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Gasoil Hydro-desulfurization using Catalyst synthesized from Iraqi Kaolin Clay: Optimization with Response Surface Methodology (RSM)

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K E Y W O R D S

Hydro-desulfurization; Kaolin clays; Experimental Design; Gasoil.

A B S T R A C T

This search aim to study the feasibility of hydro-desulfurization (HDS) of gas oil in fixed bed reactor by using economic support catalyst alumina meta kaolin (AMK) under various operating condition, i.e. Temp. (240−320 ◦C), Press. (3–12 bar), WHSV (2–6 h^{-1}) at H_2/HC ratio (50 vol./vol.). The support catalyst was prepared from Iraq kaolin and characterization by using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and Fourier transform infrared (FTIR) spectroscopy. Experimental design was used to determine which parameter (e.g. temperature, pressure and WHSV) has a greater influence on the obtained HDS and the optimum condition of process. The result shows that optimum condition given (Temp. 300 C, Press. 12 bar and WHSV 2 h^{-1}) and all parameter have significant implication in the process.

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1. INTRODUCTION

Deep sulfur removal issues are becoming more serious in refineries due to increased sulfur content in crude oil and lowered regulatory sulfur limits in petroleum products [1]. Combustion of organic sulfur compounds produce harmful and hazardous sulfur oxides, from fuel oils [2]. Heavy hydro-carbons derived from fossil fuel such as bitumen, oil sand and heavy oil contain very high amounts of

sulfur. There are many desulfurization techniques, i.e. bio-desulfurization (BDS), hydro-desulfurization (HDS), extractive desulfurization and oxidative desulfurization (ODS), it is being studied worldwide to produce ultraclean petroleum fuels. Hydro-desulfurization (HDS) is the most widely operations for removing sulfur from heavy and light fuel in refineries and it usually includes treatment by catalyst to convert hydrogen (H_2) to different sulfur (S) compounds to hydrogen sulfide such as (H_2S). [3-4].

Kabe et al., [5] investigated HDS of heavy gas oil (Sulfur Concentration 4000 ppm) over Co-Mo/Al_2O_3 and Co/Al_2O_3 catalysts in a Fixed Bed reactor at 300 ºC and pressure 30 MPa. The objective is the influence of catalysts to remove dibenzothiophene from heavy gas oil. Results indicated that HDS% is 50% and 80% respectively and show increase the HDS% with increasing temperature. Choi et al., [6] studied HDS of gas oil over CoMo supported in alumina-silica and alumina-zeolite and NiMo supported in alumina-silica and alumina-zeolite catalysts through two-stage or layer catalyst bed at 340 ºC and 25 MPa through HDS (90%). Vishwakarm [7] used the impregnation and sonochemical methods to prepare catalysts with W (7 – 13) wt % and Co (1 – 3) wt % loadings based on γ- Al_2O_3 supported for (HDS) of middle distillates by trickle-bed reactor. The performance tests with impregnated catalysts indicated a maximum in activity for HDS reaction. Sulfur conversions was (93.0%) at 360 °C and 10.3 bar for (3Co - 10W)/γ-Al_2O_3. The reaction kinetics for HDS was best fitted with a pseudo-first order power law model with a reasonable accuracy ($0.90 < R^2 < 0.95$). Mapiour et al., [8] investigated The effects of H_2 purity, pressure, gas/oil ratio, temperature, and LHSV on HDS activities of heavy gas oil were studied in a micro-trickle bed reactor using a commercial NiMo/Al_2O_3 catalyst. The author studied the effect of space velocity in range of (0.65–2 h^{-1}) and temperature of (360 - 400 °C) in a separate set of experiments. Results showed that HDS% is 96.6% and it was observed that the HDS efficiency was not significantly affected by H_2 purity, pressure, or ratio of H_2/ HC. An increase in space velocity led to a decrease in the efficiency of hydrodesulphurization while an increase in temperature led to an increase in hydrodesulphurization the maximum activity at around 360 °C.

The kinetic fit of the data to the pseudo-first-order power law model suggested that inferences regarding the responses of hydro treatment efficiency to the variable hydrogen pressure could be equally drawn from the inlet or outlet of the hydrogen partial pressure. To obtain a better HDS operation, studies have been triggered on the preparation of most efficient desulfurization catalysts for petroleum fuels. The origin of the virtually use of alumina as a support has to be attributed to its outstanding textural and property of mechanical and alumina as a support is relatively low cost. [9]. Kaolin ($Al_2Si_2O_5(OH)_4.2H_2O$) is shown in Figure 1 belonging to phyllo-silicates and ideally consisting of continuous sheets of octahedral and tetrahedral. All tetrahedral contains of a silica atom coordinated into four (O) atoms and bonds to the neighboring tetrahedron by sharing three angles (basic oxygen atoms) to form an infinite two-dimensional "hexagon" mash pattern parallel to (x & y axes). Each octahedral is formed either from an atom or vacant atom and is coordinated by six atoms (i.e. oxygen and hydroxyl) and is associated with octahedral dull by sharing edges. The octahedral with common edges form sheets of hexagonal or pseudo-hexagonal symmetry and display different topologies contingent on the octahedral hydroxyl location [10-11].

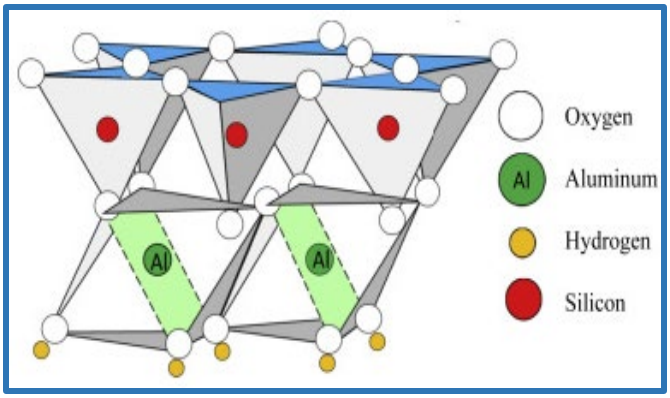


Figure 1: Crystal structure of kaolin [12]

The aim of this study is to prepare and characterize economic support catalyst then test it to examine hydrodesulphurization reactions beneath processing condition in packed bed reactor and investigate the efficiency of parameters for the catalysts preparation (Temperature, pressure and WHSV). It was necessary to establish a detailed estimation the compositional parameter and appropriate correlation between the obtained HDS transformation and the properties of the prepare catalyst. The experiment was designed to determine the optimum condition upon the hydrodesulphurization result obtained from the variables and their interactions. This model was obtained by using the residual analysis and their response of dispersion, and the effect of parameters such as temperature, pressure and WHSV with respect the support prepared, and the effect of metal loading ratio on hydrodesulphurization efficiency. The experiment was designed according to Response Surface Methodology (RSM) based on the hydrodesulphurization results process. The mathematical model for catalyst determined the most favorable and optimal conditions to prepare for the highest hydrodesulphurization conversion. Study of HDS reaction kinetic for gas oil was made using the pseudo-first order to estimate the activated energy of reaction and related parameter.

2. USED MATERIALS AND PROCEDURES

I. Used material

Kaolin clay (K) was received from Iraqi mining & geological commission, aluminum oxide (99% γ/Al_2O_3, with M. wt. = 101.96), Ammonium Chloride (99% NH_4Cl with M. wt. = 53.3) and sodium hydroxide (95% NaOH with M. wt. = 39.99) were supplied by BDH England. Iraqi gasoil was produced and supplied by Al-Daura Refinery (Midland Refinery Company) with sulfur content of 12600 ppm.

II. Catalyst Characterization

Scanning electron microscopy analysis (SEM) showed that morphology of alumina meta kaolin (AMK) and EDAX analysis (energy dispersive x-ray) for (kaolin and AMK) were performed with instrument [Type: VEGA (3) LM, Origin- Germany]. The Fourier-Transform Infrared spectroscopy was used to study chemical active bond of (kaolin and AMK) prepared, [Type: Bruker-Tensor (27), Origin-Germany]. Measurement of sulfur content was obtained using the (EDXRF) method energy dispersive x-ray fluorescence. This analyzer is proper for total sulfur revelation with a lower reservation limit of 1ppm. The measurements were conducted in Al-Daura Refinery (Midland Refinery Company) / Oil Ministry, Baghdad-Iraq.

III. Experimental setup

The experimental setup involves of three sections: (1) the feeding sections, (2) the reactor sections, and (3) the gas and liquid products separation sections. The feeding sections has two feeding modules, the liquid supplier module and gas supplier module. The gas supplier module offers to Hydro-treating (HDT) system pressure hydrogen gas essential for HDS% reactions. The H_2 gas was feed to the reactors over a preheated line with pressure. The feed equipping module includes a feed reservoir and dozen pumps. The 5 liters feed reservoir is made from stainless steel, which operate under pressure, and supplied with a pump that introduce the feed inside HDT reactors.

A flow-meter was connected to the pump to control the flow rate of the feedstock. The reactor is a stainless steel tube with an ID of 12.5 mm and a length of 50 cm heated via an electrical oven. It is a fixed-bed reactor with maximum pressure 12 bar, and temperature 320 °C, respectively, supplied with 30 g AMK. The system is supplied four temperature sensors; the first one is in the HDT reactor, the furnace, the reactor inlet to measure the temperature of the liquid, and the fourth one is to measure the temperature of hydrogen prior to entering the reactor. The product section contains a chiller, high-pressure gas and liquid separator and the liquid output buffer reservoir. The reactor exit feeds to the chiller at high pressure to separate the liquid and gas. Finally, the liquid is cumulative in a buffer reservoir. The HDS system schematic diagram and photographically are shown in Figure 2(a & b).

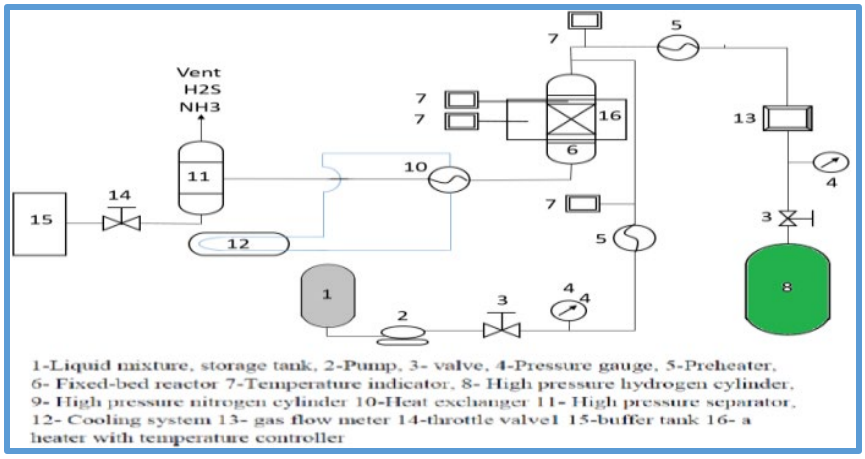


Figure 2(a): Schematic of the HDS setup

Figure 2(b): Experimental setup of fixed bed reactor.

IV. Procedure of HDS Process

1- The reactor was loaded with catalysts.
2- The heating period require 1 hour for hydrogen gas used in this HDT system.
3- The liquid feed was injected at the regulated flow rate.
4- The reaction temperature was increased to the desired value because the exothermic reaction and the heating element in the oven.
5- The product of reaction was liquefied and taken for investigation.
6- Range of operating conditions is listed in Table 1.
7- The HDS efficiency was calculate from equation 1 [13].

$$Xs\% = \frac{s(f)-s(p)}{s(f)} * 100 \quad \ldots (1)$$

Table (1): HDS range of operating conditions

No	Parameter	Operating conditions
1	Temperature, °C	(240-320)
2	WHSV, h^{-1}	(2-6)
3	Pressure, bar	(3-12)
4	(H_2/HC)	50 ratio (vol./vol.)

V. Experimental Design

The statistical method was applied using Response Surface Methodology (RSM) in order to determine the effect of significant parameter on HDS%. Therefore, improvements of the applied variables are adopted during the elimination operation [14]. Optimal design is a particular class of experimental refinements with respect of many statistical criteria. For the determination of statistical value, optimal design deals with parameterization without bias and with minimal variability.

The non-optimal design requires a greater number of experimental operations performed to estimate the parameters with the same accuracy as the optimum condition. In practice, optimal trials reduced trial costs [15-16]. Finally, in order to prepare a mathematical model to evaluate the actual experimental results, an experimental design procedure was used in this paper. In the present work, a 95% confidence interval was used to assess the significance of the involved parameter [17]. Thus the (P-value) is 5%; the level of interest in F-tests (meaning; Fisher-) is considered to be the most important for interpreting the investigated effects [18]. Finally, prepared experiments were performed according to this design at three parameters.

Reaction effects were assessed by analysis of variance (ANOVA) when converting the HDS onto the prepared catalyst from which the quantitative response to the experiments was provided. These responses were then analyzed with Design-Expert software (version 7.0.0).

3. RESULTS AND DISCUSSION

I. Scanning Electron Microscopy

SEM analyzes were performed to find the morphology of the support catalyst prepare (AMK) [19]. Figure 3 presents and indicates the superposition of alumina with meta-kaolin and the image shows that several objects of arrangement form the surface of the MK samples after cementation.

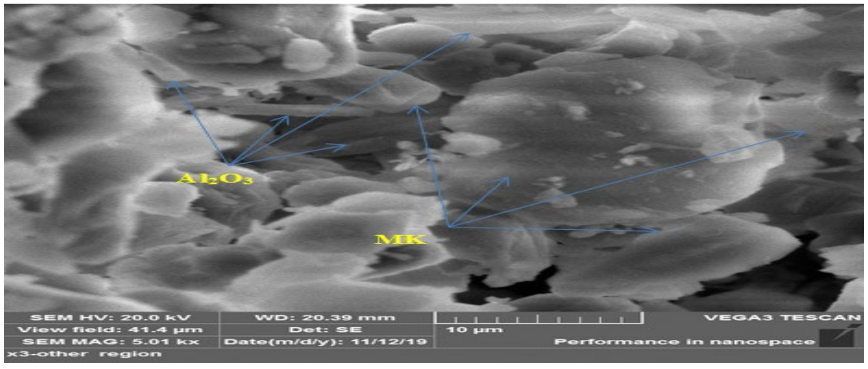
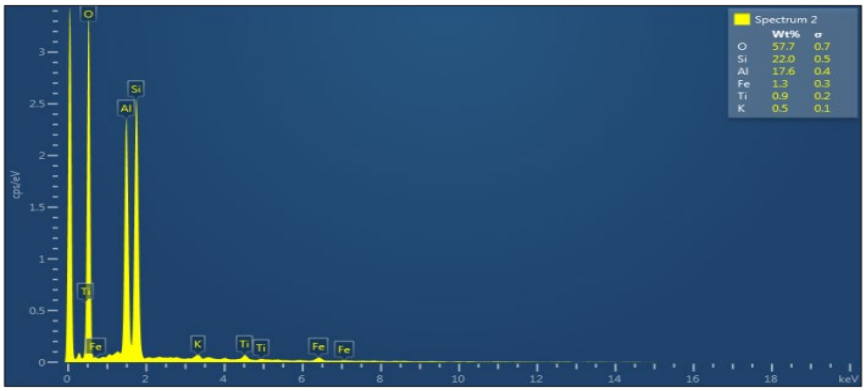


Figure 3: SEM image of the AMK

II. Energy Dispersive X-Ray Analysis (EDAX)

This technique used to identify the elemental composition of materials. Figure 4 show the kaolin composition and catalyst after cementation by alumina.



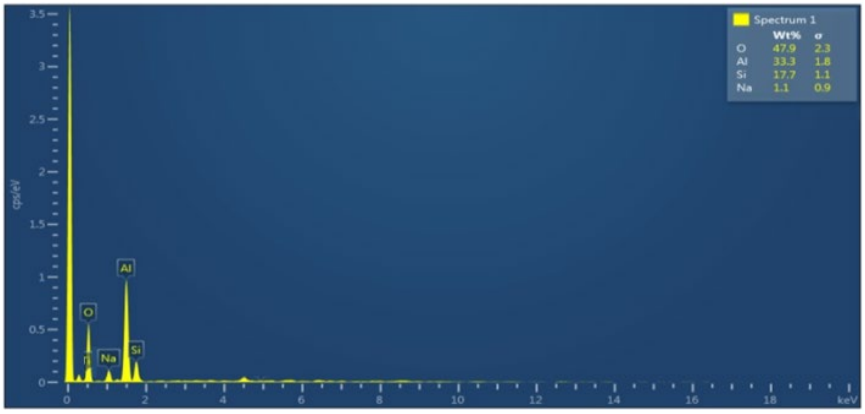


Figure 4: Typical EDAX spectrum for Kaolin and AMK.

III. Fourier-Transform Infrared spectroscopy

FTIR spectra of kaolin (K) and alumina meta-kaolin (AMK) supporter are shown in Figure 5. Figure 5 (a) shows spectrum for (K) showed bonds at (3692, 3650 and 3630 cm^{-1}), consistent to the OH- stretching vibration. H-O-H stretching was also found at (1290 cm^{-1}) in kaolin. Bands at (1052, 1022 and 997 cm^{-1}) were given to Si-O bond in the SiO_4 molecule. The other bands at (634 and 710 cm^{-1}) were attributed to Al-O vibrations where the Al is in octahedral coordination; the obtained results are in agreement with the publication of Granizo et al., [20]. Figure 5 (b) shows the stronger broadening band at (634 cm^{-1}) refers to Al-O after cementing the MK by gamma alumina to prepare AMK and lower frequency at (1052 cm^{-1}), which was the amorphous SiO_2 representing the Si-O stretching vibration. The obtained results are in agreement with the publication of Liew et al., [21].

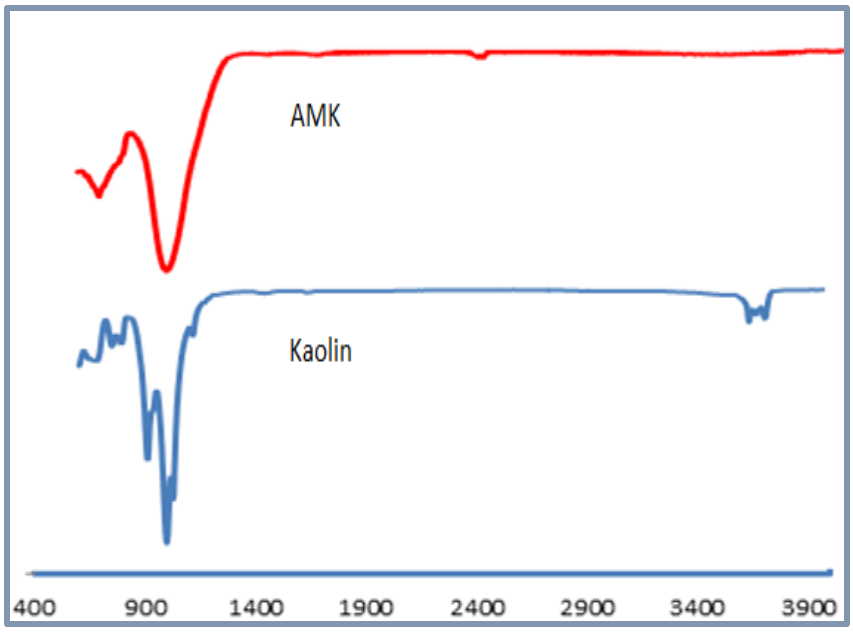


Figure 5: FTIR spectra for (a) kaolin (blue spectrum), (b) AMK (red spectrum)

4. Response Surface Methodology Analysis for HDS Result (RSM)

I. Mathematical Model

The results obtained from the HDS experiments are shown in Table 2 and analyzed using the Design Expert to estimate the mathematical expression of the HDS% as a function of operating condition to obtain regression equations responses as demonstrated in equation 2. Experimental values and predicted values obtained from model are displayed in Figure 6. The prediction error helped in evaluating the validity of the generated regression equations. The linear correlation between actual

form and prediction was obtained. For validation of linear response surface model in the form of analysis of variance (ANOVA), the experimental values of the responses were compared with the predicted value and the predictions error. The linear relationship plots drawn between the predicted vs. experimental values and the displayed values of R^2 appear in Table 3.

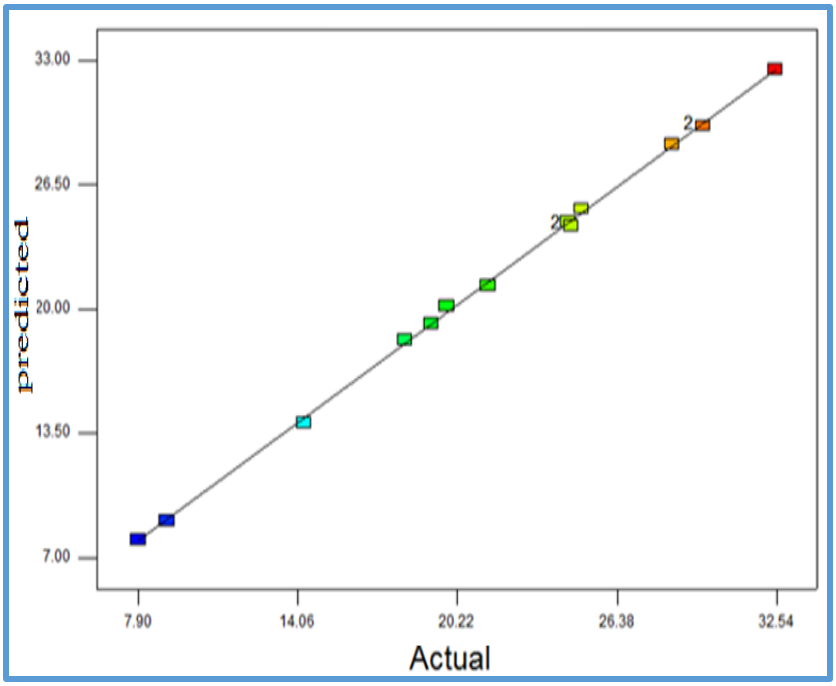


Figure 6: Show predicted vs. Actual plots for HDS%

$$HDS\% = 16.89 + 10.99 * A + 8.72 * B - 8.93 * C - 3.92 * A^2 - 6.14 * B^2 + 0.64 * C^2 - 2.69 * A^3 + 1.61 * B^3 + 2.28 * C^3 \ldots . (2)$$

Table (2): Data sheet of result of experimental work

Temp.	Press.	WHSV	HDS%
240	7	3	7.9
260	7	3	14.3
280	7	3	19.8
300	7	3	24.6
320	7	3	24.5
300	3	3	9
300	5	3	18.2
300	7	3	24.6
300	10	3	28.5
300	12	3	29.7
300	12	2	32.5
300	12	3	29.7
300	12	4	25
300	12	5	21.4
300	12	6	19.2

Table (3): The R^2 values of linear, quadratic and cubic models of HDS% process.

	linear	Quadratic	Cubic
R^2	0.909	0.993	0.999
Adj-R^2	0.885	0.989	0.998
Pred-R^2	0.8121	0.933	0.937

II. Response Surface Analysis for HDS% Process

Figure 7 shows the effects of two factors in response on (HDS%) when the another factors are held at the central level. Figure 7 (a) shows the effect of pressure and temperature on (HDS%), when the space velocity at 3 h^{-1} and confirms that all the relationships among the variables were non-linear, and this was observed upon increasing temperature and pressure , the HDS efficiency increases with increasing factors until riches 300 C^o. The maximum HDS% was revealed under 12 bar pressure. Figure 7 (b) shows the effect of temperature and WHSV on (HDS%), when the pressure at 7 bar. Figure 7 (c) shows that when pressure increases, the HDS% also increases with decreasing the WHSV, which may indicate the reduced contact time between aromatics hydrocarbons and the hydrogenation sites of the catalyst.

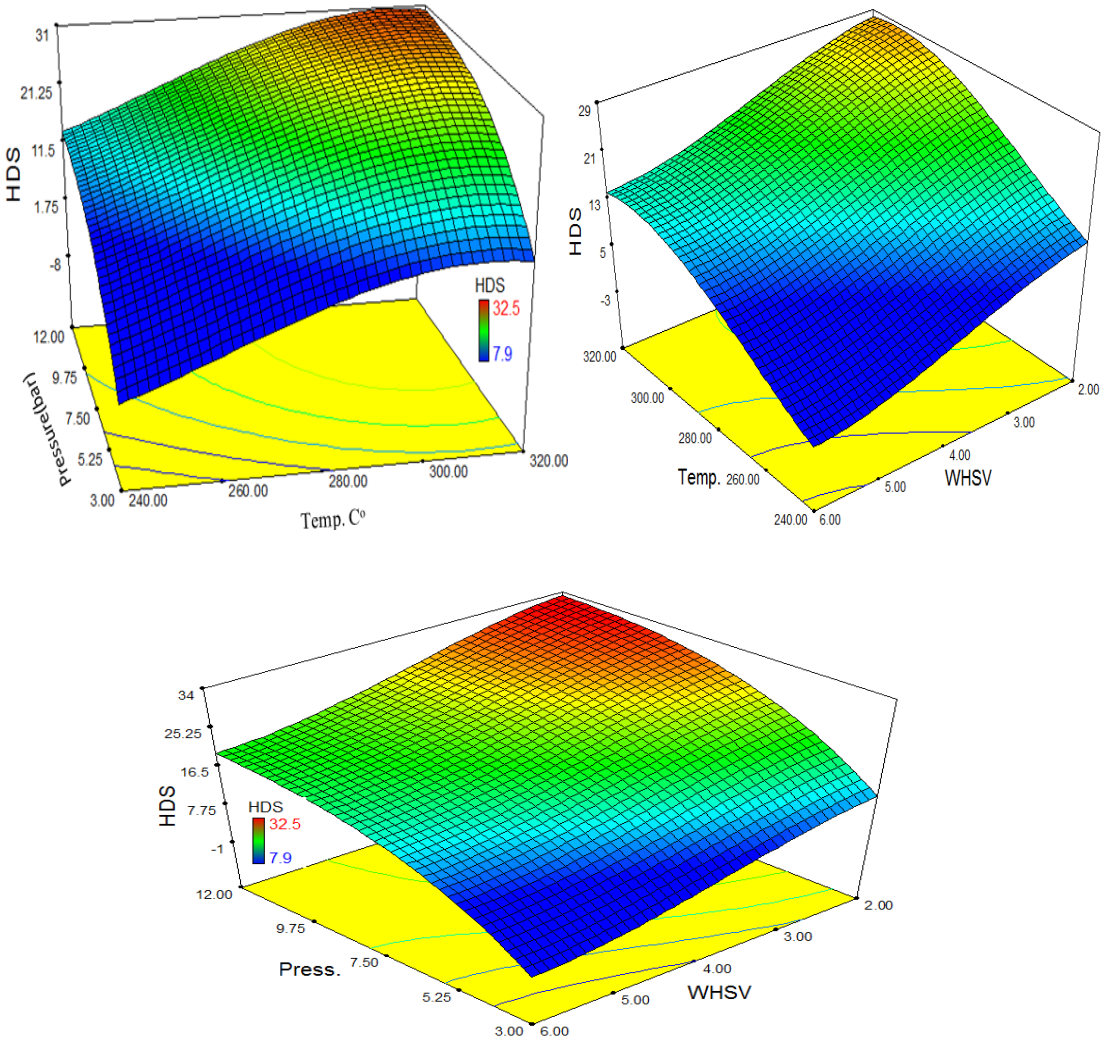


Figure 7: 3D surface plot for effect of factors on HDS%

III. Experimental validation of optimization and Significant Parameter

The main purpose of optimization is to determine optimal value of HDS% factors from the regression equations. The optimum parameter is found by Design Experts at (Temp. = 300 °C, Press. = 12 bar, WHSV = 2 hr^{-1}) to reach the best removal of sulfur compound of about 32.5%. By ANOVA software for cubic model, Table 4 below illustrates the significant parameter in the process. The model of F-value 820.38 implied that the model is significant. There is 0.01% only as chance that "F-value model" that this large volume can be caused by noise. Prob> F values of less than 0.05 indicate the importance of the model terms. In this case, temperature, pressure, and WHSV are important model terms. When values greater than 0.1 indicate that the conditions of the model are not important. If there are many form terms that are not important (not counting the terms required to support the hierarchy), then reducing the form may improve the model.

Table (4): The significant parameter on HDS process

Source	F-Value	p-value	
Model	820.3	>0.0001	Significant
Temp.	526.1	>0.0001	Significant
Press.	221.7	>0.0001	Significant
WHSV	301.3	>0.0001	Significant

5. CONCLUSIONS

Hydro desulfurization experiments of gas oil in a continuous flow fixed bed reactor revealed that the sulfur removal would be enhanced by increasing temperature and pressure, while increasing the WHSV has an opposite effect. Maximum HDS efficiency obtained over meta-kaolin cemented by gamma alumina as a catalyst was achieved in a HDS% system at temperature of 300 °C, pressure of 12 bar and WHSV of 2 h^{-1}, which is about 32.5% using DESIGN-EXPERT version 7.0.0. The regression analysis of the experimental data resulting from equation 2 represents the polynomial related to the objective function such as hydrodesulfurazation efficiency of the studied operating condition with correlation coefficient R^2 = 0.9993; Adj. R^2 = 0.9981; and Pred. R^2 = 0.9372. The "Pred. R^2" is in reasonable fitting with the "Adj. R^2" with difference less than 0.06. Positive values are shown in equation 2 for the parameters A and B means positive effect of the temperature and pressure respectively on the HDS efficiency while negative value of the C coefficient means a negative effect for WHSV on the HDS efficiency

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