

# Design of a new synthetic nanocatalyst resulting high fuel quality based on multiple supports: experimental investigation and modeling

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## Abstract

In order to meet the environmental legislations related to sulfur content, it is important to find an alternative techniques for deep removal of sulfur components from fuels. So, in this study, a novel nano-catalyst based on iron oxide ( $\text{Fe}_2\text{O}_3$ ) as active component prepared over composite support ( $\gamma$ -Alumina + HY-zeolite) is developed here for efficient removal of sulfur compounds from fuel via oxidation process. The precipitation method is employed first to prepare the composite support and then the impregnation method is utilized to generate a novel synthetic homemade ( $\text{Fe}_2\text{O}_3$ / composite support) nanocatalysts that has not been developed in the literature (iron oxide over composite support). The characterizations of the prepared catalysts display that the surface area of the catalyst increases with increasing the amount of Y-zeolite in composite support. The effectiveness of the catalysts is tested by utilizing oxidative desulfurization (ODS) operation under several operating conditions. The results of the experimental work show that the activity of oxidative desulfurization enhances with increasing Y-zeolite, temperature, and batch time under moderate operating conditions. The oxidative desulfurization efficiency followed the order: CAT-1 < CAT-2 < CAT-3. The CAT-3 performed the high removal of sulfur compounds (90.73%) at 100 min and 423 K. The best values of the kinetic parameters of the ODS process are then determined based on experimental data and model based techniques within gPROMS package. Finally, the reactor model is used to determine the optimal operating conditions while maximizing the removal of sulfur compounds leading to cleaner fuel. Where, 99.3% of the sulfur removal has achieved at batch time of 190.6 min, temperature of 543.56 K and initial sulfur content at 0.8668 wt% in the presence of CAT-3 based on the optimal kinetic parameters (order of reaction (n) of 1.9865719, activation energy (EA) at 29.942 KJ/mol and pre-exponential factor (ko) with  $622.926 \text{ wt}^{0.9865719} \cdot \text{min}^{-1}$ ).

**Key words:** Nano-catalyst; composite support; iron oxide; gamma alumina; HY-zeolite

## 1. Introduction

Crude oil and petroleum distillates containing sulfur are undesirable due to severe health/environmental problems. Sulfur dioxide (SO<sub>x</sub>) is emitted due to the combustion of fuels in oil refineries or in transportation. These emissions are dangerous due to its reaction with water in the atmosphere leading to acidic rains harmful to soil, buildings, forests and ecosystems [1-3]. Fuel oil contains four main groups of sulfur compounds (mercaptans, thiophenes (TH), benzothiophenes (BT), and dibenzothiophenes (DBT)) [4]. Sulfur compounds should be removed from crude and fractionated oil for the following reasons [5-9].

- Combustion of transport fuels can lead to the emission of sulfur oxides (SO<sub>x</sub>) resulting in acid rain.
- Sulfur compounds cause many problems of corrosion in pipelines, pumps, and other refining units.
- Sulfur emissions also lead to diseases of respiratory, aggravate illness of heart, trigger asthma and contribute to the formation of atmospheric particulates.
- Catalyst poisoning occurs due to organic sulfur compounds in the reforming process.
- Organic sulfur compounds cause early failures for engines of combustion and poisoning the catalytic converters, which are utilized in the engines of automotive and other different manufacturing processes.

Therefore, environmental regulations have been suggested on the accepted level of sulfur content in the diesel and gasoline to be within the range from 10 to 15 ppm [10].

Consequently, various methods such as hydrodesulfurization (HDS), extractive distillation, selective adsorption, biodesulfurization, and oxidative desulfurization (ODS) have been developed to eliminate sulfur compounds from transportation fuels [11]. HDS is widely employed in modern refinery for elimination of sulfur content in fuel [7,12]. HDS has a high removal efficiency for thiols and mercaptan but it is a less effective method for eliminating sulfur compounds such as TH and its higher derivatives like, BT, DBT and their alkylated derivatives, particularly 4,6 dimethyldibenzothiophene (4,6-DMDBT), as a result of their steric hindrance [13,14]. Therefore, low cost and less dangerous non-traditional processes have become the focus of attention for many research and petroleum companies. ODS is the most alternative promising technique for deep desulfurization of diesel fuel. Typically, it includes liquid-phase biphasic oxidation of sulfur compounds with H<sub>2</sub>O<sub>2</sub> at atmospheric pressure and low reaction temperatures. This technique is highly effective for eliminating refractory aromatic sulfur compounds like thiols and benzothiophenes, which are difficult to remove by utilizing HDS [7, 10, 15]. Note, the ODS process is more effective where the organic sulfur compounds are slightly more polar than the hydrocarbons compounds [5]. The ODS operation relies on electron loss, so as the electron density of the organic sulfur compounds increases, the electron loss increases, which leads to increased efficiency of the oxidation process. The electron density of the organic sulfur compounds is listed in Table 1 [9].

Oxidants (mainly hydrogen peroxide [16-18], air [19,20] and oxygen [21,22]) can give oxygen atom to the sulfur compounds in order to formulate sulfones or sulfoxides, where, mercaptan oxidizes to disulfide directly,

sulfide oxidizes to sulfone then oxidizes to sulfoxide and thiophenes oxidizes to thiophenes sulfoxide then oxidizes thiophenes sulfone. The chemical reactions of these organic sulfur compounds (OSCs) that occur in ODS process summarize as following [23-30]:

- Mercaptan oxidizes to disulfide directly:



- Sulfide oxidizes to sulfone then oxidizes to sulfoxide.



- Thiophenes oxidizes to thiophenes sulfone then oxidizes thiophenes to sulfoxide.



Also, the catalyst is considered a very fundamental part in the oxidation operation owing to its responsibility for the activation of oxidants [31].

The catalytic system can be distinguished as supported and non-supported catalyst. Supported catalysts are frequently utilized due to their comparatively higher dispersion feature (amount of active sites) with an elevated thermal stability of the catalytic component [32]. It mainly comprises of support and active metal such as  $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$  [33] and  $(\text{CuO}+\text{NiO})/\text{HY-zeolite}$  [34]. Recently, nanostructures with particle size less than 100 nm have been applied in catalytic fields [35-39]. Most nano-catalysts utilized in such operation are cost-effective, environmentally friendly and have high chemical and thermal stability [40,41]. In addition, nanostructured materials have high purities, high porosity, high mechanical strength and tunable density [42]. Nanocatalysts also have an excellent recyclability in the ODS process [43-45].

**"Table 1: The electron density of sulfur compounds**

Organic sulfur compound	Electron density
$\text{C}_4\text{H}_4\text{S}$	5.696
$\text{C}_5\text{H}_6\text{S}$	5.106
$\text{C}_6\text{H}_6\text{S}$	5.902
$\text{C}_6\text{H}_8\text{S}$	5.716
$\text{C}_7\text{H}_8\text{S}$	5.915
$\text{C}_8\text{H}_6\text{S}$	5.739
$\text{C}_{12}\text{H}_8\text{S}$	5.758
$\text{C}_{12}\text{H}_{10}\text{S}$	5.860
$\text{C}_{13}\text{H}_{10}\text{S}$	5.759
$\text{C}_{14}\text{H}_{12}\text{S}$	5.760

Zeolites are crystal microporous alumina silicates widely employed in various operations, like ion exchange, separations, adsorption and catalysis owing to their premium specifications in terms of excellent acidity, ion exchange, thermal stability, molecular sieving, capacities, adsorption and shape selectivity [46, 47]. Nano crystalline zeolites possess regular crystals with particles size not more than 100 nm and have excellent specifications compared to traditional zeolites that have micrometer-sized crystals [48]. Zeolites-Y have higher selectivity for substituted TH and DBT than for TH in the order 4,6- DMDBT > 4-MDBT > DBT > BT > TH, where its selectivity rises with raising electron density of the organic sulfur compounds [49]. Alumina is important material being utilized in several industrial applications such as petroleum, adsorbents, treatment of wastewater and surface coatings in different manufacturing scopes. The diversity of utilization is owing to combination of several specifications (amphoteric and textural) of alumina that have excellent pore distribution, pore size, controllable pore volume, tunable surface functionality, high surface area and low coking activity in addition to the gamma alumina structure involves acidic sites that has good porosity [50-51]. Also, the advanced process simulator (gPROMS) is regarded as promising software to attain the difficult goal with respect to the optimal control variables affecting the performance of the reactor or the catalyst used. As a chemical operation simulator, gPROMS has a model library of standard process units and is so easy to build novel models coded in a symbolic form for s specific chemical issues [52]. Several last studies related to the important factors affecting the performance of the catalysts used the in ODS process have extensively been reported in the literature. For instance, Hasan et al. [53] investigated the effect of calcination temperature of the catalysts prepared on the oxidative desulfurization (ODS) by using  $WO_x/ZrO_2$  catalyst, which was calcined at various temperatures (550oC to 850oC). It was found that the conversion process increases with increasing the calcination temperatures from 550oC to 700oC and further increasing in the calcination temperature results, a decrease of oxidative conversion is noted. Si et al. [54] has studied the impact of active metals on the oxidative desulfurization by loading different metals loaded on Ti-MWW. The results showed that the activity of ODS were affected by the kind of active metal based on the following order: Au/Ti-MWW, Pd/Ti-MWW > Ag/Ti-MWW, Cr/Ti-MWW> Fe/Ti-MWW>Cu/Ti-MWW. Jarullah et al. [55] studied the effect of multiple actives compounds on the activity of sulfur removal through loading different amount of copper oxide and Nickel oxide loaded over HY-zeolite. Their results showed that the activity of sulfur removal is significantly affected by loading multiple active materials. Cedeño-Caero et al. [56] have investigated the influence of the catalyst support on the removal of sulfur compounds for a series of  $V_2O_5$  catalysts supported on titania, alumina, ceria, niobia and silica. It was found that the oxidative activity of sulfur compounds depends on the support and the activity of the catalyst in the next order: alumina > titania > niobia > Al-Ti mixed oxide > SBA-15.

In this study, the role of the composite support nano-catalysts in promoting the removal of sulfur compounds from light gas oil (LGO) under different operating conditions is studied using the oxidation method in a batch reactor. Three types of the novel homemade nano composite supports are initially prepared for this purpose (i) 85%  $\gamma$ -alumina +15% HY zeolite, (ii) 75%  $\gamma$ - alumina +25% HY-zeolite and (iii) 65%  $\gamma$ -alumina +35% HY-zeolite. Three nano-catalysts are then designed by loading iron oxide ( $Fe_2O_3$ ) over the three

composite supports mentioned earlier. The effectiveness of the catalysts are investigated under different reaction temperature batch operating time and amounts of HY-zeolite within the composite supports. Finally, a mathematical model of the ODS process is developed and the best kinetic parameters for the reactor model are obtained using the experimental data and model based techniques within gPROMS software package. The process model thus developed and validated is then used within an optimization framework to determine the optimal operating conditions and the most effective catalyst (out of the 3) which will maximize the removal of the sulfur compounds leading to a cleaner/greener fuel.

The novelty of this paper lies in the enhancement of the removal of sulfur compounds in LGO by utilizing composite support ( $\gamma$ -alumina +HY zeolite) that has not been reported or applied in such area. Also, the loading of  $\text{Fe}_2\text{O}_3$  on composite support ( $\gamma$ -alumina +HY zeolite) has not been utilized in an ODS process in the last studies. The ODS process is implemented in a batch reactor by using real light gas oil (LGO) fraction as feedstock and air as an oxidizing agent.

## 2. Experimental section

### 2.1 Preparation of the catalyst

#### 2.1.1 Material

Ferric nitrate hydrate  $\{\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}, 98\%, (\text{Himedia})\}$ , Aluminum Nitrate  $\{\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}, 98\%, (\text{Himedia})\}$ , Ammonium hydroxide  $\{\text{NH}_4\text{OH}, 28\%, (\text{GCC})\}$ , Ethanol  $\{\text{C}_2\text{H}_5\text{OH}, 98\%, (\text{Hayaman})\}$  and deionized water were utilized to prepare the composite support and catalyst. HY-zeolite, was prepared in the previous study Jarullah et al. [55], and characterized at the Laboratory of Petroleum Research and Development / Ministry of Oil / Iraq. The HY-zeolite properties (mainly, pore volume (PV), surface area (SA), bulk density (BD), pore size (PZ) and particle size (PRZ) are illustrated in Table 2.

**Table 2: The properties of HY-zeolite nanoparticle**

Property	units	Values
pore volume (PV)	$\text{cm}^3/\text{g}$	0.388
bulk density (BD)	$\text{g}/\text{cm}^3$	0.648
surface area (SA)	$\text{m}^2/\text{g}$	499.400
pore size (PZ)	nm	31.140
particle size (PRZ)	nm	94.310
Crystallinity	%	92.300
$\text{SiO}_2 / \text{Al}_2\text{O}_3$ molar ratio	-	5.183

### 2.1.2 Composite support preparation

The composite support ( $\gamma$ -Alumina +HY-zeolite) was prepared by precipitation method. Prepared composite supports contain different amounts of HY-zeolite to investigate its impact on the desulfurization operation. The amount of materials used for composite supports preparation is illustrated in Table 3.

**Table 3: The amount of materials used for composite support preparation**

Chemicals and Materials	The amount of materials		
	Support-1 (85% $\gamma$ -Alumina +15% HY-zeolite)	Support-2 (75% $\gamma$ -Alumina +25% HY-zeolite)	Support-3 (65% $\gamma$ -Alumina +35% HY-zeolite)
Aluminum Nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ )	60 g	50 g	45 g
HY-zeolite	1.5 g	2.5 g	3.5 g
Ammonium hydroxide	150 ml	125ml	113 ml
Ethanol	50 ml	50 ml	50 ml
Deionized water	150 ml	150 ml	150 ml

The composite support preparation was carried out by dissolving 60 gm of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 1.5 g of HY-zeolite in 100 mL of deionized water. After that, the ammonium hydroxide solution was added by using a burette in the presence of an ice bath at temperature  $0^\circ\text{C}$  under stirring speed 700 rpm by using magnetic stirring. After the solution mixture is turned into foaming solution, the addition of ammonium hydroxide solution was stopped. The pH of the solution mixture was determined by using pH meter, which was initially 2 and was gradually raised to 7.5 during the addition of ammonium hydroxide solution to produce composite support. Then, the foaming solution was washed by adding 100 ml of  $\text{C}_2\text{H}_5\text{OH}$  solution (50 %  $\text{C}_2\text{H}_5\text{OH}$  + 50%  $\text{H}_2\text{O}$ ) to remove any insoluble impurity. After that, filter paper and a vacuum pump were employed to dry the foaming solution. Also, the furnace is used to dry the filtered foaming solution at temperature of  $120^\circ\text{C}$  for 12 hours. The drying step led to the conversion the foaming solution into a solid state and it has noticed that the color of the foaming solution changed from grey to white. After that, the dried samples were calcinated at a temperature of  $650^\circ\text{C}$  [57] at a rate of  $60^\circ\text{C}/\text{min}$  for 6 hours to get the nano composite support. The powder was cooled to room temperature by switching off the furnace. Finally, The calcinated sample is crashed by hand using a mortar and hammer to obtain nano composite support. The preparation steps of the composite support are shown in Figure1.

**Figure 1: The steps of composite support ( $\gamma$ -Alumina +HY-zeolite) preparation by precipitation method**

### 2.1.3 Preparation of Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>) / (γ-Alumina +HY-zeolite) Catalyst

Figure 2 shows the steps of catalysts preparation. The impregnation method was utilized to generate the homemade nano-catalysts. The catalyst was generated by dissolving 0.95 gm of ferric nitrate hydrate in 23 ml of deionized water and mixed by magnetic stirrer for one hour at temperature of room to obtain the salt solution.

#### Figure 2: The preparation steps of (Fe<sub>2</sub>O<sub>3</sub>/ γ-Alumina +HY-zeolite) catalyst by impregnation method

Then, the impregnated solution is prepared by gradually adding 7.125 gm of the prepared composite support nanoparticles to the salt solution for one hour at room temperature until the solution is fully impregnated. Magnetic stirrer was used to facilitate the mixing. After that, the solution was dried by placing it in the furnace at 120 °C overnight. Then, the furnace temperature was elevated to 400 °C for two hours and finally to 550 °C for three hours. The calcination step is employed to transform ferric nitrate hydrate that was loaded over the composite support to active iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and to deposit the active metal oxide over the prepared composite support.

### 2.1.4 Instruments

The following tools and equipment are utilized to characterize the prepared composite supports and catalyst: X-ray fluorescence (XRF) type (SPECTRO XEROS), (Germany), X-Ray Diffraction (XRD) type (SHIMADZU), (Japan), Thermal gravimetric analysis (TGA) type (LINSEIS 1600), (Germany), Scanning Electron Microscopy (SEM) type (Zeiss-EM10C-100 KV), Fourier transform infrared (FTIR) type (SHIMADZU), (Japan), Atomic Force Microscopy (AFM) type (AA3000 Scanning Probe Microscope) and Brunauer–Emmett–Teller (BET) type (micromeritics), (USA).

## 2.2 Oxidative desulfurization reactions

### 2.2.1 Oil feedstock

Real light gas oil (LGO), which contains initial sulfur concentration of 0.7510 wt%, was obtained from KAR refinery/north of Iraq (Erbil). LGO was employed as liquid feedstock for oxidative desulfurization operation. The physical properties of the feedstock are measured at the central laboratory of petroleum/ Erbil as listed in Table 4.

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**Table 4: Light Gas Oil feedstock specifications**

Physical property	Values	Physical property	Values
Sp.gr @ 15.5°C	0.821	Pour Point, °C	<-20
API gravity	39.230	Distillation, °C	-----
Initial sulfur concentration, wt %	0.751	IBP, °C	195
Flash Point, °C	73	10 vol % recovered, °C	212
Viscosity @ 40°C (cSt)	3.210	50 vol % recovered, °C	246
Cetane Number	54	90 vol% recovered, °C	300
Cetane Index	54	Final boiling point, °C	328

### 2.2.2 Batch reactor

Three-necked flask of 500 ml is employed to check the effectiveness of the homemade nano catalyst. The first neck, which is in the middle, is linked to a vertical condenser that used to prohibit any loss of oil feedstock by evaporation and only allow air to leave. The second neck is utilized to inject air, which is fed from the compressor while, the temperature of the flask is measured by putting a thermometer through the third neck to the sample found in the flask. Also, the product is withdrawn from the third neck upon consummation of the experiment. The heating and mixing of the sample in the batch reactor were carried out by using the heating mantle stirrer. The ODS process is illustrated in Figure 3.

**Figure 3: ODS batch reactor system**

## 2.3 Experimental evaluation

### 2.3.1 Operating conditions"

The operating conditions used for the ODS process are summarized in Table 5.

**Table 5: The operating conditions of ODS process**

Operating conditions	specifics
Type of catalyst	CAT-1= Fe <sub>2</sub> O <sub>3</sub> / (85% $\gamma$ -Alumina +15% HY-zeolite) CAT-2= Fe <sub>2</sub> O <sub>3</sub> / (75% $\gamma$ -Alumina +25% HY-zeolite) CAT-3= Fe <sub>2</sub> O <sub>3</sub> / (65% $\gamma$ -Alumina +35% HY-zeolite)
Reaction temperature	90°C, 110°C, 130°C, 150°C
Batch time	40min, 60min, 80min, 100min
Air flow rate	120 L/h
Pressure	1 atm



For each catalyst prepared, the first temperature is kept fixed (90 °C) and the batch time is changed for each run (starting with 40 min, 60 min, 80 min and then 100 min) under the same air flow rate (120 L/h) and pressure (1 atm) for all experiments. The same procedure is repeated for the second, third and fourth reaction temperature (110 °C, 130 °C, 150 °C).

### **2.3.2 Oxidation of sulfur: experimental procedure**

In all experimental runs:

- 80 ml of light gas oil was injected to the three-necked flask.
- The three-necked flask was placed on the heating mantle stirrer and linked to the condenser and the air supply. It was ensured that there was flowing cooling water through the condenser to prohibit any loss of LGO by evaporation. A thermometer was placed to gauge the process temperature. When the desired temperature of reaction was obtained, 0.8 gm of the catalyst was added to the flask and the time was recorded
- At the end of the run, the heating mantle stirrer was switch off and the product of the process was filtered.
- The flask was cleaned and dried to get it ready for the next run.
- All products, after the reaction was completed were tested for sulfur content.

### **2.4 Liquid samples testing**

The concentration of sulfur compounds in the oil feedstock (real light gas oil) and products was inspected by utilizing X-ray fluorescence following the ASTM D4294 method."

## **3. Mathematical model of the batch reactor for ODS reaction"**

The mathematical model consists of a collection of equations obtained from the literature while the kinetic parameters are obtained by reducing the sum of the squared error between experimental results and predicted result that obtained from mathematical model. The gPROMS software is used to develop the process model. The process model equations are listed in Table 6.

The set of the mathematical model equations above are encoded for the oxidation interaction and solved by employing the gPROMS (general Process Modeling System) software.

#### 4. Kinetic parameter estimation technique

Model based parameter estimation technique is well known in the literature [58]. The suitable kinetic parameters for the process are evaluated based on reducing the errors between experimental data and predicted data from the mathematical model.

In this paper, the optimum values of kinetic parameters of the oxidation interaction are estimated using two approaches. These approaches are illustrated in Table 7.

**Table 6: Equations utilized in the mathematical model**

Parameter	Equations/values	Eq. No.	Reference
Reaction rate	$(-r_{sulfur}) = \eta_0 k C_{sulfur}^n$	(1)	[58]
Arrhenius equation	$k = k_0 e^{(-\frac{EA}{RT})}$	(2)	[59,60]
The final sulfur concentration	$C_{sulfur} = [C_{sulfur,t}^{(1-n)} + (n-1).t.K_{in}\eta_0]^{\frac{1}{1-n}}$	(3)	[61]
The effectiveness factor ( $\eta_0$ )	$\eta_0 = \frac{3(\phi \coth\phi - 1)}{\phi^2}$	(4)	[61,62]
Thiele modulus ( $\phi$ )	$\phi = \frac{V_p}{S_p} \sqrt{\left(\frac{n+1}{2}\right) \frac{k_{in} C_{sulfur}^{(1-n)} \rho_p}{D_{ei}}}$	(5)	[61,62]
$D_{ei}$	$D_{ei} = \frac{\epsilon_B}{\mathcal{J}} \frac{1}{\frac{1}{D_{mi}} + \frac{1}{D_{ki}}}$	(6)	[58,62]
$\epsilon_B$	$\epsilon_B = V_g \rho_p$	(7)	[58,62]
Particle density ( $\rho_p$ )	$\rho_p = \frac{\rho_B}{1 - \epsilon_B}$	(8)	[58,62]
The tortuosity factor ( $\mathcal{J}$ )	The value of tortuosity factor ( $\mathcal{J}$ ) of the pore network ranged between (2 to 7)	----	[62]
The Knudsen diffusivity ( $D_{ki}$ )	$D_{ki} = 9700 r_g \left(\frac{T}{M_w}\right)^{0.5}$	(9)	[58,61]
Mean pore radius ( $r_g$ )	$r_g = 2V_g/S_g$	(10)	[63]
The molecular diffusivity ( $D_{mi}$ )	$D_{mi} = 8.93 * 10^{-8} \left(\frac{v_l^{0.267} T}{v_s^{0.433} \mu_l}\right)$	(11)	[64,65]
Sulfur molar volume ( $v_{sulfur}$ )	$v_{sulfur} = 0.285(v_{csulfur})^{1.048}$	(12)	[64]
Light gas oil molar volume ( $v_l$ )	$v_l = 0.285(v_{cl})^{1.048}$	(13)	[62]

Critical volume of light gas oil ( $v_{cl}$ )	$v_{cl} = (7.5214 * 10^{-3}(T_{meABP})^{0.2896}(\rho_{L15.6})^{-0.7666})Mw_L$	(14)	[62]
The external volume of the catalyst ( $V_p$ )	$V_p = \frac{4}{3}\pi(r_p)^3$ , (For sphere particle)	(15)	[65]
The external surface of the catalyst ( $S_p$ )	$S_p = 4\pi(r_p)^2$ , (For sphere particle)	(16)	[65]
Oil viscosity ( $\mu_l$ )	$\mu_l = 3.141 * 10^{10}(T - 460)^{-3.444}(\log API)^\alpha$	-(17)	[66]
Dimensionless No. ( $\alpha$ )	$\alpha = 10.313[\log_{10}(T - 460)] - 36.447$	-(18)	[66]
American petroleum institute (API)	$API = \frac{141.5}{sp. gr_{15.6}} - 131.5$	-(19)	[67]

**Table 7: The approaches for estimating the kinetic parameters**

Linear regression	Non-linear regression
The interaction order (n) and constant of reaction rate (k) are evaluated. After that, the Arrhenius equation is employed in order to appreciate the pre-exponential factor (ko) and activation energy (EA).	The interaction order (n), the pre-exponential factor (ko) and activation energy (EA) are immediately calculated.

For estimating the kinetic parameters, the objective function as shown below is minimized:

$$OBJ = \sum_{n=1}^{Nt} (C_{sulfur}^{exp} - C_{sulfur}^{pred})^2 \quad (20)$$

In equation (20), Nt,  $C_{sulfur}^{exp}$  and  $C_{sulfur}^{prd}$  express the numbers of runs, the concentration of sulfur content that obtained from experiments and sulfur concentration predicted by the mathematical model respectively. The estimation of sulfur compound conversion is obtained using equation (21):

$$X_{sulfur} = 1 - \frac{C_{sulfur}}{C_{sulfur.t}} \quad (21)$$

#### 4.1 Optimization problem formulation for parameter estimation

The estimation of parameter carried out through the configuration of optimization problem, which is expressed as follows:

**Given:** The catalyst, the formation of reactor and the process operating conditions.

**Obtain:** For the 1<sup>st</sup> approach: The orders of oxidation interaction (n1, n2, n3) for each prepared catalyst and interaction rate constant (k) at various temperature (363, 383, 403, 423) K respectively. After that, (EA) and (ko) can be estimated by applying linear regression through Arrhenius equation. With regard to the second approach: the parameters ( n, EA and ko) can be concurrently determined for each catalyst.

**So as to minimize:** The sum of squared error (SSE).

**Subjected to:** Constraints of operation

Mathematically the optimization problem can be described as:

(a) Linear regression method

**Min:** **SSE**

$$n^j, k_i^j, (i = 1 - 4, j = \text{CAT}_{1,2,3})$$

$$\text{s.t.} \quad f(z, x(z), \dot{x}(z), u(z), v) = 0$$

$$C_L \leq C \leq C_U$$

$$n_L^j \leq n^j \leq n_U^j$$

$$k_{iL}^j \leq k_i^j \leq k_{iU}^j$$

(b) Non-linear regression method

**Min:** **SSE**

$$n^j, EA^j, k_i^j, (i = 1 - 4, j = \text{CAT}_{1,2,3})$$

$$\text{s.t.} \quad f(z, x(z), \dot{x}(z), u(z), v) = 0$$

$$C_L \leq C \leq C_U$$

$$n_L^j \leq n^j \leq n_U^j$$

$$EA_L^j \leq EA^j \leq EA_U^j$$

$$k_{oL}^j \leq k_i^j \leq k_{oU}^j$$

s.t.  $f(z, x(z), \dot{x}(z), u(z), v) = 0$  : describe the process model that presented previously.

$z$  : is independent variable.

$u(z)$  : is the decision variable.

$x(z)$  : describe the set of all variables.

$\dot{x}(z)$  : describe the derivative of the variables with respect to time.

$v$  : is the design variable.

$C, C_L, C_U$  : concentration , lower and upper bounds of concentration.

$L, U$  : are lower and upper bounds.

The solution of optimization involves two steps [67]:

- (1) Simulation process is applied, where all the equality constraints are converged as we as satisfying the inequality constraints.

(2) The optimization process is performed, where all the decision variables are updated.

## 5. Results and discussion

### 5.1.1 Chemical composition

XRF test is utilized for the purpose of determining the structural formula of the prepared samples and the quantity of HY-zeolite in the prepared composite support as well as effective metal oxide loaded ( $\text{Fe}_2\text{O}_3$ ). The results of XRF test for the prepared nano-catalysts are illustrated in Table 8. The quantity of  $\text{SiO}_2$  was raised in the catalysts owing to add the HY-zeolite and it is observed that a good percentage of the composite supports and active metal is obtained.

**Table 8: XRF results of the prepared catalysts**

Sample\ Compounds	$\gamma\text{-Al}_2\text{O}_3$ (%)	HY-zeolite (%)	$\text{Fe}_2\text{O}_3$ (%)
CAT-1	81.747	14.132	4.120
CAT-2	70.666	25.552	3.781
CAT-3	60.316	35.788	3.895

### 5.1.2 X-ray diffraction (XRD)"

The XRD behaviors of the prepared composite support (support-1) after calcination at  $650^\circ\text{C}$ , are illustrated in Figure 4. As presented in Figure 4, the characteristic diffraction peaks ( $2\theta = 45.5^\circ$  and  $66.7^\circ$ ) and ( $2\theta = 12^\circ$ ,  $23.7^\circ$  and  $27.1^\circ$ ) refer to presence  $\gamma\text{-Al}_2\text{O}_3$  and HY-zeolite respectively, which indicates the formation of the composite support [68,69]. The crystallites size can be evaluated by applying Scherrer's equation [70] as follows:

$$d = 0.94\lambda/\beta \cos \Theta \quad (22)$$

Where:  $\lambda$  is the X-ray wavelength of,  $d$  is the crystal diameter, the half-maximum intensity of the broadening line is described by  $\beta$ , is at which represents the full width at half-maximum (FWHM) and  $\Theta$  is the Bragg angle at which the scattering wave was reflected or scattered at lattice plane producing intense peaks. The average crystallite diameter is 20.11 nm for the prepared composite support."

**Figure 4: XRD patterns for composite support (support-1) and for CAT-1, CAT-2 and CAT-3**

Also, The XRD results of the three generated catalysts are displayed in Figure 4. With the increase of HY quantity in the composite support, it was observed an increase the diffraction peak intensities of HY, while those of  $\gamma$ - $\text{Al}_2\text{O}_3$  decreased as shown in this Figure.

After loading of  $\text{Fe}_2\text{O}_3$  over the composite support (support-1), the peaks intensity of composite support-1 reduced while the diffraction peak intensities corresponding to  $\text{Fe}_2\text{O}_3$  (at  $33.2^\circ$ ,  $35.6^\circ$ ,  $49.4^\circ$ ,  $54.1^\circ$ ,  $62.4^\circ$  and  $63.9^\circ$ ) was raised as presented in the Figure 5 (a). This behavior indicates that there is a high dispersion of the  $\text{Fe}_2\text{O}_3$  over the prepared composite support.

### 5.1.3 Surface area (SA), pore volume (PV) and pore size (PZ) analysis''

Table 9 summarizes the PZ, SA and PZ of the designed composite supports and catalysts. It was observed that with increasing amount of zeolite in the composite support, the PZ and SA of composite supports increase due to the large SA and PZ of the zeolite [40,48]. It can also be noticed that after the loading of  $\text{Fe}_2\text{O}_3$  over the composite support, PV and the SA slightly reduced because  $\text{Fe}_2\text{O}_3$  occupied some areas inside the composite supports.

Also, the bulk density of the designed catalysts was listed in Table 10. With the addition of HY-zeolite to the support, an increase in the bulk density was noticed due to the occupation of some spaces within the samples by the HY-zeolite component.

**Table 9: SA, PV and PZ of prepared composite supports and catalysts**

Sample	SA ( $\text{m}^2/\text{gm}$ )	PV ( $\text{cm}^3/\text{gm}$ )	PZ (nm)
Support-1	281.400	0.354	5.036
Support-2	333.810	0.429	5.146
Support-3	348.570	0.429	4.928
CAT-1	271.250	0.306	4.516
CAT-2	316.800	0.358	4.514
CAT-3	341.140	0.429	5.036

**Table 10: Summary of bulk density of the prepared catalysts**

Catalyst	Bulk density (gm/cm <sup>3</sup> )
CAT-1	0.543
CAT-2	0.551
CAT-3	0.586

#### 5.1.4 Fourier transform infrared (FTIR)

Figure 5 displays the FTIR spectra of the designed nano composite supports containing various amounts of  $\gamma$ -alumina and HY-zeolite. The anti-symmetric stretching vibration -OH functional group produces a broad peak at 3350-3500  $\text{cm}^{-1}$  [71], and the band at approximate 1650  $\text{cm}^{-1}$  was associated with the H-O-H symmetric stretching vibration of water molecules which were physically or chemically adsorbed. The absorption bands located at 650 is owing to stretching vibrations of Al-O, which is characteristic of  $\gamma$ -alumina [72-75]. The band at 1041.32  $\text{cm}^{-1}$  corresponds to the characteristic absorption peaks of Si-O stretching due to the presence of HY-zeolite [76,77]. With increasing HY-zeolite content within composite support, the peak at  $\sim 1041.32 \text{ cm}^{-1}$  has increased due to increase in the  $\text{SiO}_2$  present in the HY-zeolite.

**Figure 5: FTIR for synthesized supports (a) Support-1, (b) Support-2, (c) Support-3**

Figure 6 shows the FTIR spectra of the designed nano-catalysts after impregnation process. It is observed from Figures 6 and 7 that there was no variation in the wave number regions before and after the loading of  $\text{Fe}_2\text{O}_3$  over the composite supports. These good results demonstrate that there was no chemical change in the composition of the composite supports after the process of catalyst preparation. Also,  $\text{Fe}_2\text{O}_3$  bonds did not appear because the amount of iron oxide was insufficient to show any peaks.

**Figure 6: FTIR for synthesized catalysts (a) CAT-1, (b) CAT-2, (c) CAT-3**

#### 5.1.5 Thermal gravimetric analysis (TGA)

The TGA profiles of the composite supports and catalysts samples are displayed by Figure 7.

**Figure 7: TGA of the designed catalysts (a) Support-1, (b) Support-2, (c) Support-3, (d) CAT-1, (e) CAT-2, (f) CAT-3**

From these Figures, it can be observed that there is no variation in the loss of mass for the samples before and after loading of  $\text{Fe}_2\text{O}_3$  over the composite support. Two mass loss regions are appeared in these Figures where, the first region is located between 20-120°C, with loss of mass values of about 10%. This occurs owing to the water evaporation which was physically adsorbed onto the sample [78,79]. The mass loss that ranged between 180-350°C, is associated with the releasing of the water which was chemically adsorbed [78]. At temperatures above 450°C, there is a tendency for the weight of all samples to be stable. The loss of mass, evaluated by the TGA tests, is ranged between (18-25%) for the composite supports and (14-24%) for the catalysts. These results show that the designed supports and catalysts have a good thermal stability. The highest thermal stability is obtained by CAT-3, where the loss of mass is approximately 14.57%.

### 5.1.6 Particle size (PRZ) distribution

The average PSD of the designed catalysts is determined by the PSD distribution test. Figures 8 displays the results of the PSD distribution test for the designed nano-catalysts.

**Figure 8: Particle size distribution of the prepared catalysts**

this Figure indicates that the average size of particle for all generated catalysts are reported to be < 100 nm, where, the average nano particle size is 89.06 nm for CAT-1, 88.75 nm for CAT-2 and 91.48 nm for CAT-3.

### 5.1.7 Scanning Electron Microscopy (SEM)

The SEM test has displayed the surface nature of the catalysts. Generally, the large surface area of the composite supports enhances the dispersion of nanomaterial of small sizes [7]. Also, the particle size for all the prepared catalysts is <100 nm. The particles have spherical shapes as presented in Figure 9 below.

**Figure 9: Scanning electron microscopy images of (a) CAT-1 (b) CAT-2 (c) CAT-3**

## 5.2 Oxidative desulfurization results

The effectiveness of the designed supports and catalysts in terms of the conversion of sulfur compounds was evaluated in a batch oxidative desulfurization process. Real light gas oil (LGO) was used as an oil feedstock and air as an oxidizing agent. The removal of the sulfur compound is studied under several operation conditions such as HY-zeolite percent in the composite supports, reaction temperature and reaction time (batch operation time).



### 5.2.1 Determination of the most active catalyst

The highest sulfur removal was achieved with the presence of CAT-3 as illustrated in the Figure 10. This result is attributed to the composite support of CAT-3 that contain the highest quantity of the zeolite, available acid sites, large surface area and a unique pore structure, which improve the removal of sulfur particles [80].

**Figure 10: The ODS efficiencies of supported Fe<sub>2</sub>O<sub>3</sub> catalysts. (Experimental conditions: catalyst dosage = 0.01 g/mL (0.8 g in 80 mL), air flow rate=120 L/h , light gas oil volume =80 mL, reaction temperature=423 K and reaction time=100 min)**

### 5.2.2 Impact of reaction temperature

The impact of the interaction temperature on the activity of sulfur components removal in ODS operation was investigated at 363 K, 383 K, 403 K and 423 K, and the results are presented in Figure 11.

As presented in this Figure, with the increasing temperature of reaction, the efficiency of the ODS process increases. Such behaviors are interpreted by the following points:

- The reaction constant of the reaction will increase with increasing temperature, which causes an enhanced removal rate of the sulfur compound in step with Arrhenius' equation [59]. According to Arrhenius' equation, the removal rate of sulfur compounds is increased by increasing the reaction temperature wherever the reaction rate constant is completely affected. Hence, increasing the temperature of the reaction can increase the number of the molecules that have the energy of activation (the activation energy depends on the reaction rate) and thus increase the number of molecules concerned within the reaction interaction ensuing high sulfur removal [58].
- Also, many physical properties of liquid and gas are influenced by the reaction temperature mainly Henry's constant, density, viscosity, and gas diffusivity. With increasing reaction temperature, Henry's constant and gas diffusivity increased and opposite phenomena related to viscosity was noted [81]. This behaviour positively affects the oxidation reaction and leads to an increase in the removal rate of sulfur compounds.
- The temperature of oxidization process powerfully influences the development of surface properties and therefore the section structure of the prepared composite support [57]. Also, the activities of the catalyst are extremely affected by its calcination temperatures. With increasing calcination temperature, the acid sites density will increase promoting the efficiency of the ODS process.

**Figure 11: Temperature impact on the efficiency of ODS operation for the prepared catalysts at (a) 40 min (b) 60 min (c) 80 min (d) 100 min. (Experimental conditions: catalyst dosage = 0.01 g/mL (0.8 g in 80 mL), air flow rate=120 L/h, light gas oil volume =80 mL)**

### **5.2.3 Influence of Batch Reaction time**

The effect of the reaction time on the removal rate of sulfur compounds by ODS operation was investigated utilizing 40 min, 60 min, 80 min, and 100 min as the batch operation time. Figure 12 displays the experimental results at various temperatures for each designed catalyst. In general, it was observed that the desulfurization activity rises with the reaction time. The increase in the reaction time provides more residence time leads to interaction time between reactants [64, 71]. As conferred in Figure 12 (d), the sulfur compounds conversion enhanced from 61.85% to 79.56% by raising the reaction time from 40 min to 100 min at 423 K, for CAT-1. Also, the conversion of sulfur compounds increased from 71.54% to 86.52% for CAT-2 and 80.19% to 90.73% for CAT-3.

**Figure 12: Time impact on the activity of ODS process for the prepared catalysts at (a) 363 K (b) 383 K (c) 403 K (d) 423 K. (Experimental conditions: catalyst dosage = 0.01 g/mL (0.8 g in 80 mL), air flow rate=120 L/h, light gas oil volume =80 mL)**

### **5.2.4 Impact of HY-zeolite added to the catalyst support**

The influence of the addition of HY-zeolite to the composite support of catalyst on the removal rate of sulfur compounds has been investigated here. Three composite supports were prepared containing numerous quantities of HY-zeolite (15%, 25%, and 35%). The experimental results are conferred in Figure 13 for various reaction times and temperatures.

**Figure 13: Influence of HY-zeolite on the efficiency of ODS process at different time and at (a) 363 K (b) 383 K (c) 403 K (d) 423 K. (Experimental conditions: catalyst dosage = 0.01 g/mL (0.8 g in 80 mL), air flow rate=120 L/h, light gas oil volume =80 mL)**

In general, the behavior of sulfur compounds conversion seems that the ODS chemical change efficiency were increased with increasing the number of HY-zeolite within the composite support of the catalyst. Aluminum in the framework structure of HY-zeolite has hydrophilicity/hydrophobicity, and Lewis acidity which were greatly related to Ion exchanged capacity. These zeolites possessed comparatively high hydrophilicity, which maybe helpful for the surface assimilation process. The Lewis acid sites are often generated from extra-framework that are liable for the superb chemical action performances for aerophilic desulfurization process to the rise within the total quantity of active sites and therefore the increase in the active expanse for adsorption, the removal rate of sulfur compounds enhanced with increasing the amount of zeolite in composite support [82]. Also, the mesoporosity of HY-zeolite had with success doubled once

modification by ion exchange method. The promotion result of Fe was allotted to the high dispersion of active  $\text{Al}_2\text{O}_3$  / HY composite [83]. The prepared nanocatalyst had associate degree acceptable performance in removing all types of sulfur compounds at the utilized operating conditions because HY-zeolite in composite support provides a larger contact area for the sulfur compounds to react with the oxidant leading to higher removal rate of sulfur compounds [40, 84].

Based on the results of the catalyst characterization and the oxidation reaction, the prepared nanocatalysts have high stability and excellent performance in the removal of sulfur compounds.

### 5.3 Kinetic parameters estimation

The optimal kinetic parameters are evaluated using model-based techniques that aimed to obtain predicted values as close as possible to the experimental values [85]. The mathematical process model utilizes the constant parameters given in Table 11.

**Table 11: Values of fixed parameters employed in the modeling process of ODS**

Parameter, unit	Value
Initial concentration (Ct), wt%	0.751
Time <sub>1,2,3,4</sub> , min	40, 60, 80, 100
Temperature (T <sub>1,2,3,4</sub> ), K	363, 383, 403, 423
Sp.gr of LGO at 15.5°C, gm/cm <sup>3</sup>	0.821
T <sub>meABP</sub> , °R	957
Acceleration gravity (g), m/sec <sup>2</sup>	9.810
R, J/mole.°K	8.314
V <sub>gCAT1,2,3</sub> , cm <sup>3</sup> /gm	0.306, 0.358, 0.429
S <sub>gCAT-1,2,3</sub> , cm <sup>2</sup> /gm	2712500, 3168000, 3411400
V <sub>pCAT-1,2,3</sub> , cm <sup>3</sup>	3.698*10 <sup>-16</sup> , 3.660*10 <sup>-16</sup> , 4.008*10 <sup>-16</sup>
S <sub>pCAT-1,2,3</sub> , cm <sup>2</sup>	2.492*10 <sup>-10</sup> , 2.474*10 <sup>-10</sup> , 2.629*10 <sup>-10</sup>
(ρ <sub>B,CAT-1,2,3</sub> ), gm/cm <sup>3</sup>	0.543, 0.551, 0.586
M.Wt of LGO (M <sub>wL</sub> ), gm/mole	200.468
M.Wt of sulfur (M <sub>wi</sub> ), gm/mole	32.060
Γ <sub>g,CAT-1,2,3</sub> , nm	2.258, 2.257, 2.518

#### 5.3.1 Linear regression

The best model parameters evaluated by employing linear approach are given in Tables (12- 14) for each catalyst:

**Table 12: Best model parameters optimized by utilizing 1<sup>st</sup> way for CAT-1**

Parameter	Value	Unit
n	1.993351	–
k1	$954.772 \times 10^{-5}$	$(wt^{-0.993351}).min^{-1}$
k2	$175.642 \times 10^{-4}$	$(wt^{-0.993351}).min^{-1}$
k3	$304.615 \times 10^{-4}$	$(wt^{-0.993351}).min^{-1}$
k4	$545.335 \times 10^{-4}$	$(wt^{-0.993351}).min^{-1}$
SSE	$286.741 \times 10^{-5}$	–

**Table 13: Best model parameters optimized by utilizing 1<sup>st</sup> way for CAT-2**

Parameter	Value	Unit
n	2	–
k1	$173.232 \times 10^{-4}$	$(wt^{-1}).min^{-1}$
k2	$317.228 \times 10^{-4}$	$(wt^{-1}).min^{-1}$
k3	$584.754 \times 10^{-4}$	$(wt^{-1}).min^{-1}$
k4	$895.587 \times 10^{-4}$	$(wt^{-1}).min^{-1}$
SSE	$235.177 \times 10^{-5}$	–

**Table 14: Best model parameters optimized by utilizing first approach for CAT-3**

Parameter	Value	Unit
n	1.975312	–
k1	$293.844 \times 10^{-4}$	$(wt^{-0.9754122}).min^{-1}$
k2	$491.453 \times 10^{-4}$	$(wt^{-0.9754122}).min^{-1}$
k3	$796.204 \times 10^{-4}$	$(wt^{-0.9754122}).min^{-1}$
k4	$123.069 \times 10^{-3}$	$(wt^{-0.9754122}).min^{-1}$
SSE	$911.384 \times 10^{-6}$	–

As shown in Tables 13 to 15, the order of the reaction is different for each type of the catalyst. The orders of the ODS reactions are found to be 1.993 for CAT-1, 2 for CAT-2 and 1.975 for CAT-3 for sulfur compounds contained in LGO.

According to Arrhenius equation, the activation energy is calculated by plotting of  $\ln k$  versus  $(1/T)$  that results in a straight line with slope equal to  $(-EA/R)$  as illustrated in Figures from 14 to 16 for each catalyst. The activation energy values obtained are given in Table 15.

**Figure 14:  $\ln k$  versus  $(1/T)$  for kinetic parameters of the oxidation process using CAT-1**

**Figure 15:  $\ln k$  versus  $(1/T)$  for kinetic parameters of the oxidation process using CAT-2**

**Figure 16:  $\ln k$  versus  $(1/T)$  for kinetic parameters of the oxidation process using CAT-3**

**Table 15: Mathematical results of activation energies**

Catalyst	EA(kJ/mol)	Frequency factor
CAT-1	36.844	1880.513
CAT-2	35.422	2178.954
CAT-3	30.510	718.166

Activation energy can be affected by many factors as follows:

- The activation energy is strongly influenced by the catalyst type. In this study, the activation energy is found to be (36.844 kJ/mol for CAT-1), (35.422 kJ/mol for CAT-2) and (30.510 kJ/mol for CAT-3 for sulfur compounds found in light gas oil.
- The activation energy can be notably influenced by the types of sulfur compounds. The value of ODS activation energy of DBT and 4,6-DMDBT found in light gas oil is about 32.1 kJ/mol.

### 5.3.2 Non-linear regression

The parameters of ODS interaction ( $n$ ,  $EA$  and  $k_0$ ) have been evaluated based on this approach and the values of these parameters are summarized in Tables 16 - 18 below

**Table 16: Best model parameters optimized by utilizing 2<sup>nd</sup> way for CAT-1**

Parameter	Value	Unit
n	1.986900	–
EA	34.911	KJ/mol.
k <sub>o</sub>	1014.744	$wt^{-0.9869}.min^{-1}$
SSE	$270.007 \times 10^{-5}$	–

**Table 17: Best model parameters optimized by utilizing 2<sup>nd</sup> way for CAT-2**

Parameter	Value	Unit
n	1.975313	–
EA	34.775	KJ/mol.
k <sub>o</sub>	1681.534	$wt^{-0.975313}.min^{-1}$
SSE	$159.999 \times 10^{-5}$	–

**Table 18: Best model parameters optimized by utilizing 2<sup>nd</sup> way for CAT-3**

Parameter	Value	Unit
n	1.986572	–
EA	29.942	KJ/mol.
k <sub>o</sub>	622.926	$wt^{-0.9865719}.min^{-1}$
SSE	$5.716 \times 10^{-4}$	–

Based on the results illustrated in these Tables, it is detected that the CAT-3 is preferable than the other catalysts depending on the activation energy obtained at the similar operating conditions. The activation energy of the other catalysts is greater than CAT-3, where the rate of reaction is inversely proportion to the activation energy.

#### 5.4 Experimental and simulation results

The process simulation is implemented by utilizing the gPROMS program. The results of experimental work and predicted are shown in Figures 17 to 22 below:

**Figure 17: Experimental and simulation results using 1<sup>st</sup> way for CAT-1**

**Figure 18: Experimental and simulation results using 1<sup>st</sup> way for CAT-2**

**Figure 19: Experimental and simulation results using 1<sup>st</sup> way for CAT-3**

**Figure 20: Experimental and simulation results using 2<sup>nd</sup> way for CAT-1**

**Figure 21: Experimental and simulation results using 2<sup>nd</sup> way for CAT-2**

**Figure 22: Experimental and simulation results using 2<sup>nd</sup> way for CAT-3**

As illustrated in these Figures, more accurate parameters were obtained by depending on the nonlinear approach because the sum of squared errors (SSE) of nonlinear approach is lower than the linear approach, depending on objective function shown in Table 19. The values of kinetic parameters obtained by employing non-linear method gives low error as comparison with those evaluated through linearization of Arrhenius equation.

**Table 19: Comparison between the sums of squared errors (SSE)**

Parameters	Sum of squared errors (SSE)	
	Linear approach	Non-linear approach
CAT-1	$28.674 \times 10^{-4}$	$27.001 \times 10^{-4}$
CAT-2	$23.517 \times 10^{-4}$	$15.999 \times 10^{-4}$
CAT-3	$9.113 \times 10^{-4}$	$5.716 \times 10^{-4}$

## 6. Maximization sulfur removal

The optimization problem is formulated as follows:

**Given:** The order of reaction, the description of reactor, the catalyst and  $k_0$  and EA for the reaction.

**Obtain:** The optimal operating conditions (temperature, reaction time)

**So as to minimize:** The concentration of sulfur compounds.

**Subjected to:** Process constraints

The problem is represented mathematically as follows:

$$\begin{aligned}
& \text{Min} && C_{sulfur} \\
& T^j, time_i^j, C_{sulfur}^j && (j= \text{CAT-1,2,3}) \\
& \text{S.t.} && f(z, x(z), \dot{x}(z), u(z), v) = 0 \\
& && time_L^j \leq time^j \leq time_U^j \\
& && C_{sulfur.tL}^j \leq C_{sulfur.t}^j \leq C_{sulfur.tU}^j \\
& && T_L^j \leq T^j \leq T_U^j \\
& && X_{sulfur.tL}^j \leq X_{sulfur.t}^j \leq X_{sulfur.tU}^j
\end{aligned}$$

The optimization problem was solved using the method available in gPROMS program.

## 6.1 Optimal operating conditions for maximum sulfur removal

The optimal operating conditions for each prepared catalyst are displayed in Table 20 below.

**Table 20: Optimal operating conditions for ODS operation utilizing CAT-1, CAT-2 and CAT-3**

Parameter, unit	Values		
	CAT-1	CAT-2	CAT-3
$C_{sulfur.t}$ , wt%	0.758	0.756	0.867
T, K	550	537	543
Time, min	200	189.66	190
Conversion, %	98.73	99.10	<b>99.30</b>

As illustrated in Table 20, the maximum sulfur removal (higher than 99%) has been attained in the presence of CAT-2 and CAT-3 at the optimal operating condition (reaction temperatures of 537K and 543.56K, contact time at 189.66 min and 190 min and initial concentration of sulfur compound at 0.7558 wt% and 0.8668 wt%), respectively satisfying the environmental regulations and obtaining a clean and almost sulfur-free fuel.

## 7. Conclusions

In this work, nanocatalyst ( $\text{Fe}_2\text{O}_3$ ) over composite support ( $\gamma$ -alumina +HY zeolite) has successfully used for ODS operations. It is found that the composite support has a significant impact on the catalyst activity, where the catalyst activity increases with increasing the amount of HY-zeolite in composite support. The highest experimental removal of sulfur compounds obtained is (90.73%) over CAT-3 at 423 K and 100 min.



The simulation and optimization techniques were applied to estimate the best values of kinetic parameters. Linear and Non-Linear approaches were utilized to estimate the optimal kinetic parameters. It is observed that the nonlinear approach has higher accuracy based on the value of the sum of the squared error (SEE) between the experimental data and predicted data. Finally, environmentally friendly fuel was achieved by removing 98.73, 99.10 and **99.30** of sulfur compounds in the presence of CAT-1, CAT-2 and CAT-3, respectively.

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### "Nomenclature

$X_{\text{sulfur}}$	Conversion of sulfur compound.
$C_{\text{sulfur}}$	Concentration of sulfur compound at the end of the reaction.
$C_{\text{sulfur.t}}$	Initial concentration of sulfur present in light gas oil.
$k$	Reaction Rate Constant
$k_{\text{App}}$	Apparent Rate Constant
$D_{ki}$	Knudsen diffusivity
$D_{ei}$	Effective diffusivity
$D_{mi}$	Molecular diffusivity
EA	Activation Energy
Sp. gr <sub>15.6</sub>	Specific gravity of of light gas oil at 15.6°C
$MW_L$	Liquid molecular weight of
R	Gas constant
$n$	Order of reaction
$-r_{\text{sulfur}}$	Reaction rate of sulfur
$r_p$	Particle radius
$r_g$	Pore radius (nm)
$S_g$	Specific surface area of particle
$S_p$	External surface area of catalyst particle
$V_p$	External Volume of catalyst particle
$T_{\text{meABP}}$	Mean average boiling point

$V_g$  Pore volume

## Greek Symbols

$\eta_0$  Effectiveness factor

$\varepsilon_B$  Porosity

$\rho_{L15.6}$  Density of light gas oil at 15.6°C(gm/cm<sup>3</sup>).

$\mathcal{T}$  Tortuosity

$\rho_B$  Bulk density

$\mu_l$  Viscosity of liquid

$v_l$  Liquid molar volume

$v_{csulfur}$  Critical volume of sulfur compound.

$v_{cl}$  Critical molar volume of liquid

$o$  Initial (at time = 0)

$\Phi$  Thiel modulus

$v_{Sulfur}$  Molar volume of sulfur

$\rho_p$  Particle density"

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