrodearomatization (HDA) of diesel fuels requires either severe process conditions such as temperature, pressure and space velocity or the use of novel effective catalysts that able to convert the less reactive-non-desirable compounds at an acceptable rate. Among these, the process parameters play a key role on ultra deep desulfurization as well as dearomatization since removal of the sulfur compounds and reduction of aromatics is achievable by employing modified operating conditions for hydrotreating units with respect to the important independent variables (temperature, pressure and space velocity). However, HDS reactions at high reaction temperature will result in increasing the coke formation on the catalyst, which tends to deactivate the catalyst rapidly, and using low Liquid Hourly Space Velocity (LHSV, h^{-1}) will result in decreasing hydrotreating efficiency. Hence, deep understanding of chemistry involved in removing the sulfur and the influences of the important operating conditions are extremely necessary. Consequently, optimization of the above-mentioned variables is required.

Therefore, the main objective of the present study is to determine the correlation between process variables (reaction temperature, total pressure and space velocity), and the Hydrodesulfurization activity (HDS, %), Hydrodearomatization activity (HAD, %) and Cetane Index (CI) via desulfurization of real gasoil (SRGO). In the present work, a systematical parameteric case study was undertaken using one-variable-at-a-time (OVAT) strategy to investigate if the simple mild hydrotreating technology is adequate for producing diesel fuel meeting the new international specification. However, this paper addresses the preliminary assessment of the optimization of the above-mentioned variables using Response Surface Methodology (RSM) approach.

2.0 MATERIAL AND METHODS

2.1 Catalyst Activation (*In-situ Sulphidation*)

An industrially applied CoMo/ γ-Al$_2$O$_3$ catalyst bearing molybdenum oxide (MoO3) and cobalt oxide (CoO) was purchased from *AKZO Chemie catalyst, Ketjen catalyst, Nieuwendammerkade, 13 1022 AB, Amsterdam the Netherlands*. The hydrotreating catalyst comprised of 11.59 weight % Mo, 7.87 weight % Co and a remainder of alumina (γ-Al$_2$ O$_3$) as support. The catalyst

Extrudates as received in the oxidic form have a blue cylindrical geometry (1.5–2.0 mm × 5.0–8.0 mm). The chemical composition and the metal content of the catalyst measured by quantitative Energy Dispersive Spectroscopy (EDX) were comparable with the technical data sheet of chemical properties of the catalyst as reported in Table 1.

Table 1 Physical properties of Co-Mo/ γ-Al$_2$O$_3$ catalyst obtained from EDX analysis

Catalyst	Co, wt.,%	Mo, wt.,%	Al, wt., %	O, wt., %
CoMo	7.87	11.59	41.83	38.71

The catalyst has been activated (converted from oxide form to the sulfide form) in a fixed bed stainless steel reactor using a proper amount (1.45 gm) of n-Di-ButylSulfide (n-DBS) added to a model hydrocarbon solvent (145 gm n-decane) to give a solution containing 1.0wt % sulfur. Prior to sulphidation (*in-situ*) procedure, the loaded catalyst was dried under hydrogen flow at 120°C temperature and atmospheric pressure for 2 h. Next, the catalyst was wetted using decane as solvent under hydrogen flow at 150 °C and atmospheric pressure for extra 2 h to avoid the presence of dry parts in the catalyst bed, which ultimately decrease the overall activity.

The sulphidation of the catalyst was initiated at low temperature and slowly raised to high temperature in order to prevent the catalyst from being reduced and attained complete sulphidation. Catalyst sulphidation was performed by injecting the sulphiding feed at a starting temperature of 260°C at a rate of 30°C h^{-1} and total pressure of 24 bar. After 1 h, the catalyst bed temperature was further increased to 360°C at a rate of 25 °C h^{-1} and the pressure increased up to 50 bar for 3 h keeping flow of sulfiding mixture. The other sulphidation parameters were as follows: LHSV=2 h^{-1}, H$_2$: HC ratio = 300 vol/vol. After sulphidation , the SRGO feed was introduced to the system by a metric pump. The operating conditions were adjusted to the required activity test conditions for each run.

2.2   Feed and Product Analysis

A gas oil fraction (SRGO) derived from Terenganu and Sarawak oil fields was obtained from PETRONAS-Penapisan-Melaka Sdn. Bhd. (PPMSB) Refinery Complex. The atmospheric SRGO fraction have a boiling range of 235-350°C. Both crude oil and its gas oil were subjected to detailed characterization (see Table 2) in order to assess the quality of the feed based on the bulk physical properties.

Table 2   Properties of PETRONAS crude oil and its gasoil (235-350°C)

Oil Properties		Gasoil Properties	
API°	37.5	Yiel d Vol %	19.3
Total Sulfur ppmwt	1700	Total Sulfur ppmwt	1100
Total N ppmwt	1000	Total N ppmwt	386
Viscosity@ 37.8°C cSt	10.73	Viscosity @ 37.8°C cSt	3.961
Pour Point °C	21	Pour Point °C	3
Vanadium ppm wt.	<1	Vanadium ppm	< 0.1
Nickel ppm wt.	1	Nickel ppm	< 0.1
(K) Factor	12.5	(K) Factor	12.2
Con. Carbon wt%	4.6	Cetane Index	61
Asphaltenes wt%	0.3	Arom. wt%	21
RVP Kpa	12	Flash Point °C	107
Acidity mg KOH/g	0.085	Aniline Pt °C	84.8

The composition of the feed and liquid hydrocarbon products were analyzed for their specific gravity, Cetane index (CI), aromatic carbon by ASTM D-1298 using a glass hydrometer, ASTM D-976 using Calculated Cetane Index formula and UV spectroscopy , respectively . The total nitrogen content in the liquid effluent was measured by Combi-Soufrazote Nitrogen analyzer (VINCCI, France). The total sulfur content of the feed and product liquid hydrocarbons was determined by using sulfur-in-oil analyzer (SLFA-20) manufactured by Horiba, Inc. Horiba sulfur analyzer has a detection range from 0.002 to 5 wt% of sulfur, using the X-Ray Fluorescence (XRF) technique in compliance with the ASTM D4294 method. The ASTM D 976 method used two variable equations to determine Cetane Index (CI) from the diesel's mid-boiling point and density. CI was calculated according to Equation (1).

$$CI = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log B)^2 \tag{1}$$

where

D = density (g/mL) at 15°C determined by Test Method ASTM D 1298

B = mid-boiling temperature (°C) determined by Test Method ASTM D 86 and corrected to standard barometric pressure.

HDS,% and HDA,% activities were calculated and compared in terms of percentage of sulfur removal and aromatics reduction. The hydrodesulphurization (HDS) activity of the catalysts was calculated by Equation (2).

$$HDS, \% = 100 \times (S_{T\text{-feed}} - S_{T\text{-product}})/S_{T\text{-feed}} \tag{2}$$

where

HDS: Hydrodesulphurization activity, %,

$S_{T\text{-feed}}$: Total sulphur content of feed, %,

$S_{T\text{-product}}$: Total sulphur content of product, %,

The percentile reduction in total aromatics was determined and defined as HDA activity and calculated by the Equation (3)

HDA: Hydrodearomatization activity, %

$$HDA, \% = 100 \times (A_{T\text{-feed}} - A_{T\text{-product}})/A_{T\text{-feed}} \tag{3}$$

$A_{T\text{-feed}}$: Total aromatics content of feed, %,

$A_{T\text{-product}}$: Total aromatics content of product, %,

2.3   Hydrotreating Activity Tests

The catalytic activity tests of gas oil fraction were carried-out using a catalytic pilot plant manufactured by GEOMECHANICS, France. The unit has an integral fixed bed down-flow reactor in once-through mode of 19 mm internal diameter and volume of 150 ml and designed to run at high pressure up to 150 bar and 700°C. The reactor was operated in isothermal mode by temperature controller corresponding to four-zone electric furnace jackets. The axial temperature profile of the catalyst bed was measured by four thermocouples located in a thermowell

mounted at the center of the reactor. The loaded catalyst of 75 ml was charged to the middle of the reactor. The catalyst bed was diluted with equal volume of inert material (silicon carbide, 0.5/2.4 mm particle diameter). Liquid reactants feed were injected with a high-pressure metering pump. Prior to the activity test, the unit underwent leakage test. The unit was pressurized under nitrogen flow up to 90 bar and was maintained for 120 min to check for leakage. After confirming that there was no leak (less than 0.1 MPa/h), the unit was depressurized (pressure was released). The operating conditions used for the hydrotreating tests were carefully chosen based on the conditions often used in literature and commonly employed in the industrial site (11-13). Table 3 tabulated the hydrotreating operation conditions used for the gas oil. Hydrotreated product samples were collected every hour for each condition for 240 min time-on-stream (TOS).

Table 3 Operating conditions used for Hydrotreating activity tests of SRGO

Operating variables	Value
Temperature,°C	200, 300, 330, 350, and 370
Pressure, bar	20, 30, 40 and 50
LHSV, hr-1	1.0, 2.0, 3.0 and 4.7
TOS, min	0, 60, 120, 180 and 240

3.0 RESULTS AND DISCUSSION

3.1 Effect of Process Variables

The influence of operating conditions (temperature, pressure, and LHSV) for the prepared sulphided catalysts (CoMo-S) on HDS, HDA activities and CI were investigated. Results of the activity tests obtained with real total sulfur and aromatics compounds demonstrated that both saturation of aromatics and elimination of sulfur took place, but to different extent. The catalytic HDS and HDA activity tests of CoMo-S/γ-Al$_2$O$_3$ catalysts were optimized based on the one-variable-at-a-time (OVAT) approach. However, the "one-variable-at-a-time" technique of optimization has some major flaws because the experimental space is not explored very well and the solution may be missed if there are interactions among the variables [14]. Despite that, the experimental data provided some interesting information about the influence of each process variable, as described

in the following section. The following section discusses the HDS reactivity and HDA activity of the catalyst and the CI of the liquid product as a function of temperature, pressure, LHSV and TOS.

3.1.1   Effect of Temperature

The employed (CoMo-S/γ-Al$_2$O$_3$) catalyst showed expected responses to temperature with higher HDS activity at higher temperatures and good stability over the time course of the reactions. Figure 1 shows the variation of HDS activities of catalyst for sulfur removal at different temperatures as a function of pressure, while the other variables remained constant. HDS activity of the employed catalyst increased from about 39.9 to 80.9% when the temperature was

increased from 300 to 370°C (LHSV =2.0 hr^{-1}, P= 50 bar and H$_2$: HC=100%$\dfrac{\text{vol}}{\text{vol}}$).

The extents of HDS activity were 39.9%, 57.8%, 76.9% and 80.9% when the temperature were 300 °C, 330 °C, 350 °C and 370°C, respectively. However, deep HDS desulfurization to <200 ppm sulfur was not achieved even at a temperature as high as 370 °C. It could be that these sulfur compounds such benzothiophenes and DBTs (and to some degree 4-MDBT) were mainly desulfurized via the direct desulfurization pathway (DDS), for which the CoMo-S/γ-Al$_2$O$_3$ catalyst had the highest HDS activity.
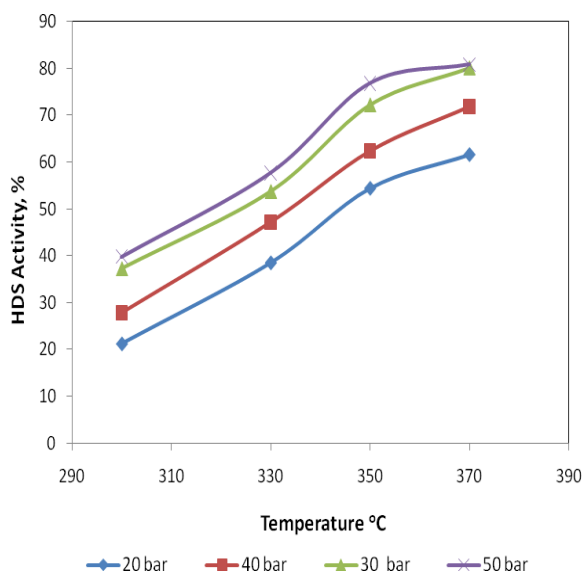
Figure 1 Effect of temperature as a function of pressure on the HDS activity (**LHSV** = 2.0 h⁻¹ H₂:

$$HC = 100\% \frac{vol}{vol}$$

The above results can be explained on the basis of the characteristics of the feed; the sulfur, basic nitrogen compounds and total aromatics content of the feed (see Table 2). However, the **SRGO** cut derived from Terengganu and Sarawak oil fields has high organic total nitrogen and total aromatics content. However, these nitrogen compounds and polyaromatic were adsorbed competitively with the sulfur species on the active catalytic sites at temperatures where the hydrodegnation step was proposed to be rate limiting [15- 18].

According to Van Looji *et al.*[19] and Knudsen *et al.*[20] who reported that low concentrations of basic nitrogen compounds present in the feedstock played a major role in hindering deep HDS of diesel feeds and strongly inhibited the HDS reactions. Moreover, the operating conditions used in sulphidation procedure offered a conventional type of the (**Co-Mo-S**) I model. However, this typical Type I model formed at lower temperatures was probably chemically bound with the support as evident by the presence of the Al-O-Mo entities [21], which is believed difficult to be converted to the sulphide form into the active phase below 600°C [22]. However, the supported catalyst linkages in **Co–Mo–S I** model probably

hindered the reactant molecules from approaching the active phase sites of the catalyst even at higher temperatures. As can be noticed from Figure 1, the HDS activity slightly improved (76.87 to 80.9%) as the temperature increased from 350°C to 370°C. Moreover, the thermodynamic equilibrium reached at higher reaction rates at higher temperature. A combination of all the above factors could have caused low HDS reactivity of the catalyst at high temperatures.

Farage *et al*. [23] and co-workers reported that at low temperatures (T < 340°C), the hydrogenation (HYD) reaction path way is the dominate reaction route, while at higher temperatures (e.g. 370°C), the DDS reaction path way becomes significant. However, the HYD reactions path way enhanced up to maximum as the temperature was increased from 300 °C to 370 °C and becomes un-favored as the temperature raised higher than 370°C, which could attributed to the thermodynamic equilibrium limitation of the hydrogenation of the least alkyl substituted compounds (4,6-DMDB to 4,6-dimethyl tetrahydrodibenzothiophene). Whitehurst *et al*.[24] concluded that the favored approach of sulfur removal from refractory alkyl substituted sulfur compounds was about 90% by the hydrogenation (HYD) pathway at 300°C while at 370 °C the preferred route was about 90% by the direct desulfurization (DDS) route.

3.1.2 *Effect of Pressure*

The effect of total pressure on HDS activity as a function of reaction temperature at 2.0 h^{-1} LHSV and 100 vol/vol H$_2$: HC is illustrated in Figure 2. The results show that HDS activity was slightly enhanced with pressure on a TOS of 240 min. By increasing the pressure from 20 bar to 50 bar, the HDS activity increased from 61% to 80.5% at temperature of 370°C and from 21.2% to 39.8% at 300°C. Furthermore, it is worthy to mention that increasing pressure from 40 to 50 bar exhibited no significant improvement in the HDS activity as the HDS activity remained stable at this operating pressure (50 bar) (see Figure 2). It seems that high pressures mainly served to saturate the catalyst and any increase in the pressure will slightly affect the HDS activity [25]. Moreover, the conversion also decreased with increasing reaction rate between hydrogen and aromatics (alkyl-substituted compounds) and nitrogen-containing organic compounds constituents of the feedstock [26].
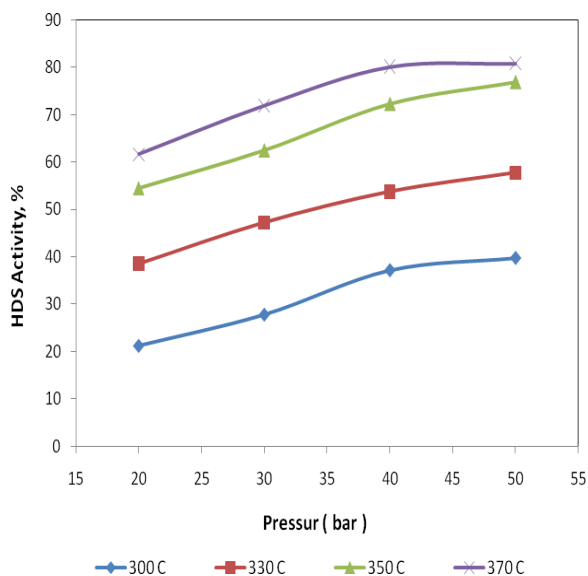
Figure 2 Effect of pressure as a function of temperature on HDS activity (LHSV = 2.0 h^{-1} H_2:
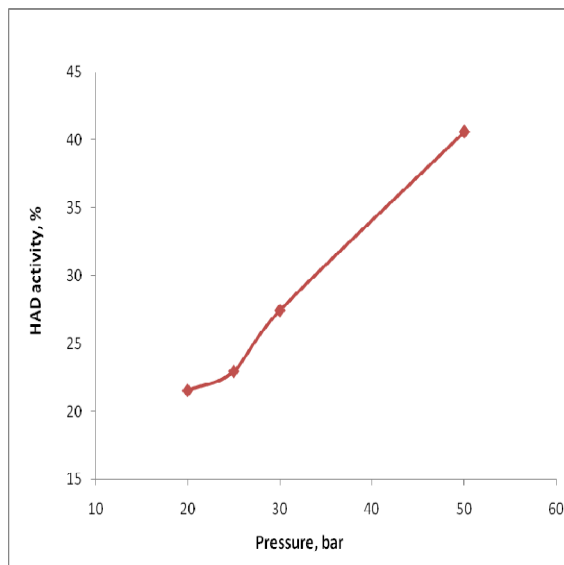
$$HC = 100\% \frac{vol}{vol}$$

Landau MV *et al.* [27] reported that the hydrogen pressure has a much smaller impact on the effectiveness of the HDS activity even if the increase of pressure reached up to 80-100 bar, it will give a moderate decrease from 200 ppmwt to 60 ppmwt by weight in residual sulfur. One possible reason for this phenomenon could be extra reduction of the catalyst active Co-Mo-S sites on the surface of catalyst at high pressures, which tends to change the sulfidation phase and decrease the concentration of active sites responsible for the direct desulfurization. This might explain the low effect of hydrogen pressure on the HDS activity. As demonstrated in Figure 1 and 2, where the HDS activity was exhibited as a function of temperature and pressure, it can be noticed that the effect on the HDS activity for temperature is more pronounced than pressure. Many researchers and co-workers reported that for HDS of distillate fuels at high temperature and low pressure, CoMo catalysts are more favorable by/ via the direct extraction pathway. Contrary to high operating pressure and low reaction temperature conditions, CoMo catalyst show lower HDS activity via hydrogenation pathway [27].

Figure 3 displays that Hydrodearomatization reactivity (HDA) of the catalyst increased slightly with temperature (200-350℃) at P=25 bar and LHSV of 2.0 h^{-1} from about 18% to 22%. The Hydrodearomatization activity peak was at 350 ℃. According to the proposed mechanism of HDS of alkyl DBTs compounds, two successive subsequent steps occurred; the hydrogenation of one of the aromatic rings (HYD reactions) in the first step, followed by sulfur removal (HYG reactions) in the second step. The hydrogenation pathway was most likely less effective in the presence of alkyl compounds and organic nitrogen compounds that tend to poison the hydrogenation sites of the catalysts at low pressure thus resulted in low HDA-HDS activities [28].

On the other hand, increasing pressure induces the saturation of aromatics even when CoMo catalyst is used which usually employed when sulfur removal is the main target. Figure 4 shows the effect of pressure on HDA activity at 350℃. By raising the pressure from 20 to 50 bar, the rate of HDA activity increased from 21.5% to 40.6% (LHSV of 4.7 h^{-1} and 100 vol/vol H_2:HC). Hydrodearomatization activity improved more significantly with pressure rather than temperature as shown in Figures 3 and 4. The explanation of the different effect of pressure on HDS and HDA activities can be explained on basis of the pressure dependency of the catalyst. However, the direct desulfurization pathway (DDS) via hydorgenolysis activity for which the CoMo-S catalyst owning the highest activity, where as that DBT is mainly might be being desulfurized via this pathway, always show a relatively low hydrogen pressure dependency [27]. In addition, removal of sulfur via the hydrogenation route suffers from a thermodynamic equilibrium limitation in the hydrogenation step, and the apparent activation energy for HDS via the hydrogenation route is therefore, relatively low.
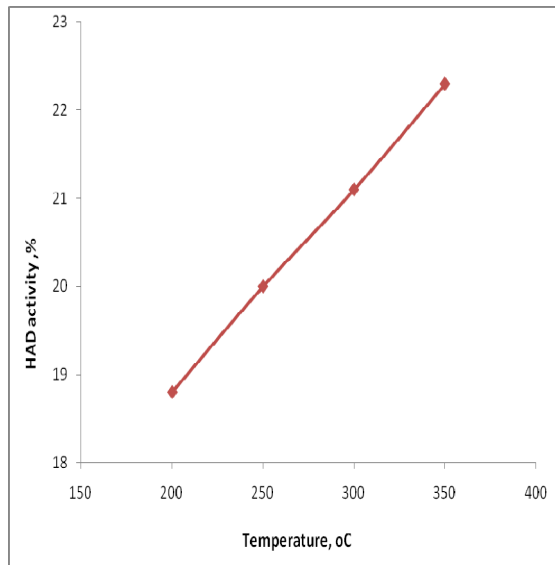
Figure 3 Effect of temperature (200,250,300,350°C) on the HDA activity (P=25 bar, LHSV = 2.7 h^{-1} H2: HC = 100 vol/vol)

Figure 4 Effect of pressure (20, 25, 30, 50 bar) on HAD activity at (T= 370 °C, LHSV = 2.7 h^{-1} H$_2$: HC = 100 vol/vol)

As shown in Figure 5, Cetane Index (CI) enhanced more pronouncedly as the degree of aromatics saturation improved at high pressure; however, loss of aromatics up to 40.6 % over CoMo-S catalyst accompanied by a considerable increase in CI. Since, CI is a calculated number based on the ASTM boiling point curve, deep aromatic saturation up to 40.6% leads to improvement of CI by 1-3 degrees. This can be referred to the fact that Cetane Index (CI) is not characterized to directly depend on sulfur. Reduction of aromatics and polyaromatics in the hydrotreated cut enhanced the CI of the diesel fuel since there is a boiling point shift when aromatics are saturated [29].
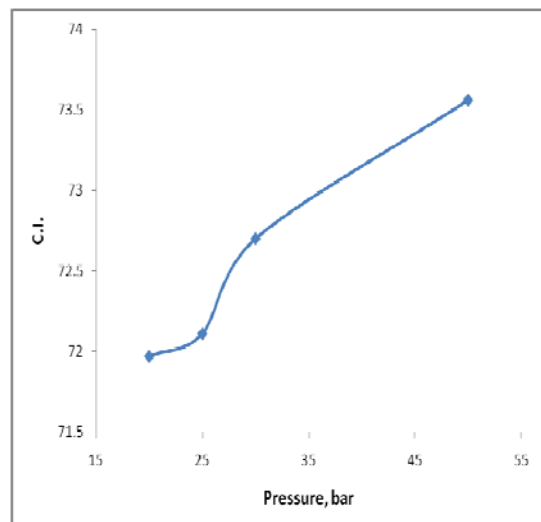

Figure 5   Effect of pressure (20, 25, 30, 50) on CI at (T= 350 bar, LHSV = 2.7 h⁻¹ H₂: HC = 100 vol/vol)

3.1.3 Influence of Space Velocity

Liquid hourly space velocity (LHSV) and the catalyst bed volume are interacted parameters that affect both the HDS/HDA activity and the process high throughput [30]. The available LHSV range can be derived from the above-mentioned parameters since the volume of the catalyst bed for the process will be constant, the space velocity will vary directly with the feed rate from the pump. However, the maximum LHSV of the feed is limited by the maximum accessibility of the reactor volume and maximum hydrogen flow at 75 ml catalysts

loading, which is 4.7 h^{-1} gasoil theoretically. The selected minimum LHSV value (1 h^{-1}) was slightly under that of the value used in the industry (2 h^{-1}). This space velocity range was divided into four parts, and the tests were performed at 1, 2, 3 and at 4.7 h^{-1} values. The HDS activity and HDA activity values obtained at different space velocities are shown in Figure 6.
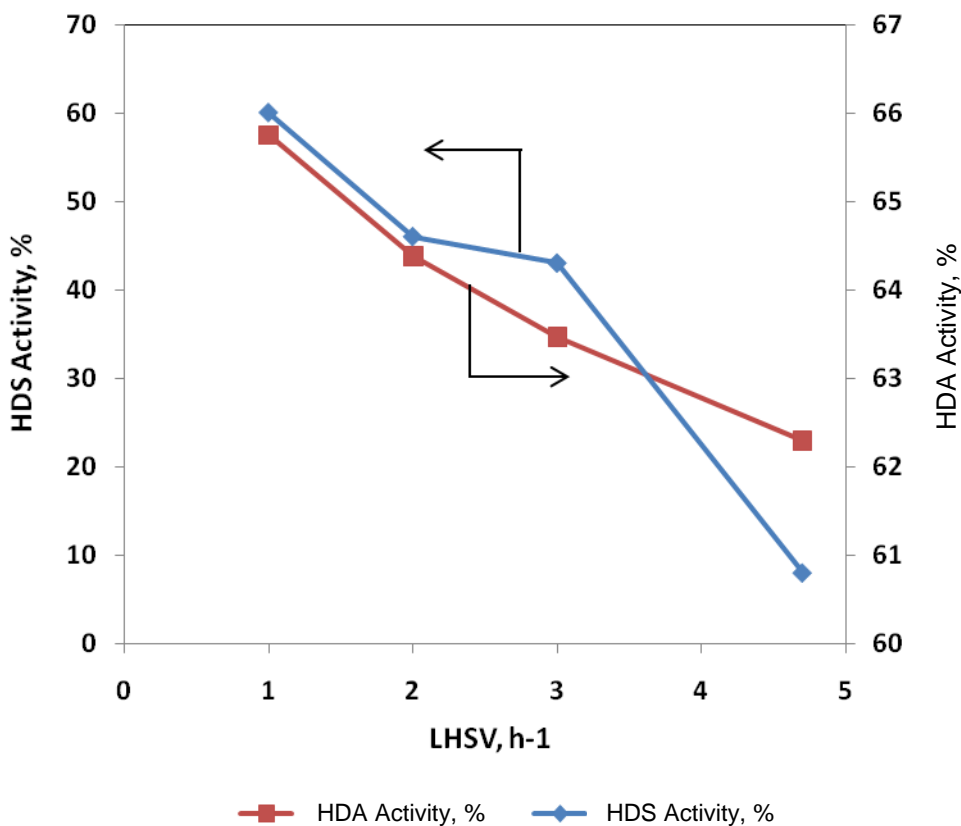
Figure 6 Effect of LHSV on HDS and HDA activities at (T= 350 °C, P= 25 bar and H$_2$: HC = 100 vol/vol)

It has been found that changes in space velocity could have significant effect on the HDS% activity as well as HDA activity to a large extent. The HDS/HDA activities improved as the space velocity decreased. Indeed, as shown in Figure 6, reducing liquid hourly space velocity increased the contact time between reactants and catalyst, thus improved the HDS/HDA activity via direct and indirect desulfurization pathways mechanism. However, this can be attributed to the fact

that lower space velocity tends to facilitate the sulfur and aromatics compounds to access the active sites. Thus, HDS/HDA activities improved via the two pathways. Frost and Cottingham [31] reported that decrease in the liquid hourly space velocity will usually bring about an increase in the efficiency (or extent) of the Hydrodesulfurization (HDS) activity.

Since higher hydrogenation activity required for the saturation of aromatic compounds was favorably enhanced by the decrease of space velocity, the HDA activity improved up to 57.4% at minimum space velocity of $1h^{-1}$. Contrary, higher space velocity led to suppressing the HDA activity of the catalyst and reduced the concentration of total aromatics (low HDA activity). The decrease in HDA reactivity may refer to the low contact time between aromatics hydrocarbons and the hydrogenation sites of the catalyst. In addition, the presence of nitrogen and sulfur compounds which competitively approached the catalytic active sites tended to poison the catalyst and led to reduce the hydrogenation activity of the catalyst [32- 34].
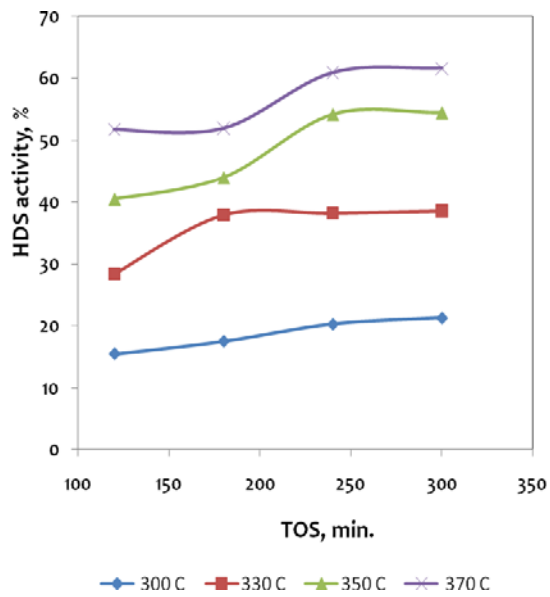
3.1.4 Effect of TOS

The results for different HDS activities against TOS at different temperatures and pressures for CoMo-S/ γ-Al$_2$O$_3$ sulphided catalysts are shown in Figures 7 and 8 respectively. As expected, the CoMo-S catalyst shows much lower activity but more stable for the HDS at low temperatures. Figure 7 shows that all HDS activities were marginally stable with TOS particularly at 300-370°C reaction temperatures. However, the decline in activity for different temperatures against time-on-stream is very similar, which indicates that the catalytic sites remain constant or vary similar with time for all catalytic activities.
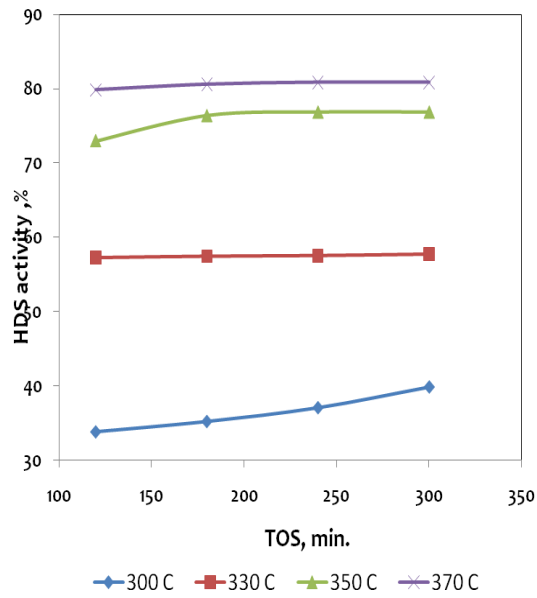
Figure 7 Effect of TOS as a function of temperature on HDS activity

Figure 8 Effect of TOS on HDS activity as a function of pressure

On contrary, and expectedly, the HDS activity was unstable at low pressure as a function of TOS (see Figure 8); it has been observed a more or less similar fluctuation/deactivation trend for the low operating pressures at 20 bar and 30 bar. However, they show different initial activities that slowly decrease at 20 bar and slowly increase at 30 bar until about 240 min TOS. On the other hand, for high pressure (40 bar), the HDS activity displayed high initial activity that slowly increased until about 240 min TOS. After this time, a stationary state was reached. This is in good agreement with the finding by Ho [35] who referred this phenonena to numerous reasons related to the hydrogen supply to the catalyst surface where hydrogen is activated and dissociated. The active sites of the catalyst surface may be famished of adsorbed hydrogen due to low mass transfer / or slow solubility of hydrogen. The Hydrodenitrogenation activity rate (HDN %) has a signifcant role in this phenomenon as being responsive to H_2 pressure. In fact, nitrogen compounds block almost all active sites that are accessible for HDS. Moreover, the thermodynamic equilibrium at high temperature may limit HDS rates.

The thermodynamic equilibrium was probably attained after certain TOS (180 min) at pressure of 40 and 50 bar at temperatures of 350, 370°C, respectively rather than at low pressure of 20, 30 bar and high temperature 370°C. In contrast the increment in the HDS activity is evident that the catalytic activity improved as the temperature and pressure increased since the conversion reached its equilibrium and remained stable after 240 min TOS at 370°C, 50 bar, 2.0 hr^{-1} and 100 vol/vol H_2:HC ratio. Chen *et al*. [36] concluded that at high temperature (above 370 C), the hydrogenation/dehydrogenation equilibrium effect became considerable and the kinetics of HDS of each individual sulfur species was no longer of pseudo-first order.

4.0 CONCLUSION

Three Hydrotreating process variables namely, temperature, pressure and space velocity were altered and their effects on the performance of the catalyst and the quality of products were studied. The results indicate that in general the quality of product improved (total sulfur in the product passed through a minimum) as the space velocity decreased or reaction temperature increased. Hydrodearomatization activity (HDA) was significantly more affected with

pressure compared to Hydrodesulfurization (HDS). The results show that the LHSV has to be reduced to 2 and the reactor temperature as well as the total pressure has to be increased to 370 ℃ and 40 bar respectively to reach the desired 200 ppm sulfur and reduction of aromatics up to 40.6 % in the liquid gasoil product. However, mild hydrotreating with the above-mentioned conditions is not a satisfactory solution that enables local and international refineries to meet the new specifications. Future specifications cannot be met except with a dual-stage reactor operating at low pressure or deep high-pressure hydrotreater.

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