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Kinetics of oxidation of sulfur compounds: Rapid oxidation in new design of oscillatory baffled reactor

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Abstract

Recently, one of the most crucial objectives for the petroleum refining industries is producing clean or eco-friendly fuel. The world demands clean diesel utilizing simple processes under safe conditions (i.e., moderate operating conditions). For this purpose, an oscillatory helical baffled reactor (OHBR) was designed to improve the oxidative desulfurization (ODS) process, which is achieved here by converting sulfur compounds found in diesel fuel using a new homemade nanocatalyst. First, the homemade catalyst support, γ-alumina nanoparticles, was prepared using precipitation technology. The γ-Al_2O_3 was then used to design the synthetic nanocatalyst made of iron oxide using the IWI technology with 5% Fe_2O_3. A good distribution of the metal oxides has maintained a good surface area (SA) and pore volume (PV), resulting in high activity. The ODS of sulfur compounds and the performance of the modified nano-catalyst at different safe reaction conditions (frequency of oscillation from 0-2 Hz, amplitude of oscillation from 2-8 mm, reaction temperature from 50-80 oC and residence time only 9 min) were evaluated in the new designed OHBR. The best removal of sulfur was 73.23% at an oscillation frequency of 2 Hz, oscillation amplitude of 8 mm, and oxidation reaction of 80 oC with a residence time of 9 min under constant pressure. A kinetic model related to the sulfur oxidation from real diesel fuel by the ODS process in the OHBR was also investigated in this manuscript to estimate the best kinetic parameters of the relevant reactions in the first order.

Keywords: Kinetics model; Oxidation reaction; Sulfur removal, Nanocatalyst; Oscillatory baffled reactor.

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1- Introduction

The world's demand for feedstock, such as crude oil and its derivatives as a low-cost energy source, has grown, and it is expected to continue at its current rate until 2035. Crude oil is the most significant energy source in the world. With an increasing global energy requirement, crude oil has a crucial role in the global energy resource. The use of low-quality fossil feedstocks, such as heavy oil and sour, has become inevitable due to the depletion of fossil fuel resources and rising energy demand [1-2].

Crude oils are classified and utilized as transportation fuels, such as gas oil (light & heavy), gasoline, and jet fuel. Following that, crude oils contain different types of sulfur, typically in the form of organic sulfur compounds (OSCs). The American Petroleum Institute Gravity API and sulfur content are two properties that greatly influence the values/or properties of feedstock [3]. Types of the OSCs present in petroleum distillates and crude oil are undesirable for some causes [4-6]. The primary cause of acid rain is the emission of sulfur mono and dioxides (SO/or SOx) from the burning of fuels used in transportation. Organic sulfur compounds in fuel cause several corrosion problems in heat exchangers, pipelines, reactors, flungs, and another equipment. Organic sulfur compounds poison the catalyst types used in the reforming of gasoline, which transforms low-octane linear hydrocarbons into high-octane branched and cyclic paraffins. Organic sulfur compounds cause premature failure of poisoning of the catalytic and combustion engine converters used in automotive engines.

While, the sulfur content is determined to protect the environment from pollution. The US Environmental Protection Agency (EPA) and European Union (EU) legislation set the maximum allowable S-level from 10-15 ppm [7-8].

The OSCs compounds in the lower-boiling fractions of petroleum, e.g., the gasoline range, are mainly thiols (RSH), sulfides (RSR), and disulfide (RSSR), which are relatively rapid to decrease in a low-cost process. As a result, middle-distillate fractions, e.g., the fuel oil and diesel range, contain significant amounts of benzothiophenes (TH) and dibenzothiophenes (DBTs), which are considerably more difficult to remove by hydrodesulfurization process (HDS). Mainly, the strictly hindered ones, 4-methyl-dibezothiophene and 4,6-dimethyl-DBT are the most resistant compounds in the current HDS processes, and they retard the rate of HDS [9-10].

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The refining industry has recently actively researched several alternatives to HDS to provide deep desulfurization procedures. These new technologies, such as bio-desulfurization, method of oxidative (ODS), electrochemical desulfurization, process of adsorption, alkylation desulfurization, catalytic distillation, method of precipitation, and ionic liquid extraction technology, may be completed under mild /or low operating conditions and not need the H_2. Most alternative technologies have not yet been shown to be economically feasible on a large scale. Many reasons contribute to the lack of progress in these processes, including the efficacy of hydrodesulfurization technology, opposition to change in the existing refinery community, and the expense of implementing novel methods. The oxidative desulfurization process (ODS) technology, ultradeep desulfurization, rapid oxidation, and without extractive are the more economical and more applicable through the new design of the reactor [11]. The present work aims to provide a suitable kinetic model for the new design (oscillatory baffled reactor (OBR)) and evaluate a new method such as oxidative desulfurization ODS. The work explains a detailed apparent kinetic analysis of the oxidation reaction of OSCs using peracetic acid CH_3CO_3H as an oxidant by new design over (iron oxide loaded on gamma alumina nanoparticles) to produce sulfoxides/or and sulfones.

2- Materials used and experimental work

2.1. Materials used

Real diesel fuel (RDF) is used as a feedstock with sulfur content (0.046413 wt%) supplied by the *Ministry of Oil Iraq-Refineries/Karbala Refinery*. The chemical compounds used for the preparation of nanocatalysts and the main details of RDF are presented in Table 1. Peracetic acid is used as an oxidizing agent. Peracetic acid is produced from the mixing of acetic acid with hydrogen peroxide (1.4 ml H_2O_2/CH_3CO_2H).

Table 1. Specifications of materials and chemicals used for nanocatalyst preparation with the main properties of RDF

Substance	Chemical structure	State of materials	Boiling Point, (ºC)	Melting points, (ºC)	Molecular weight	Purity%	Supplier
Alumina nitrate	$Al(NO_3)_3.9H_2O$	Solid	135	73	375.13	Above 97%	*SIGMA-ALDRICH*
Ammonium hydroxide	NH_4OH	liquid	38	-58	35.064	up to 30%	*SIGMA-ALDRICH*
Ferric nitrate	$Fe(NO_3)_3.9H_2O$	Solid	125	47.2	404	98%	*SIGMA-ALDRICH*
Hydrogen peroxide	H_2O_2	liquid	150.2	-0.43	34	50%	*Merck Millipore /Germany*
Acetic acid	CH_3CO_2H	liquid	117.9	16.73	60.052	99.9%	*J.T.Baker/United States*
Deionized water	H_2O	liquid	100	0	18	DDW	*PPEL-Iraq*

Properties of real diesel feedstock			
API	40.76	Initial boiling point, (ºC)	182
Sulfur content, (ppm)	464.13	10%	201
Flash point, (ºC)	64.2	50%	235
Diesel-color	0.5	90%	318
Content of water	37.9	Boiling point, (ºC)	345

2.2. Nanocatalyst preparation

2.2.1. Precipitation procedure

γ-alumina has been designed according to precipitation technology [12]. Support has been designed in petroleum process engineering [13]. Three stages of such technology to prepare the suitable amount of the γ-alumina are achieved as follows: in the first stage, 15 g of alumina nitrate was dissolved in 80 ml from DDW. When a homogeneous solution is achieved, ammonium hydroxide (NH_4OH) drops were injected into the alumina nitrate solution under a steady magnetic stirring of 450 rpm to form a gel solution. Then, in the second step, the pH of the solution will be increased rapidly from 2.8 to 8.1 to form boehmite. The gel solution is then treated with ethanol and water to remove insoluble contaminants. After washing, the product (boehmite) was filtered utilizing a vacuum pump, and after that, a centrifuge (TG16-WS) was used to remove the water and ethanol from the product. The gel solution is dried in an electric oven at 120 °C overnight. γ-alumina produced after calcination steps until 570 ºC.

2.2.2. IWI procedure

The Incipient Wetness Impregnation technology (IWI) was used to prepare the new nanocatalyst [14]. The dissolution process was carried out as follows: 0.534 g of salt (ferric nitrate $Fe (NO_3)_3.9H_2O$) g was dissolved in 20 ml of double deionized water (DDW) for 60 min in a magnetic stirrer until a total dissolution of ferric nitrate. The mixture was blended in a container with homemade (1.45) g γ-alumina nanoparticles with continuous stirring for 60 min at room temperature to increase impregnation. The sample was transferred to an ultrasonic homogenizer sonicator processor mixer (type: LC-JY92-IIN) and mixed conditions (rate of power 82%, 3 pulses-OFF, 5 pulses-ON, for 100 min, the sample was left to rest for 5 h) to increase the impregnated of iron. Following that, the drying and calcination processes of the impregnated γ-alumina were completed in the furnace using four-stage processes using a programmable furnace (Safe-therm, China). The temperature is firstly raised to 120 °C for one hour, then to 250 °C for one hour, and after that at 400 °C for 1.5 hours, and finally to 570 °C for 2.5 hours under an oxygen flow rate of 5 ml/ min supplied by O_2 generate (NG-300P, volume 0-300 ml/min, 0.4 Mpa, and 650 W) to increase the conversion of the ferric nitrate to iron oxides.

2.3. Field emission scanning electron microscopy (FESEM) technology

The surface morphology for material products such as ($Fe_2O_3/\gamma\text{-}Al_2O_3$) is investigated utilizing FESEM pictures. This technique is used in TESCN MIRA3 FRENCH to notice the nature of the surface of metal oxide Fe_2O_3 particles supported on $\gamma\text{-}Al_2O_3$. The tests are performed at the University of Tehran /Iran.

2.4. Experimental work

The following steps were carried out for the evaluation of the nanocatalyst $Fe_2O_3/\gamma\text{-}Al_2O_3$ prepared in the (OHBR): The first pump1, used to provide diesel fuel to tubular reactors, was made by (*Taiwan*-MFG. NO. 5228). Turning on the heater outside the tubular reactor to heat the tubular reactor to the desired oxidation temperature utilizing the temperature controller. Adding 0.4 g from of ($Fe_2O_3/\gamma\text{-}Al_2O_3$) nanocatalyst inside the tubular reactor through the slot. Injection of oxidant (peracetic acid) supplied through slot. The diesel oscillation (frequency and amplitude) was supplied inside the tubular reactor via turning on the second pump 2 (oscillation pump), which was set at the desired amplitude and frequency of oscillation by the change of the central plunger and voltage regulator, respectively. After reaching steady-state conditions (oscillation frequency, oscillation amplitude, residence time, and oxidation temperature with 1 atm), the product samples were withdrawn from the reactor outlet. Fig. 1 represents the OHBR.

3- Kinetic model section

3.1. Mathematical modeling of OBR for oxidation reaction

The following assumptions were made in the development of the present model for the ODS process in the oscillatory baffled reactor without the effect of the dispersion:

1. Operating conditions for the process are not effective on the fuel phase (no condensation or evaporation occurs into or from the RDF).
2. Operating conditions of experimental unit (oscillatory baffled reactor (OBR)) at (heterogeneous reaction, isothermal conditions, constant pressure).
3. The nanocatalyst is thoroughly wetted inside the OHBR.
4. Perfect mixing in OBR to obtain uniform concentration input and output reactor, as well as temperature throughout the reaction volume.
5. The heat capacity and density of the components are constant.
6. Reaction order (n) with respect to the concentration of sulfur (C_S^n) and order (m) of peracetic acid C_{PA}^m) equal to zero.
7. The Arrhenius equation was applicable to all the oxidation processes.
8. The catalyst was prepared assuming the spherical particle form. Also, the porosity was assumed to be 0.5.

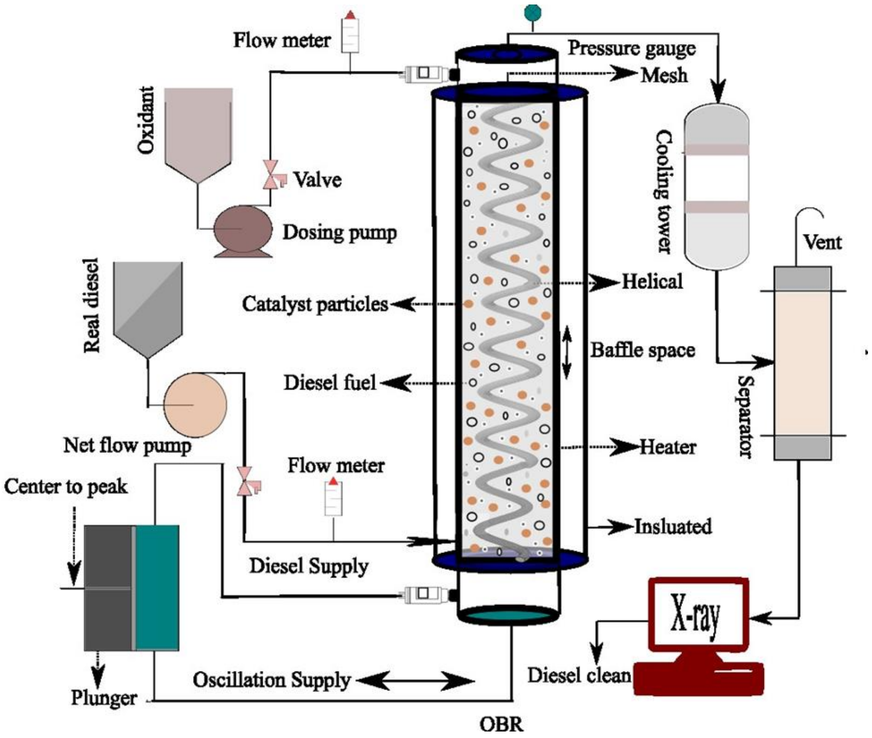

Fig. 1. Pilot plant oscillatory helical baffled reactor

Fig. 2 represents the available tools and required data with the assumptions for modeling the processes of oxidative desulfurization of real diesel fuel.

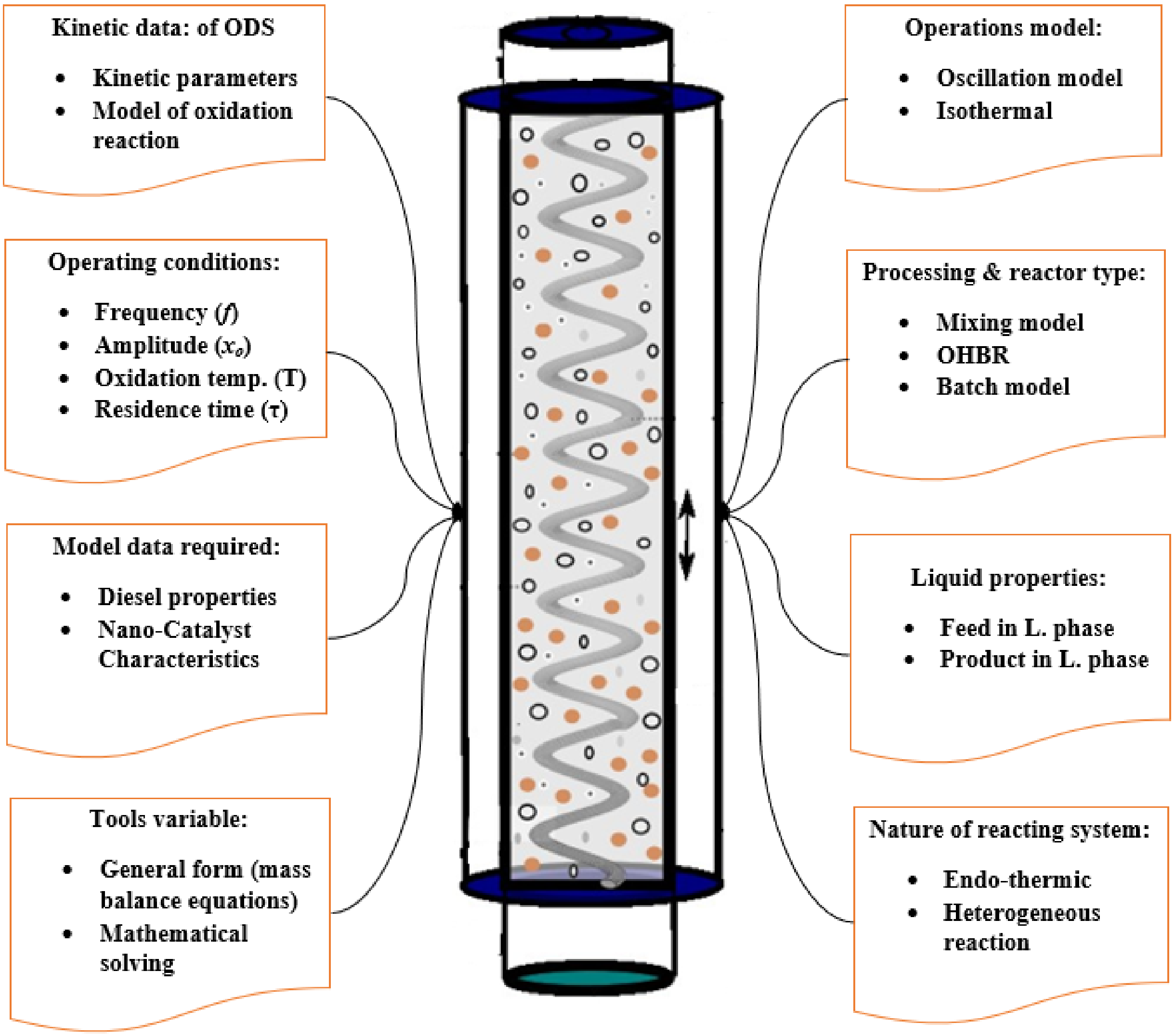

Fig. 2. Required data and available tools for mathematical modeling of ODS reactions

3.2. Mass balance equation for oxidation reaction in OBR

Mass balance equations in the oscillatory helical baffled reactor (OHBR) for the oxidative desulfurization process (ODS) are described with the following set of differential and algebraic equations. The general mass balance over the catalytic reactor for sulfur compound entering the tubular reactor is [17-18]:

The oscillatory helical baffled reactor (OBR) for the ODS process can be described using the following mole balance equation on a batch system:

Overall mole balance in the OBR unit for desulfurization process using nanocatalyst (Fe_2O_3/γ-alumina):

$$[Mole\ of\ S\ in\ OBR] = [Mole\ of S\ out\ OBR] + [Accumulation] + [Dissapparance\ by\ reaction] \qquad (1)$$

Mole of the sulfur and oxidant in the input and output in the oscillatory baffled reactor equal to zero. Therefore, Eq. 1 becomes equal to:

For the batch mode in the OBR

$$[Mole\ of\ S\ in\ OBR] = [Mole\ of\ S\ out\ OBR] = 0 \qquad (2)$$

As a result, Eq. 1 becomes:

$$-[Accumulation\ of\ reaction] = [Dissapparance\ by\ reaction] \qquad (3)$$

The design of the oscillatory baffled reactor to enhance the mass and heat transfer, concerning results of the ODS process improving in the OBR, the sulfur oxidation can evaluate the value of the chemical reaction accumulation and the reaction disappearance, as given below [19]:

$$-[Accumulation\ of\ reaction]_{OBR} = [R_S][V_{T.R}] \qquad (4)$$

$$[Dissapparance\ of\ reaction]_{OBR} = \frac{dN_S}{dt} \tag{5}$$

Where, R_S represents the reaction rate of sulfur oxidation in the ODS technology and $V_{T.R}$, volume of the tubular reactor is the same as the oxidation reaction volume. Substitution, Eq. 4 and Eq. 5 in Eq. 3, the reaction rate of oxidative desulfurization process at constant density (no change in the phase) is observed:

$$-[R_S][V_{T.R}] = -\left[\frac{dN_S}{dt}\right] \tag{6}$$

Following that, the Eq. 6 arrangement is represented as follows:

$$-[R_S] = -\left[\frac{d(\frac{N_S}{V_{T.R}})}{dt}\right] \tag{7}$$

$$-[R_S] = -\left[\frac{dC_S}{dt}\right] \tag{8}$$

C_S: $Concentration\ of\ sulfur, moles/volume$

Sulfur conversion (X_S) can be described by the following equation:

$$C_S = C_o(1 - X_S) \tag{9}$$

$$X_S = \frac{C_{so} - C_S}{C_{so}} \tag{10}$$

In general, kinetic models can be used to obtain intrinsic parameters of any rate of reaction. There are several experimental proposals, such as a reduction of catalyst amount and flow rate in order to maintain a specific residence time, etc. The only way to obtain kinetic information is to assume a kinetic model and adjust its parameters by comparing the predicted (model) results with the observed (experimental) data. Therefore, we will assume the kinetic model of the ODS process in the OBR as follows:

1. First-order kinetic model for the ODS in OBR

When the sulfur oxidation reaction followed first-order kinetics, the equation of reaction rate can be expressed as follows:

$$\text{For pseudo order equation of ODS} = -[R_S] = KC_S^n\, C_{PA}^m \tag{11}$$

The concentration of oxidant (C_{PA}^m) and constant reaction rate (K) equal to the apparent rate constant ($K_{app.}$) can be represented as [20]:

$$K_{app.} = K\, C_{PA}^m \tag{12}$$

Firstly, assuming the $K_{app.} = K_p$ and in the pseudo-first-order oxidation reaction (n=1) and from Eq. 12, Eq. 11 can be rearranged to become:

$$-[R_S] = K_p\, C_S \tag{13}$$

The Eq. 13 sub in Eq. 8 and can be rearranged to become, as shown below:

$$-\left[\frac{dC_S}{dt}\right] = K_p\, C_S \tag{14}$$

$$\int_{C_{S_0}}^{C_{S_f}} \frac{dC_S}{C_S} = -\int_0^t K_p\, dt \tag{15}$$

$$ln\frac{C_{S_f}}{C_{S_0}} = K_p\, t \tag{16}$$

Reaction rate constant for oxidation reaction (K_p) can be determined for each reaction using the Arrhenius equation as follows:

$$K_p = K_o e^{-\frac{EA}{RT}} \tag{17}$$

Sub., Eq. 17 in Eq. 16 and rearrangement:

$$C_{S_f} = C_{S_0} Exp\left[K_o e^{(-\frac{EA}{RT})}\ t\right] \tag{18}$$

2. 2nd Order kinetic model for ODS in OBR

The pseudo-second-order oxidation reaction (n=2), the following reaction rate equation for the ODS process can be noticed below:

$$-\frac{dC_S}{dt} = -[R_S] = K_p\, C_S^n \tag{19}$$

$$-[R_S] = -\left[\frac{dC_S}{dt}\right] \tag{20}$$

$$\int_0^t dt = \int_{C_{S_0}}^{C_{S_f}} \frac{dC_S}{R_S} \tag{21}$$

$$t = \int_{C_{S_0}}^{C_{S_f}} \frac{dC_S}{R_S} \tag{22}$$

$$-[R_S] = K_p\, C_S^n \tag{23}$$

Following that, by separating and integrating Eq. 22, we obtain:

$$\int_{C_{S_0}}^{C_{S_f}} \frac{dC_S}{C_S^n} = \int_0^t K_p\, dt \tag{24}$$

The final expression for the pseudo-second-order reaction can be written as:

$$C_{S_f} = \left[K_o e^{(-\frac{EA}{RT})}\ t(1-n) + \frac{1}{{C_{S_0}}^{n-1}}\right] \tag{25}$$

The effectiveness factor (ɳ) can be determined as a function of Thiele modulus (M_T) with the following equation valid for sphere particles [21]:

$$\eta = \frac{1}{M_T}\left[\frac{1}{tanh3M_T} - \frac{1}{3M_T}\right] \tag{26}$$

M_T, Represent of the Thiele modulus is equal to:

$$M_T = L\sqrt{\frac{(n+1)K\, C_{PA}^{m-1}}{2D_{eff}}} \tag{27}$$

L is the characteristic size of the (Fe_2O_3/γ-Al_2O_3) nanoparticle. For sphere particles

$$L = 0.33\, r_p \tag{28}$$

r_p is the radius of the nanocatalyst pellet (cm)
D_{eff}, is effective diffusivity can be expressed as:

$$D_{eff} = \frac{catalyst\ porosrsity * Molecular\ diff.of\ sulfur}{Catalyst\ tortuosity} = \frac{\epsilon_p D_m}{\tau_p} \tag{29}$$

Where, porosity is represented as the ratio of pores volume of catalyst nanoparticles to total volume. In contrast, tortuosity is defined as the actual distance traveled by the compound divided by the unit length of the medium. The porosity of the nanoparticles is measurable, whereas tortuosity is hard to characterize. The tortuosity can be expressed approximately by the relation:

$$\tau_p = \frac{1}{Catalyst\ porosity} = \frac{1}{\epsilon_p} \tag{30}$$

If the porosity is unknown, sufficient accuracy is obtained by approximating porosity = 0.5; thus Eq. 29 can be rewritten [22]:

$$D_{eff} = 0.25\, D_m \tag{31}$$

The molecular diffusion coefficient of the sulfur in RDF was measured by the empirical Wilke–Chang equation [23]:

$$D_{AB} = \frac{7.4 * 10^{-8} [\emptyset_B M_B]^{0.5} T}{\mu_B v_A^{0.6}} \tag{32}$$

The diffusivity function with temperature can be stated as follows:

$$D_{AB} = D_{ABo} \left[\frac{T}{T_o}\right]^{1.5} \tag{33}$$

From Table 2, it has been observed that the ODS of RDF employing the prepared nanocatalyst is followed by the pseudo-first-order kinetics, giving a better fit than pseudo-second-order kinetics. While in Table 3, Thiele modulus (M_T) results for real diesel fuel oxidative desulfurization reactions utilizing the prepared nanocatalyst (Fe_2O_3/γ-Al_2O_3) at various reaction temperatures are presented here. The findings presented in Table 3 demonstrate that every product's Thiele modulus (MT) value is less than 0.4[24], demonstrating that the impact of internal mass transfer on the total oxidation rate can be disregarded/or neglected.

From the Arrhenius equation, the activation energy can be obtained, with respect equations below [18]:

$$K = A_o Exp\left[-\frac{E_A}{RT}\right] \tag{34}$$

$$lnK = lnA_o - \left[\frac{E_A}{RT}\right] \tag{35}$$

Following that, a plot of (1/*T(K)*) against (ln *K*) [25] will give a straight line with a slope equal to (*-EA/R*), where (EA) activation energy and *(R)* gas constant is then linearly evaluated, as shown in Fig. 3, for nanocatalyst, respectively. The values of the activation energy for these nanocatalysts at different frequencies of oscillation are 9.061 KJ/mol, 9.550 KJ/mol, 5.389 KJ/mol, and 9.539 KJ/mol at 2 Hz, 1.5Hz, 1Hz, and 0.5 Hz, respectively.

4- Results and discussion

The surface morphologies of the prepared supported (γ-alumina) and nanocatalyst (Fe_2O_3/γ-alumina) have been displayed by the FESEM, represented in Fig. 4 a and b. The micrographs observe a good distribution of the metal oxide in Fig. 4bon the surface of the nano-catalyst with a well-developed pore and the particles with a uniform shape [15]. Also, particles of Fe_2O_3 were deposited well on the surface of γ-alumina without any agglomeration.

The oscillation (amplitude and frequency) effect upon the removal of oxidative desulfurization process of sulfur compounds has been investigated at 4 mm, 6 mm, and 8 mm and 0.5 Hz, 1Hz, 1.5Hz and 2 Hz at different oxidation temperatures of 50 ^oC, 65 ^oC, and 80 ^oC and residence time only 9 min under atmosphere pressure, and the results of such an effect are demonstrated in Fig. 5 and Fig. 6. Based on the results presented in these figures, it has been observed that increasing the amplitude of oscillation leads to an increase in the oxidation reaction of sulfur compounds. The amplitude of oscillation causes the formation of the eddies propagated inside the OHBR [16]. It increased the oscillation's amplitude, which enhanced the OHBR's mixing efficiency and improved the oxidation reaction rate, reaction rate, and decreasing residence time (i.e., only needed 9 min to obtain optimal removal). Increasing the oscillation amplitude of the reaction offers the chance for the reactants to contact and then react. The removal of sulfur compound increased from 43.29% to 53.74% when the oscillation amplitude increased from 4 mm to 6 mm and improved the removal to 64.04% with increasing amplitude to 8 mm at 1.5 Hz and 80 ^oC, as shown in Fig. 5. These results indicate that the best removal was 73.23% under moderate conditions: amplitude of oscillation of 8 mm, frequency of oscillation of 2 Hz, reaction temperature of 80 ^oC, and constant pressure, and a short residence time of only 9 min, as shown in Fig. 6.

From the experimental result, it is noticed that small amplitudes give poor vortex propagation and the high value of the amplitude of oscillation will cause random mixing (not good mixing/or not investigated the radial mixing). Therefore, it will affect the ODS process.

Table 2. Kinetic model result for the oxidation reaction

Nanocatalyst	**Oxidation reaction order**	**Oxidation temperature, °C**	**$K_{app.}$ $(Con)^{1-n}$ $(min)^{-1}$**	**Standard deviation**	**Parameter**
Nanocatalyst (Fe_2O_3/γ-Al_2O_3)	1st order	50	$6.67*10^{\wedge -2}$	0.011709	Frequency of oscillation= 0.5 Hz
		65	$7.95*10^{\wedge -2}$		
		80	$9.04*10^{\wedge -2}$		
		50	$8.44*10^{\wedge -2}$	0.007908	Frequency of oscillation= 1 Hz
		65	$9.38*10^{\wedge -2}$		
		80	$10.01*10^{\wedge -2}$		
		50	$8.43*10^{\wedge -2}$	0.016002	Frequency of oscillation= 1.5 Hz
		65	$11.08*10^{\wedge -2}$		
		80	$11.36*10^{\wedge -2}$		
		50	$10.99*10^{\wedge -2}$	0.018407	Frequency of oscillation= 2 Hz
		65	$13.23*10^{\wedge -2}$		
		80	$14.64*10^{\wedge -2}$		
	2nd order	50	$1.97*10^{\wedge -4}$	5.2E-05	Frequency of oscillation= 0.5 Hz
		65	$2.51*10^{\wedge -4}$		
		80	$3.01*10^{\wedge -4}$		
		50	$2.72*10^{\wedge -4}$	3.91535E-05	Frequency of oscillation= 1 Hz
		65	$3.17*10^{\wedge -4}$		
		80	$3.50*10^{\wedge -4}$		
		50	$2.72*10^{\wedge -4}$	8.44E-05	Frequency of oscillation= 1.5 Hz
		65	$4.09*10^{\wedge -4}$		
		80	$4.26*10^{\wedge -4}$		
		50	$4.04*10^{\wedge -4}$	0.000125	Frequency of oscillation= 2 Hz
		65	$5.48*10^{\wedge -4}$		
		80	$6.54*10^{\wedge -4}$		

Table 3. Thiele modulus results at different operation conditions

Temperature (K)	**K(1/sec)**	**D_{AB} (cm^2/sec)**	**D_{eff} (cm^2/sec)**	**M_T**	**Standard deviation**
323	$10.99*10^{\wedge -2}$	$1.817*10^{\wedge -7}$	$4.542*10^{\wedge -8}$	0.000104	1.52753E-06
338	$13.23*10^{\wedge -2}$	$2.081*10^{\wedge -7}$	$5.203*10^{\wedge -8}$	0.000101	
353	$14.64*10^{\wedge -2}$	$2.221*10^{\wedge -7}$	$5.554*10^{\wedge -8}$	0.000103	

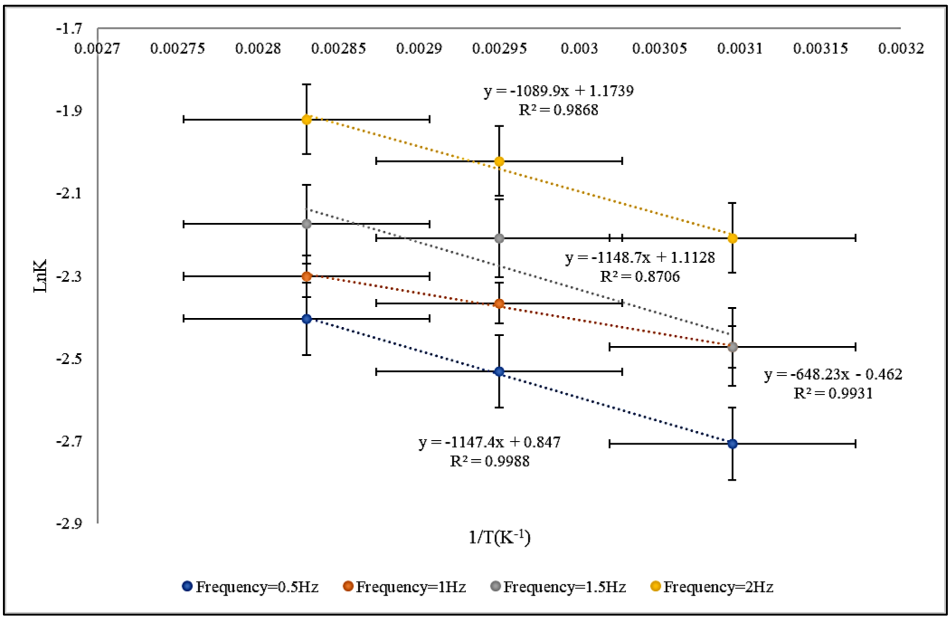

Fig. 3. lnK versus 1/T (K) of ODS for first order

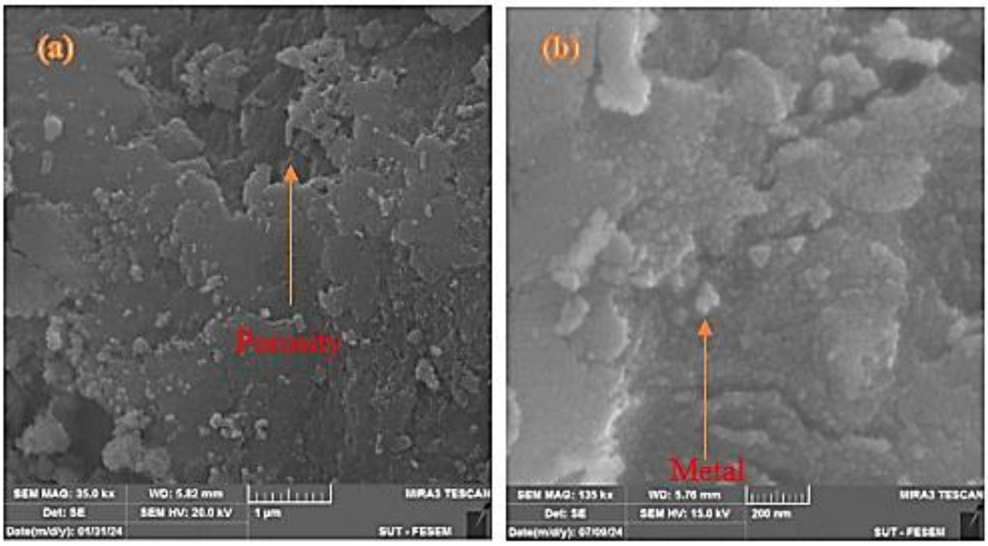

Fig. 4. FESEM analysis for support (γ-Al2O3) (a), and nanocatalyst (Fe2O3/γ-Al2O3) (b)

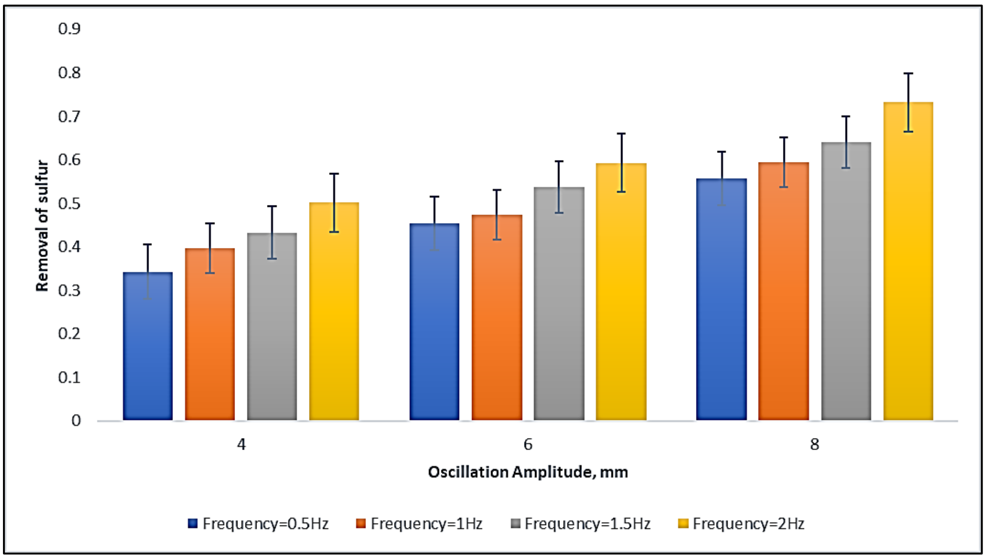

Fig. 5. Effect amplitude of oscillation on ODS process for different frequencies of oscillation, reaction temperature 80°C, and residence time 9 min under 1 atm

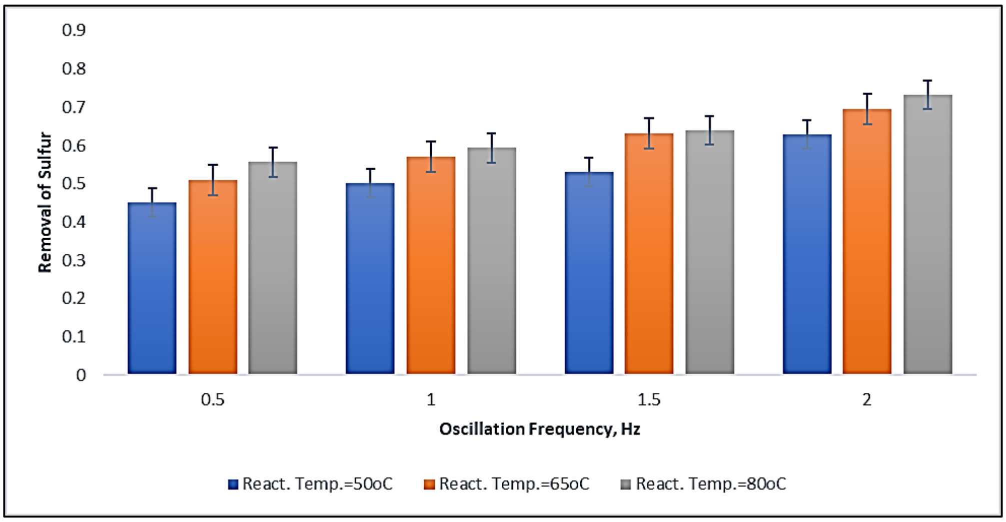

Fig. 6. Effect frequency of oscillation on ODS process for different oxidation temperatures, the amplitude of oscillation 8 mm, and residence time 9 min under 1 atm

5- Conclusion

A new synthetic nanocatalyst ($Fe_2O_3/\gamma\text{-}Al_2O_3$) has been prepared to enhance diesel fuel by removing sulfur compounds, and such a novel nanocatalyst has successfully been prepared utilizing impregnated technology. Results indicated a precisely defined morphology, high surface area, uniform distribution, and stable structure. Removal of sulfur by new oxidant peracetic acid from RDF has been conducted in the novel design of an oscillatory helical baffle reactor based on the new nanocatalyst ($Fe_2O_3/\gamma\text{-}Al_2O_3$) using different operating conditions (frequency of oscillation from 0-2 Hz, amplitude of oscillation from 2-8 mm, reaction temperature from 50-80 ^oC and residence time only 9 min). Results revealed that the ODS process appears to be technically and economically feasible for processing ultra-low sulfur fuel. The technology of IWI is a successful method for the preparation of ($Fe_2O_3/\gamma\text{-}Al_2O_3$) depending on the good distribution of the iron oxide beside the maintained high surface area and pore volume. The catalyst activity and the process conversion rely mainly on the active and the reactor type. From the result, good sulfur removal from real diesel fuel can be accomplished using the OHBR by oxidation reactions over a new homemade nanocatalyst ($Fe_2O_3/\gamma\text{-}Al_2O_3$) under mild operational conditions (frequency of oscillation= 2 Hz, amplitude of oscillation= 8 mm, oxidation temperature= 80 °C, and constant pressure 1atm), resulting in good ODS reactions and higher conversion of 73.23% of sulfur compound resulting in good fuel quality and lower pollution. The ODS reactions clearly show that such a new catalyst can be used for sulfur removal as they have followed first-order reactions.

Nomenclature

C_s	Concentration of species D	g/cm^3
C_{PA}	Concentration of species O	g/cm^3
Dm	Molecular diffusion coefficient of sulfur in fuel	cm^2 /sec
D_{eff}	Effective diffusivity	cm^2 /sec
Dp	Average crystal size of particles	nm
EA	Activation energy	kJ/mole k
K_1	Rate constant for ODS process	1/sec
K_2	Rate constant for ODS process	$(Con)^{1-n}$ $(min)^{-1}$
K_o	Frequency factor or pre-exponential factor	1/sec
L	Characteristic size of the particle	cm
m	Order of the reaction with respect to species oxidant	………
n	Order of the reaction with respect to species sulfur	………
M_B	Molar mass of solvent	g/mole
M_T	Thiele modulus	……….
R	Universal gas constant	J / mole. K
−Rs	Rate of reaction	$mole/cm^3$ .sec
r_p	Radius of catalyst pellet	cm
t	reaction time	min
T	Temperature of reaction	K
$V_{T.R}$	Volume of tubular reactor	cm^3

Greek Letters

ϵ_p	Porosity of catalyst pellet	………….
η	Catalyst effectiveness factor	…………..
μ_B	Viscosity of solvent	c.p
ν_A	Liquid molar volume of the solute	cm^3 /mole
ρ	Density of reactant	g/cm^3
τ_p	Tortuosity of the catalyst pellet	…………..

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حركية أكسدة مركبات الكبريت: الأكسدة السريعة في التصميم الجديد لمفاعل متذبذب ذي حواجز

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الخلاصة

في الآونة الأخيرة، كان أحد أهم الأهداف لعملية تكرير النفط هو إنتاج الوقود النظيف/أو الوقود الصديق للبيئة. العالم يتطلب إلى وقود الديزل النظيف وبواسطة عمليات بسطة وسهله وفي ظل ظروف آمنة (أي ظروف تشغيل معتدلة). ولهذا الغرض، تم تصميم مفاعل متذبذب ذي حواجز حلزوني (OHBR) لتحسين عملية إزالة الكبريت التأكسدي (ODS)، والتي يتم تحقيقها هنا لتحويل مركبات الكبريت الموجودة في وقود الديزل باستخدام محفز نانوي جديد محلي الصنع. أولاً، تم تحضير سطح المحفز محلي الصنع، جسيمات $\gamma-$الألومينا النانوية، باستخدام تكنولوجيا الترسيب. وبعد ذلك استخدام $\gamma-Al_2O_3$ لتصميم المحفز النانوي المصنوع من أكسيد الحديد باستخدام تقنية التنقيع (IWI) وبنسبة (Fe_2O_3%٥). لقد حافظ التوزيع الجيد لأكاسيد المعادن على مساحة سطحية جيدة (SA) وحجم مسامي (PV)، مما أدى إلى فعالية مرتفعة. المواد المستنفدة للأوزون للمركبات الكبريتية وأداء المحفز النانوي المعدل في ظروف تفاعل اعتيادية مختلفة (تردد التذبذب من ٠–٢ هرتز، سعة التذبذب من ٢–٨ مم، درجة حرارة التفاعل من ٥٠–٨٠ درجة مئوية وزمن التفاعل ٩ دقائق فقط) تم تقييمها في المفاعل المتذبذب ذي حواجز (OHBR) المصمم حديثًا. تم أيضًا دراسة نموذج حركي متعلق بأكسدة الكبريت من وقود الديزل الحقيقي بواسطة عملية المواد المستنفدة للاكسدة في مفاعل (OHBR)، في هذه المخطوطة لتقدير أفضل مرتبة حركية للتفاعلات وكانت من الدرجة الأولى.

الكلمات الدالة: النموذج الحركي، تفاعل الأكسدة، إزالة الكبريت، المحفز النانوي، مفاعل متذبذب.