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Optimization for Kinetic Model of Oxidative Desulfurization of Sour Naphtha Over a Natural Base Zeolite Catalyst in a Three Phase Oscillatory Baffled Reactor

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Abstract

The oxidative desulfurization (ODS) of Iraqi sour naphtha was studied in a novel design of a heterogeneous catalytic reactor. Molecular oxygen was used as an oxidizing agent and a clay-based zeolite was used as a catalyst. The present work of ODS was conducted in a three-phase oscillatory baffled reactor under different operating conditions; temperature =25, 35, 45, and 55°C, residence times (1 – 14 min), Reynold number of oscillation (175, 235, 315), and net flow Reynolds number (25, 50, 75). A zeolitic base ODS catalyst was prepared and applied as a heterogeneous catalyst in the OBR unit. The aim of this study is to obtain the ODS kinetic parameters and concentration profile of the sulfur compounds in the naphtha cut. The model developed was based on the properties of the feedstock, characteristics of the catalyst, and operation conditions inside the OBR according to the experimental observations. To obtain the kinetic model parameters mass transfer and flow conditions were applied in the model network. The equations were employed in gPROMS software to simulate the experimental results of sulfur concentration remaining after completion of the ODS process. The set of equations was successful in simulating the experimental results with a 5% absolute error. The predicted data were used for optimizing the kinetic parameters to get the ODS kinetic parameters based on minimizing sulfur concentration.

Keywords: Oxidative desulfurization, three-phase, oscillatory baffled reactor, optimization.

1. Introduction:

Although a lot of work has been done on creating alternative fuels, petroleum, or crude oil, continues to be the most popular and cost-effective source of energy for meeting global energy demands, notably in the transportation sector, with a share of 33.1% [1]. Crude oil reserves are

presently running out, and the oil quality is getting worse, especially in terms of density and sulfur content. It has been reported that the sulfur content will rise from 4500 to more than 6000 ppm by 2025[2]. In response to this dangerous rise and the harmful rise in pollution levels, extensive research on sulfur elimination should be conducted [3]. Naphtha cut is the main source of gasoline fuel which represent the daily fuel all over the world. Currently, and due to the massive destruction that happened in North Refineries Company, most of the naphtha produced is directly fractionated into gasoline without further sweetening resulting in high levels of sulfur oxides emitted to the atmosphere evryday[4, 5]. To be committed to the international regulations of sulfur emission, the sulfur content in gasoline should not exceed 10 ppm[5-9]. In the conventional desulfurization process, hydrodesulfurization (HDS) is conducted in the commercial packed bed reactor at severe operating conditions of temperature (not less than 280°C) and pressure (not less than 15 bar)[10]. Also, the HDS catalysts which are mostly composed of noble metals are expensive, and applying a cost-effective (naturally based) catalyst would provide more commercial benefits for the petroleum industry[11]. The HDS process also costs a lot due to the high hydrogen consumption needed for hydrotreatment per barrle[12] and the additional additives needed to prolong the lifetime of the HDS catalyst to prevent rapid deactivation due to exposure to severe operating conditions[13]. Thus, several works are conducted by different research groups to deeply clean the gasoline fuel at fairly mild operating conditions[14]. Oxidative desulfurization (ODS) is one of the promising alternatives to HDS that deeply desulfurize the light fuel cuts without using hydrogen and at mild operating conditions[15-17]. Despite these extensive efforts of research, the ODS still needs more supportive technical and scientific data to enforce the commercialization of the process. Cako et al.[18] conducted desulfurization of raw naphtha to make aviation fuels using dual-frequency acoustic cavitation (acoustic cavitation) and UV assisted advanced oxidation processes (AOPs) reaction system. They found that pseudo first order kinetic model was followed by every system of acoustic cavitation-based treatment. With treatment costs exceeding \$100 USD m⁻³, ozone-aided acoustic cavitation was the most expensive process.

Gosh et al.[19] described the selective hydro-desulfurization of FCC naphtha at low olefin saturation by a kinetic model. They used 348 molecules to represent the FCC naphtha. With the help of the structure-oriented lumping (SOL) framework, the reaction chemistry was specified in terms of reaction rules. The kinetic parameters were calculated from the experimental data set that included information from both commercial refineries and pilot plants, covering a wide

range of process conditions and feed compositions. Mohammed et al.[20] converted agricultural waste into activated carbon (AC) that had been modified to withstand the gradual loss of ODS activity. To increase the AC's lifetime of activity, it was coated with aluminum oxide and impregnated with manganese. Investigations were done into the ODS catalysts' kinetics. The ODS reaction was demonstrated to follow first-order kinetics and to be unaffected by the coating layer. Investigations were made into the activity decay. It was discovered that the coated catalyst had a higher activation energy for the deactivation reaction than the uncoated catalyst. Soltanali et al.[21] conducted desulfurization by zeolite catalysts in the naphtha reforming process in the absence of hydrogen. ZSM-5 catalyst (Si/Al = 50) was successfully synthesized to study the impact of operating conditions on the naphtha reforming process using a zeolite catalyst in the absence of hydrogen. Based on the kinetic models for the naphtha reforming process in the absence of hydrogen, the results of the experimental design were analyzed. The ideal conditions were $WHSV = 4.02 \text{ h}^{-1}$, temperature = 349.09°C , and pressure = 20 bar to achieve the highest octane number, liquid recovery, and S conversion, and the lowest coke deposition on the catalyst and benzene content. The actual results from reactor tests conducted under ideal circumstances showed that the proposed model was entirely valid. Rezvani et al.[22] prepared a novel form of inorganic-organic hybrid nanocatalyst by combining magnesiocopperite (MgCu_2O_4), polyvinyl alcohol, and the potassium salt of Cu-substituted phosphomolybdic acid. They used real gasoline and model oil to examine the activity of the prepared catalyst. After 60 minutes at 35°C , high ODS efficiency of 97% was attained utilizing hydrogen peroxide/acetic acid as an oxidant. Ahmad et al. [23] utilized hydrogen peroxide and formic acid for ODS of model sour oil in presence of Fe-ZSM-5. They achieved 96% conversion of the sulfur compounds in 60 minutes at a temperature of 60°C . Additionally, the catalyst was effective in the ODS of naphtha. Nawaf et al. [24] examined how well a heterogeneous catalyst performed ODS of S in light gas oil. Additionally, they created a trickling bed reactor process model that may be used for ODS process design and optimization. For the first time, the present study conducted a three-phase ODS process of naphtha in an oscillatory baffled reactor (OBR) unit. The reactor was used to obtain the kinetic parameters of a three-phase ODS process over a naturally based prepared ZSM-5 catalyst. This novel model is based on multi lump approach and based on real sour Iraqi naphtha cut.

2. Experimental work

2.1. Materials

The feedstock used in the present study was the naphtha cut that is produced in North Refineries Company, Iraq. The product was used as received and its specifications of it are shown in Table (1).

Table (1) Specifications of the naphtha feedstock.

Specific gravity	0.730
Viscosity (Sct)@25°C	0.8
Total Sulphur (ppm)	1091
API gravity	62.33
Distillation	
Initial boiling point (°C)	42
5%	60
10%	70
20%	88
30%	108
40%	120
50%	140
60%	153
70%	173
80%	191
90%	215
95%	230
End boiling point	248

Oxygen gas (99.9999% purity) was used as an oxidizing agent. Zeolite (ZSM-5) was used as support for the ODS catalyst. Specifications of the ZSM-5 are shown in Table (2).

Table (2) Physical properties of the ZSM-5.

Relative crystallinity, %	90
Total surface area, m ² /g	320
Microporous surface area, m ² /g	270
Silica-alumina ratio	27.5
Na ₂ O, wt%	0.04
SO ₄ , wt%	0.2
Cl ⁻ , ppm	1<

2.2 Preparation of catalyst

The ZSM-5 was impregnated with 6% Fe. The salt solution of Fe metal was prepared by

dissolving 4 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt in 30 ml of deionized water and stirring to obtain a clear solution of Fe. The dry ZSM-5 particles, 12 g, were placed in a conical flask and a funnel was used to add the impregnation solution drop-by-drop [25] with stirring by a magnetic stirrer. The impregnated ZSM-5 was further mixed in an ultrasonic sonicator (Toption, China, 650W) for half an hour and was left at room temperature overnight. The solution was heated on the hot plate magnetic heater stirrer at 60°C until all water was evaporated. The wet Fe/ZMS-5 was placed in a drying oven at 100°C for 6 h. Then the sample was calcined at 550°C for 4 hours at a heating rate of $5^\circ\text{C}/\text{min}$ under a nitrogen atmosphere inside the tubular furnace (Safetherm, China, maximum temperature: 1200°C).

2.3 Experimental setup

The experimental data for obtaining the kinetic parameters were obtained by conducting a series of experiments on the ODS of naphtha in a continuous OBR unit, a schematic diagram of the experimental rig is shown in Figure (1). The sour feedstock, naphtha cut, was stored in a feed storage tank and was flown to the reactor via a syringe pump 1 (Eurodyne Limited, UK). The flow rate of the feedstock was adjusted and oscillated via the syringe pump utilizing Sapphire commander software[26]. The volume of the flown feedstock was used to adjust the amplitude of oscillation to achieve the desired Reynolds number of oscillation while the frequency of oscillation was adjusted by setting the lead screw of the tubing that connects the pump to the feedstock tank. The molecular oxygen gas was fed through a mass flow meter and delivered to the bottom of the OBR. To generate the oscillatory eddies inside the tubular reactor a second syringe pump (syringe pump 2) was used for this purpose. It is connected to the tubular reactor via a polytetrafluoroethylene tube and a customized union. The two syringe pumps provide a very low flow rate with a high capability of adjustment of frequency and amplitude via the Sapphire commander.

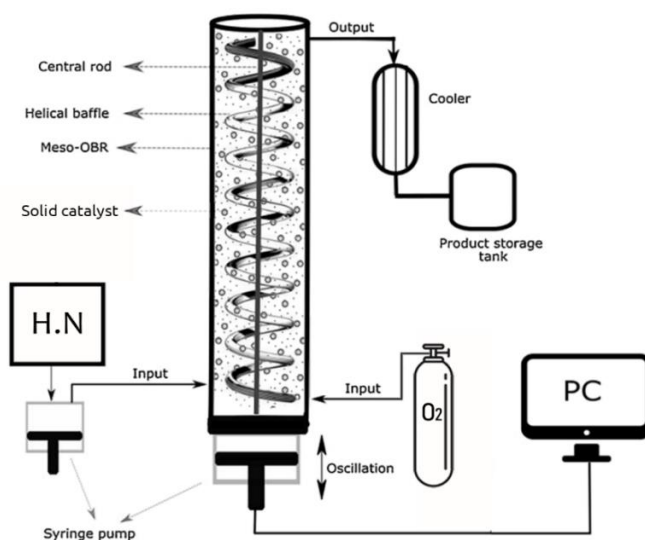


Fig. (1): The experimental setup

2.4 Running of experiments

The main operating condition of the present study is the dimensionless number of oscillations, the oscillatory Reynolds number, Re_o , which is a function of both frequency and amplitude of oscillation as shown in Equ. 1 [27]:

$$Re_o = 2\pi f x_0 \rho D / \mu \quad (1)$$

Also, temperature and residence time are other study key parameters. Moreover, the flow rate of the feedstock is represented in terms of the conventional Reynold's number (Re_n) as shown in Equ. 2

$$Re_n = \rho u D / \mu \quad (2)$$

Where:

D: Diameter of the tubular reactor

ρ : Density of feedstock

μ : Viscosity of feedstock

f: Frequency of oscillation

x_0 : amplitude of oscillation

Table (3) shows the matrix of experimental variables of the present study.

Table (3). Matrix of experiments.

Variable	Level	Value
Temperature, °C	4	25,35, 45, 55
Residence time, τ , min	8	1-14
Reynold's number, Re_n	3	25, 50, 75
Reynold's number of oscillation, Re_o	3	175, 235, 315

The OBR unit system operated at the severest operating conditions (Temperature = 100 °C, frequency of oscillation= 4.3 Hz, and amplitude of oscillation = 8 mm) for one hour to check for leaks of gas and liquid through the tubing lines and valves. Then, the experimental rig was rinsed with ethyl alcohol and water to get rid of any remnants left from previous runs.

Under the varied operating conditions described in Table 3, the ODS process was carried out in the OBR utilizing oxygen gas as an oxidant and Fe/ZMS-5 as a catalyst. [26]. The temperature of the reactor was adjusted to the required temperature (60, 70, or 80°C) using the temperature controller (0.1 oC) to perform the experimental runs. The catalyst (Fe/ZSM-5) was distributed throughout the OBR, and the naphtha cut was mixed before being supplied into the OBR. To accomplish the desired residence duration for each cycle, the feed flow rate was regulated using syringe pump 1. The mixture was oscillated using syringe pump 2 with the "Sapphire Commander" software adjusted to the appropriate oscillation frequency and amplitude. The liquid samples were collected from the cooling system's liquid outflow and labeled. To remove the sulfur compounds, a sample of the product (treated gasoline) was allowed to settle to allow separation of the polar aqueous phase. The residual sulfur content in the sample was then compared to that of the fresh sample. After the studies were completed, the naphtha was cut, the fuel syringe pumps 1, 2, and 3, the dosing pump, and the temperature controller was switched off, all open valves were closed, and all heating systems were turned off. The reactor was removed and cleaned after cooling to room temperature. To explore the influence of mixing on the ODS of the sulfur compound in the naphtha cur, preliminary ODS experiments were performed, and each experiment was replicated to ensure that the percent error was not exceeded 5%.

2.5 Analysis of samples

An X-ray sulfur analyzer (ASE-2, Bourestnik, Russia) was used to obtain the sulfur content for the sour naphtha and the treated naphtha. This device used Energy Dispersive X-ray fluorescence mechanism for testing the sulfur concentration. The efficiency of sulfur removal was calculated by Equ. 3:

$$X_S = \frac{C_{Sin} - C_{Sout}}{C_{Sin}} \times 100 \dots \dots \dots (3)$$

Where the family name may be ambiguous (e.g., a double name), please indicate this. Present the authors' affiliation addresses (where the actual work was done) below the names. Indicate all affiliations with a lower-case superscript letter immediately after the author's name and in

front of the appropriate address. Provide the full postal address of each affiliation, including the country name and, if available, the e-mail address of each author.

3. Modeling and optimization

The mathematical model can be validated by experimental data, including measurements of the accomplishment of work. In the present study, the ability of the mathematical model to predict the performance of the OBR for the ODS reactions system was estimated. gPROMS software (License ref: 27552, Version 7.017) was used to develop the model and simulate the ODS process in the OBR.

3.1 Mathematical model of OBR for ODS (general model)

The following assumption has been made in the development of the present model for the ODS process in the OBR without the effect of the dispersion: -

1. The oscillatory baffled reactor (OBR) is in steady-state operation.
2. Constant pressure operation of OBR.
3. OBR operates under isothermal conditions.
4. Feedstock and products of naphtha are in the liquid phase.
5. Ideal mixing inside OBR to get uniform concentration and temperature throughout the reaction volume.
6. For each oxidation reaction, the Arrhenius equation is applicable.
7. The order of reaction with respect to oxygen gas was (0) for the ODS of sulfur.

Figure (2) shows the required data and available tools with the assumptions for modeling and simulation processes of naphtha desulfurization.

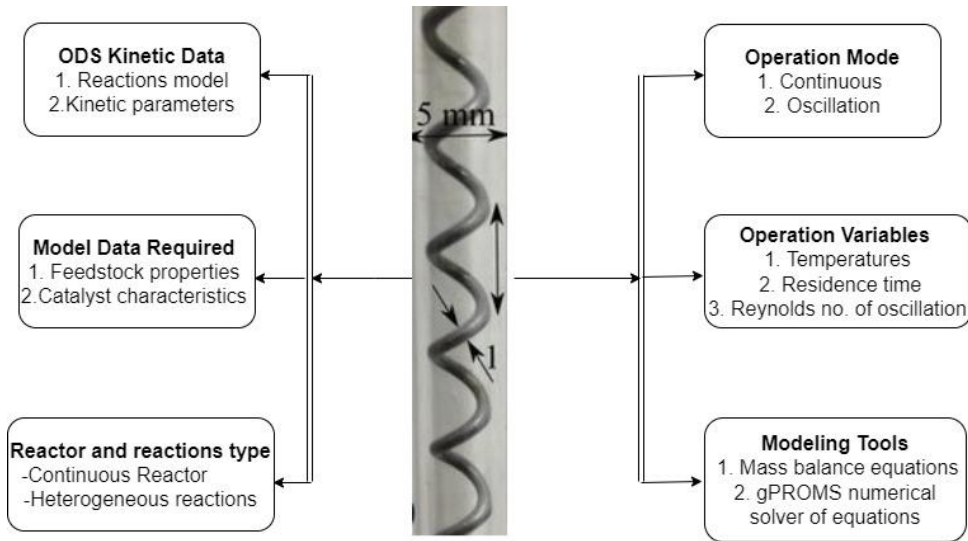


Fig. (2): Modeling and optimization tools of ODS reactions in the OBR.

3.2.1 Mass Balance Equations

The mass balance equation in the OBR for the ODS process is composed of several differential and algebraic equations.

The general mass balance over the OBR for sulfur (S) is: -

$$\text{Input} = \text{Output} + \text{Consumption by reaction} + \text{Accumulation} \dots\dots\dots (4)$$

$$\text{Input of S, moles/time} = F_S$$

$$\text{Output of S, moles/time} = F_S + dF_S$$

$$\text{Consumption of S by reaction, moles/time} = (-r_S) \cdot dV$$

$$\text{Accumulation of S} = 0$$

Inserting the above terms into equation (2) and rearranging it, we obtain:

$$-dF_S = (-r_S) \cdot dV \dots\dots\dots (5)$$

Where:

$$F_S = C_S v_t \dots\dots\dots (6)$$

C_S : Concentration of S, moles/volume

v_t : Volumetric flow rate, volume/time

Since

$$F_S = F_{S0}(1 - X_S) \dots\dots\dots (7)$$

Where:

X_S : Sulfur conversion

So, we obtain on replacement:

$$F_{S0} dX_S = (-r_S) \cdot dV \dots\dots\dots (8)$$

Equ. 8 represents the differential change of sulfur concentration inside the differential segment (dV) of the OBR reactor during the ODS reaction. The molar flow rate of sulfur in feedstock (F_{S0}) was maintained constant and the chemical reaction rate of sulfur consumption (-r_S) depends on the sulfur conversion.

3.2.2 Chemical reaction rate

For chemical reaction rate kinetics studies, it is preferred to obtain intrinsic reaction parameters rather than the apparent constants. To get the reaction rate constants for the ODS reaction, they are different approaches available: batch studies with maintaining the constant weight of catalyst and observing the reduction of the concentration of reactant with or conducting a continuous operation of the experiments with having the flow rate changes along with temperature and other specific parameters of chemical reaction engineering [28]. Therefore, we will assume the kinetic model of the ODS process in the OBR as follows:

1- If the kinetic model is the first order

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

$$-r_{DBT} = -\frac{dC_S}{dt} = KC_S \dots \dots \dots (9)$$

By separating and integrating equation (9) and combing it with the first-order reaction concentration profile, we obtain:

$$C_S = C_{S0}Exp\left(-K_0e^{\frac{-E}{RT}}\tau\right) \dots \dots \dots (10)$$

Where:

- C_S = Concentartion of sulfur at τ, M
- C_{S0} = Initial concentartion of sulfur at τ = 0, M
- τ: Space-time of naphtha
- K₀: Frequency factor of ODS reaction
- E: activation energy of the ODS reaction
- R: Ideal gas constant
- T: temperature of ODS reaction

2- If the kinetic model is n-th order

When the sulfur oxidation reaction followed n-th order kinetics, the equation of reaction rate

can be expressed as follows:

$$-r_s = -\frac{dC_s}{dt} = KC_s^n \dots\dots\dots (11)$$

By separating and integrating equation (8), we obtain:

$$\int_0^V \frac{dV}{F_{S0}} = \int_0^{X_S} \frac{dX_S}{-r_s} \dots\dots\dots (12)$$

$$\frac{V}{F_{S0}} = \int_0^{X_S} \frac{dX_S}{-r_s} \dots\dots\dots (13)$$

Since $F_{S0} = C_{S0} * v_l \dots\dots\dots (14)$

By inserting equation (14) in equation (13):

$$\frac{V}{C_{S0} * v_l} = \int_0^{X_S} \frac{dX_S}{-r_s} \dots\dots\dots (15)$$

Since $\tau = \frac{V}{v_l} \dots\dots\dots (16)$

Where:

V: Volume of the reactor, m³

v_l: Volumetric flow rate, m³/s

By inserting equation (16) in equation (15):

$$\tau = C_{S0} \int_0^{X_S} \frac{dX_S}{-r_s} \dots\dots\dots (17)$$

Where:

C_{S0}: Initial concentration of sulfur (inlet into the reactor)

C_S: The final concentration of sulfur (outlet from the reactor)

The total space-time of reactants (τ) can be expressed as follows[29]:

$$\tau = \frac{1}{LSHV} \dots\dots\dots (18)$$

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

$$X_S = \frac{C_{S0} - C_S}{C_{S0}} \dots\dots\dots (19)$$

By substituting the first order concentration profile of sulfur and equations 11 and 19 in equation

$$C_S = [(\tau * (K_0 e^{\frac{-E}{RT}}) * (1 - n)) + \frac{1}{C_{S0}^{n-1}}]^{1-1/n} \dots\dots\dots (20)$$

(17) and integrating the equation, we obtain:

3.2.3 Reactor performance

The oxidation reaction of the sulfur (S) is carried out in the OBR.

The process includes a number of parameters that affect the performance of the sulfur removal from naphtha such as the oscillatory flow conditions inside the OBR and others. These parameters are determined by using the correlations presented in this section.

❖ Total space-time (τ)

The volumetric flow rate can be determined as follows:

$$v_l = u * A_c \dots \dots \dots (21)$$

Where:

u : The mean liquid feedstock velocity, m/s

A_c : Cross-sectional area of flow, m²

By substituting equation (21) in equation (16), we obtain:

$$\tau = \frac{V}{u * A_c} \dots \dots \dots (22)$$

It was assumed that interfacial area can be expressed as[30]:

$$a = \frac{V}{A_c} \dots \dots \dots (23)$$

So, equation (23) can be rearranged as follows:

$$\tau = \frac{a}{u} \dots \dots \dots (24)$$

For the cylindrical tube of the OBR, the volume and the cross-sectional area can be expressed as follows:

$$V = \frac{\pi}{4} D^2 L \dots \dots \dots (25)$$

$$A_c = \frac{\pi}{4} D^2 \dots \dots \dots (26)$$

By inserting equations (25) & (26) in equation (23):

$$a = \frac{\frac{\pi}{4} D^2 L}{\frac{\pi}{4} D^2} \dots \dots \dots (27)$$

$$a = L \dots \dots \dots (28)$$

Where, L : Total reactor length, cm

❖ **The mean velocity (u)**

The instantaneous velocity of liquid feedstock [$u(t)$] in the continuous OBR includes two components which are [31, 32]:

$$u(t) = u_0 \pm u_{p(t)} \dots \dots \dots (29)$$

- 1- The permanent flow velocity (u_0): This velocity is due to the net flow rate.
- 2- The oscillatory flow velocity (u_p): This velocity is due to the oscillation motion inside the OBR and can be expressed by [31, 32]:

$$u_{p(t)} = \pi x_0 f \cos(2\pi f t) \dots \dots \dots (30)$$

Where:

A: The oscillation amplitude which characterizes the fluid displacement inside the reactor column, mm

f: The oscillation frequency, Hz

While the mean flow velocity (u_m) in the continuous OBR was then defined as [31]:

$$u_m = u = u_0 \pm u_{pm} \dots \dots \dots (31)$$

So, the mean flow velocity (u_m) contains two components which are [31]:

- 1- The permanent flow velocity (u_0): This velocity is due to the net flow rate.
- 2- The mean oscillation velocity (u_{pm}): This velocity is due to the oscillation motion inside the OBR and can be expressed by [31, 32]:

$$u_{pm} = 2X_0 f \dots \dots \dots (32)$$

By inserting equation (32) in equation (31):

$$u_m = u = u_0 \pm 2X_0 f \dots \dots \dots (33)$$

By inserting equation (33) in equation (24):

$$\tau = \frac{a}{u_0 \pm 2X_0 f} \dots \dots \dots (34)$$

According to Equ. (23), the net flow velocity of the feedstock (u_0) can be expressed by:

$$u_0 = \frac{a}{\tau_n} \dots \dots \dots (35)$$

Where:

τ_n : Space-time due to the net flow of feedstock

By substituting Equ. (35) in Equ. (34):

$$\tau = \frac{a}{\left(\frac{a}{\tau_n}\right) \pm 2X_0 f} \dots \dots \dots (36)$$

$$\tau = \frac{a}{\left(\frac{a}{\tau_n}\right) \pm (Re_o \mu / \pi \rho D)} \dots \dots \dots (37)$$

$$\frac{\mu}{\pi \rho D} = \frac{1}{3.14 * 1} = 0.318$$

$$\tau = \frac{a}{\left(\frac{a}{\tau_n}\right) \pm (0.318 Re_o)} \dots \dots \dots (38)$$

By substituting equation (38) in equations (10) & (20):

$$C_S = C_{S0} \text{Exp} \left[-K_0 e^{\frac{-E}{RT}} \left(\frac{a}{\frac{a}{\tau_n} \pm 0.318 Re_o} \right) \right] \dots \dots \dots (39)$$

$$C_S = \left[\left(\frac{a}{\frac{a}{\tau_n} \pm 0.318 Re_o} \right) * (K_0 e^{\frac{-E}{RT}}) * (1 - n) \right] + \frac{1}{C_{S0}^{n-1}} \Big]^{1-n} \dots \dots \dots (40)$$

Equations (39) and (40) can be rewritten according to the performance of the ODS process in the OBR which was studied experimentally and proved that the sulfur conversion increased with increasing the oscillation conditions (f and X_o). Therefore, these equations become:

$$C_S = C_{S0} \text{Exp} \left[-K_0 e^{\frac{-E}{RT}} \left(\frac{a}{\frac{a}{\tau_n} - 0.318 Re_o} \right) \right] \dots \dots \dots (41)$$

$$C_S = \left[\left(\frac{a}{\frac{a}{\tau_n} - 0.318 Re_o} \right) * (K_0 e^{\frac{-E}{RT}}) * (1 - n) \right] + \frac{1}{C_{S0}^{n-1}} \Big]^{1-n} \dots \dots \dots (42)$$

The equations (41) and (42) were derived based on the chemical engineering principles as a kinetic model of the ODS process in the OBR and used for simulating the observed and predicted results via gPROMS software. These equations were new kinetic equations because they included all process parameters that affect the conversion of the S which are: reaction temperature (T), space-time (τ), Reynold number of oscillation (Re_o), frequency factor (K_0), activation energy (E), and reaction order (n).

The equations (35-40) were derived based on the chemical engineering principles as a kinetic model of the ODS process in the OBR in the presence of the dispersion effect and used for simulating the observed and predicted results via gPROMS.

3.3 Parameter estimation techniques

Kinetic parameter estimation is a challenging step in the development of the process model based on experiments. Minimizing the error between the experimental data and the predicted data, which was calculated according to equation (65), is the method used for estimating the suitable value of the kinetic parameters:

$$\% \text{ Error} = \frac{C_S^{pred.} - C_S^{obs.}}{C_S^{pred.}} * 100 \dots \dots \dots (43)$$

Therefore, the predicted values from the process model must match as closely as possible to experimental data to reduce the error between these data[33].

Where:

% Error: Percent error between experimental and predicted results of sulfur concentration

$C_S^{pred.}$: Predicted concentration of S (calculated by the model)

$C_S^{obs.}$: The observed (experimental) concentration of S

For estimating the optimal value of the kinetic parameter, the objective function (OBJ) was minimized as shown in equation (42) below:

$$OBJ. = \sum_{n=1}^{N_t} (C_S^{obs.} - C_S^{pred.})^2 \dots \dots \dots (44)$$

Where:

N_t : Numbers of test runs.

3.3.1 Optimization problem formulation for parameter estimation

The parameter estimation problem formulation can be stated as follows:

Given	The reactor configuration, the feedstock, and the process conditions
Optimize	The activation energy (E) and pre-exponential factor (K_0)
To minimize	The sum of squared errors (SEE)
Subject to	Constraints on the conversion and linear bounds on all optimization variables

Mathematically, the problem can be presented as: -

Min SSE

E, K_0

s.t $f(H, X(H), \underline{X}(H), U(H), V) = 0, [H_0, H_f]$ (Model, equality constraint)

$E^L \leq E \leq E^U$ (Inequality constraints)

$K_0^L \leq K_0 \leq K_0^U$ (Inequality constraints)

Where:

$f(H, X(H), \underline{X}(H), u(H), v) = 0$: Represents the process model that presented in a previous section.

H: Reactor height (independent variable).

$U(H)$: The decision variables (E, K_0).

$X(H)$: Gives the set of all differential and algebraic variables

$\underline{X}(H)$: Represents the derivative of differential variables with respect to reactor height.

V: Represents the design variables or the height-independent constant parameters.

$[H_0, H_f]$: The height interval of interest.

L and U: Lower and upper bounds.

4. Results and Discussion

4.1. The ODS model in the OBR: The values of the parameters used for the ODS models in the OBR via simulation techniques were given in Table (4):

Table (4) Values of the parameters used in the ODS models.

Parameter	Unit	Value
The initial concentration of S (C_A)	mol/L	$C_A = 0.0382$
Reaction temperature (T)	K	$T_1 = 298, T_2 = 308, T_3 = 318, T_4 = 328$
Space-time (R)	s	$R_1 = 1-R_n = 14$
Reynolds number of oscillation (Re_o)	-	$Ro_1 = 175, Ro_2 = 235, Ro_3 = 315$
Net flow Reynolds number	3	$Re_1 = 25$ $Re_2 = 50$ $Re_3 = 75$
Gas constant (GC)	L. Pa/mol. K	$GC = 8314$
The ratio of reactor volume to its cross-sectional area (a)	m	$a = 0.38$

The ODS process is simulated by gPROMS software. Process simulation depended on standard engineering relationships such as mass balance and kinetic relations to predict the behavior of the S oxidation reaction.

The generated kinetic parameters obtained via the simulation technique for the ODS process were illustrated in Table (6):

Table (6) The best model parameters obtained by the simulation technique (general model).

Parameter	Unit	Value
K1 @ T1	min^{-1}	0.845
K2 @ T2	min^{-1}	0.924
K3 @ T3	min^{-1}	1.101
K4 @ T4	min^{-1}	1.153
N	-	1.203

Figure (3) shows a comparison of the experimental and simulated results obtained according to

the simulation technique.

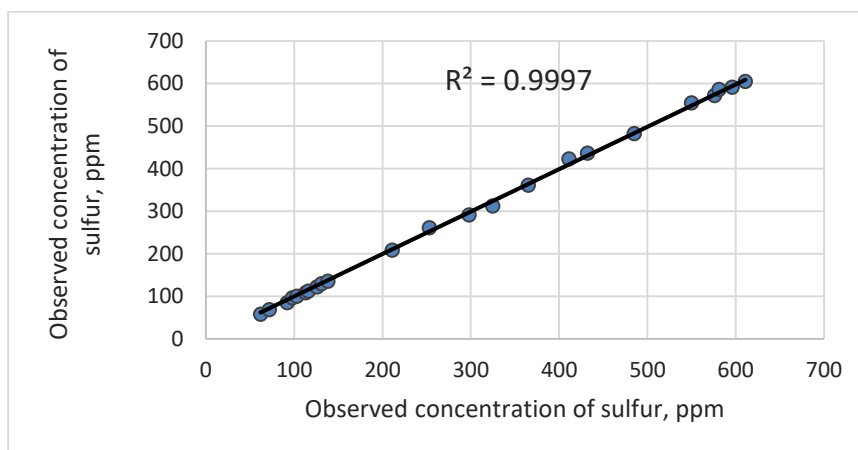


Fig. (3): Comparison between the error of predicted and observed remaining concentration of sulfur.

3.5.1. Activation energy

Activation energy is calculated by plotting ($\ln K$) versus ($1/T$) based on the linearization of the Arrhenius equation to get a straight line with a slope of $(-E/R)$, as illustrated in Figure 4. The values of activation energy (E) and the frequency factor (K_0) obtained from the plotting of the Figure were (96.56 kJ/mol) and (4027.89 min^{-1}), respectively.

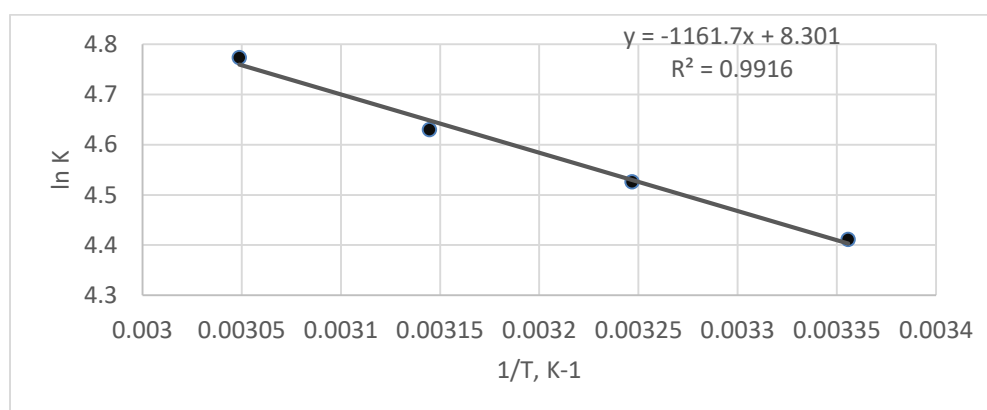


Fig. (8): $\ln K$ versus $1/T$ for kinetic parameters of the naphtha oxidation process in the OBR

3.5.2. Kinetic analysis of sulfur oxidation reaction

The oxidation reaction of the S compound found in the naphtha was carried out in the OBR under different operating conditions and a heterogeneous zeolitic catalyst. The reaction kinetics is determined by analyzing the results obtained by experimental results, kinetic model, and

gPROMS package. The reaction rate and sulfur concentration profile obtained by the simulation technique were shown below:

❖ ODS reaction rate:

$$-r_s = -\frac{dC_s}{dt} = 4027 * \exp\left(\frac{-96.56}{T}\right) * C_s^{1.203} \dots \dots \dots (45)$$

❖ Sulfur concentration profile:

$$C_{DBT} = \left[\left(\frac{a}{\frac{a}{\tau_n} - 0.318 Re_o} \right) * (4027 * e^{\frac{-96.561}{T}}) * (-0.203) + \frac{1}{C_{S0}^{n-0.203}} \right]^{(-4.926)} \dots \dots \dots (46)$$

4. Conclusions

The deep desulfurization of naphtha cut is challenging nowadays in Iraq as the hydrodesulfurization equipment is complicated and requires severe operating conditions to achieve satisfactory sweet gasoline. The present study aimed at the utilization of a ZSM-5-based catalyst for oxidative desulfurization of a sout naphtha cut in North Refineries Company. The catalytic ODS of refinery naphtha was applied using a novel composite catalyst (Fe-ZSM-5). To describe the ODS reaction in the three-phase OBR, a multi-lump kinetic model with different orders of reaction for the major routes was developed. Individual product reaction order of 1.203 was determined. The experimental results were fed along with mass transfer equations, flow equations, and properties of the catalyst and feedstock to develop a simulated three-phase ODS process. The simulation resulted in an error of 5% between the simulated and experimental results of the remaining sulfur compounds that were encouraging to obtain the Fe/ ZSM-5 ODS kinetics using optimization technique in gPROMS software. The optimization was successful in achieving the activation energy and pre-exponential factor of the prepared catalyst.

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