

Modelling and simulating a batch reactor used in kerosene oxidation desulphurization

Enas.A. eltnay, Nasser. A. Altoumi, Gummaa A. Abodera,
Amani kwadikha

Faculty of Oil and Gas and Reactivated Energy, Zawia University

Abstract

The presence of S-compounds in the petroleum fractions of the oil compounds causes pollution to the environment and operation problems such as corrosion and sulfur dioxide sulfur dioxide (SO₂) production that increases acid rain. Though catalytic hydrodesulfurization (HDS) is also often used to remove these compounds, it is necessary to use hydrogen and high pressures which results in high energy and operation costs. This paper has proposed an in-depth mathematical model based on kinetic data acquired experimentally to process the simulation of the oxidative desulfurization (ODS) of the kerosene in batch reactor. The model itself was only conducted within MATLAB R2024a which allowed the optimization of numerical process parameterization. The best kinetic constants were named as activation energy of 19.14 kJ/mol, pre-exponential factor of 2163.56 (wt)^{-0.66530} min⁻¹ and reaction order of 1.67. Such parameters have helped in the reaction conditions that took a sulfur conversion of more than 99.9 % and these are 370 K and 120 minutes. Also, a scale-up study has shown that an efficient working diameter of the reactor is 1 meter with the optimized conditions applied.

Keywords: Optimal reaction condition, Mathematical model, Optimal kinetic parameters, Scale up, Batch reactor

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Introduction:

Petroleum fractions contain different types of sulfur compounds which is harmful compound to industry and environment. These compounds are undesirable in petroleum fractions because they poison the catalyst in refinery and cause corrosion problems of internal combustion engines, also can emit SO₂ in the combustion process.

due to these dangers, many strategies have been developed for sulfur elimination One of these techniques is the oxidative desulphurisation (ODS) process, which has received more attention because it operates at low operating conditions and doesn't consume hydrogen compared to hydrodesulphurisation (HDS) [1]. Therefore, the ODS process has been studied by many researchers using different catalysts and oxidants under different operating conditions and for different petroleum fractions [2]. Despite these experimental studies, the simulation process and modelling become necessary because they provide a better understanding of the process.

The mathematical model of chemical processes involves several simulations and optimisations, which have many advantages such as estimating the optimal operations without making any changes to the real process. Finding a model that describes the experimental process under different process conditions is considered a difficult task challenge because the experimental process contains several types of structure. The mathematical model for a batch reactor can be complex due to the effect of many factors within the reactor including mixing efficiency, size and shape of catalyst particles,

kinetics on the catalyst surface and pore diffusion within the framework of effective or apparent reaction rate constant [3].

This study aims to find optimum kinetic parameters by applying a mathematical model and comparing the results from the model with experimental results, these kinetic parameters were used to find optimum reaction conditions which can give high conversion. This study also includes the scale-up study of the batch reactor based on the optimal kinetic parameters and optimal reaction conditions to find the appropriate volume of the reactor.

2- Methods and Methodology

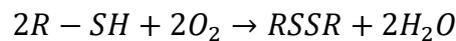
2.1. Process Description

The simulation results were made on experimental results. The experimental section is consisting of a batch reactor for oxidative desulfurization of mercaptans from kerosene using merox on activated carbon catalyst in alkaline solution by air as oxidant.

In order to easy for matching between experimental and simulation results some assumptions are used:

- Isothermal and constant pressure in the reactor.
- Steady state experimental unit.
- The gaseous reactant exists in large excess and the liquid is saturated with gas at all times.
- The reactant used in the model section consists of butanethiol and behaves as butanethiol in properties because it considers the most sulfur compound present in kerosene.

And the reaction can be stated below:



where Thoils oxidize on the catalyst using air as an oxidant to produce disulfide which can remove easily by the adsorption process because it has high polarity.

2.2. Mathematical Model

The mathematical model of chemical processes involves several simulations and optimization that have many advantages such as estimation of the optimal operations without making any change on the real process. It can be developed by the formulation of the equations of mass and energy balance. A basic mathematical model will include a chemical reaction rate and combination mass and heat transfer equations with the kinetic equation [4].

The mathematical model can be started by making material balance about batch reactor concerning mercaptan concentration and this lead to:

$$\tau = \int_{C_{RSHO}}^{C_{RSH}} \frac{-dC_{RSH}}{-r_{RSH}} \quad (1)$$

Where:

C_{RSH} : Mrcaptan concentration, Wt%

C_{RSHO} :Initial concentration of mercaptan, Wt%.

$-r_{RSH}$: Reaction rate, Wt% /sec.

Chemical Reaction Rate

The reaction rate of chemical reaction could be taken into account by assuming nth order kinetics.

$$-r_{RSH} = \eta_0 K_{in} C_{RSH}^n \quad (2)$$

Where:

η_0 : Effectiveness factor.

K_{in} : Effectiveness factor.

By substitution of eq. (2) in eq. (1) and integration to this equation we can get the final expression which is:

$$C_{RSH} = [C_{RSHO(1-n)} + (1 - n) \cdot t \cdot K_{in} \cdot \eta_0]^{(1-n)} \quad (3)$$

The reaction rate constant (k_{in}) can be calculated for ODS reaction by using the Arrhenius equation as follows:

$$K_{in} = K_o e^{\left(\frac{-E}{RT}\right)} \quad (4)$$

Where:

K_o : Pre-exponential factor, (wt)^{-0.66530} . min⁻¹ .

E : Activation energy, kJ/mol.

R : Gas constant, J/mol oK.

Eq. (4) contain effectiveness factor which can be calculated from the following equation that can be used for sphere particle [5]:

$$\eta_0 = \frac{3(\phi \coth(\phi) - 1)}{\phi^2} \quad (5)$$

Effectiveness factor is a function of Thiele modulus which is calculated from the following equation:

$$\phi = \frac{V_P}{S_P} \sqrt{\frac{(n+1)K_{in}C_{RSH}^{(n-1)}}{2D_e}} \quad (6)$$

Where:

Φ : Thiele modulus.

V_p : Particle volume, m³.

S_p : External surface area of particle, m².

D_e : Effective diffusivity, Cm²/sec

Molecular diffusivity which is present in eq. (7) can be estimated from the equation:

$$D_e = 7.8 \times 10^{-8} \frac{\psi_B MB}{(v_{RSH})^{0.6}} \times \frac{T}{\mu} \quad (7)$$

Where:

ψ_B : Non-aggregation coefficient.

MB : Molecular weight of solvent, g/gmol.

v_{RSH} : Molar volume of mercaptan, m³/mol.

μ : Viscosity, Pa.s.

The molar volume of solute is calculated from the following equation [6]:

$$v_{RSH} = 0.285(v_{CRSH})^{1.048} \quad (8)$$

Where:

v_{CRSH} : Critical molar volume of mercaptan, m³/mol.

Equations (1) to (8) were coded and solved simultaneously using MATLAB software. The mathematical model was used to estimate the optimal kinetic parameters by minimising the absolute error between experimental and predicted data.

In order to calculate the optimal kinetic parameters using the MATLAB software we must reduce the value of sum of square error (SSE) below [7]:

$$SSE = \sum_1^i (C_{RSH_{exp}} - C_{RSH_{pred}})^2 \quad (9)$$

Where : (i) represent the number of runs.

SSE: Sum of square error

The mathematical model was containing several constant parameters which showed in Table 1.

Table 1. Values of constant parameters used in ODS model

Temperature K	Batch Time (Min)	Gas constant J/mol. °K	Initial concentration (Wt%)	Molar volume g/cm ³	Particle radius Mm
300- 310-320	20- 40-60- 80 -100	8.314	0.0189	96.36	0.4

2.3. Scale up of Batch Reactor

The batch reactor model has been developed by performing a material balance over the reactor and an energy balance for the reactor and jacket, which can be used to control the temperature of the reactor.

The material and energy balance leads to the following set of ordinary differential equations [8]:

Material balance:

$$\frac{dc}{dt} = -K_{in}C^n \quad (10)$$

Energy balance

Reactor:

$$\frac{dT}{dt} = \frac{UA}{\rho_r c p_r V} (T_j - T) + \frac{\Delta H r_{SH} V}{\rho_r c p_r V} + \frac{\mu N^2 V}{\rho_r c p_r V} \quad (11)$$

Where:

U: Overall heat transfer coefficient, KW/m² °K. ρ_r: Density of solution in reactor, Kg/m³.

c_{p_r}: Heat capacity of solution in reactor, kJ/kg °K. V: Reactor volume, m³.

N: Impeller speed, RPM.

ΔH: Heat of reaction, kJ/mol.

Jacket:

$$\frac{dT}{dt} = \frac{UA}{\rho_r c p_r V} (T_j - T) + \frac{F}{V_j} (T_j - T_n) \quad (12)$$

Where:

T_j: Jacket temperature, °K. T_n: Temperature of input steam, °K.

F: Steam flow rate, kg/s. V_j: Jacket volume, m³.

The viscosity of kerosene is used as a function of temperature which is estimated from the experimental result:

$$\mu = 0.016T - 3.548 \quad (13)$$

The model of scale up of batch reactor contains several numerical values which showed in Table 2.

Table 2. Constants used in scale up model

Jacket solution Heat capacity	Jacket solution density	Reactor solution Heat capacity	Reactor solution density	Impeller speed	Heat of reaction	Overall heat transfer coefficient	Input steam temperature
4.2	1000	2.01	815	2000	225	24	410

3- Results and Discussion

3.1. Kinetic Parameters Estimation

The optimal kinetic parameters calculated from the model by minimizing the sum of squared errors (SSE) are presented in Table 3.

Table 3. Optimal kinetic parameters predicted from the model

Parameter	Value	Unit
n	1.66530	
E	19.13650	kJ/mol
k _o	2163.56	(wt) ^{-0.66530} . min ⁻¹

3.2 Simulation and Experimental Results

The experimental and simulation results are shown in Table 4. The simulation results were obtained from the model using the scale-up of the batch reactor is studied under different reactor sizes to observe the effect of size on concentration and temperature in the model. The scale up model is used in the MATLAB software to study the output temperature and concentration under different reactor sizes and these values are presented in Tables 6 and 7 below.

From these tables, the best value for diameter was at $D=1$ m due to that when $D=1$ m, the value of concentration reaches to minimum value and the temperature profile were more stable from the other value to diameter, in addition to consider the closest value to the optimum temperature of high conversion. So, from this study for scale up to batch reactor used here the diameter will be m which can be depending on it other dimensions of the reactor.

The comparison between the experimental and simulation results is shown in Figures 1 to 3.

Temperature (K)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)
300	20	89.39	30.52	97.24	26.46
300	40	59.20	70.62	66.33	66.89
300	60	32.46	84.56	32.41	84.58
300	80	21.73	90.12	23.14	89.24
300	100	16.11	93.03	15.41	93.39
310	20	79.92	35.32	87.74	31.38
310	40	48.83	75.92	49.31	72.64
310	60	25.68	87.92	23.13	88.97
310	80	16.90	92.47	15.31	93.29
310	100	12.42	94.79	13.31	94.33
320	20	70.09	36.11	78.74	31.63
320	40	40.25	80.37	39.31	80.86
320	60	20.48	90.61	18.81	91.48
320	80	13.34	94.31	14.81	93.55
320	100	9.77	96.16	10.81	95.62

These figures showed the comparison between experimental and simulation results and we can see a good agreement between the simulation and experimental results because a few assumptions are used in this work and this assumption is used to facilitate the solving of the model where reducing the number of assumptions will increase the agreement between experimental and simulation results. Also shows the effect of time on the conversion at different temperatures From these figures we can observe that the conversion was increased by increasing the temperature and time, increasing the temperature will increase the number of attractive molecules and this leads to an increase in the conversion. Also, increasing the temperature will increase the rate constant according to the Arrhenius equation and this will lead to an increase in the reaction rate, while increasing the time will increase the contact time between the reacting materials and the active sites of the catalyst.

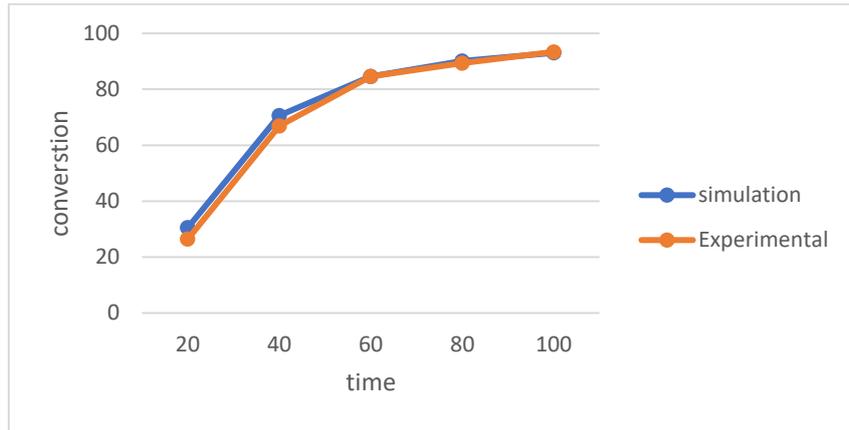


Fig. 1. Comparison between experimental and simulation results at T=300 °K

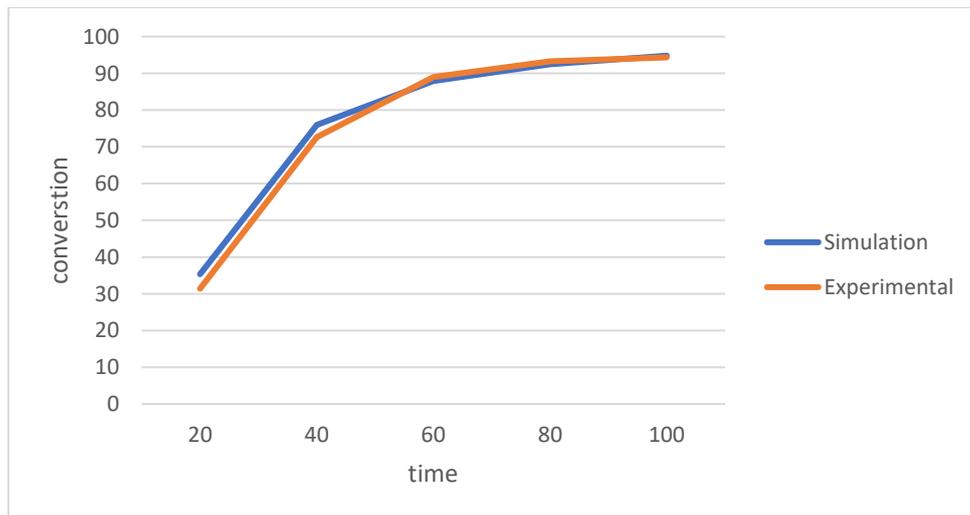


Fig. 2. Comparison between experimental and simulation results at T=310 °K

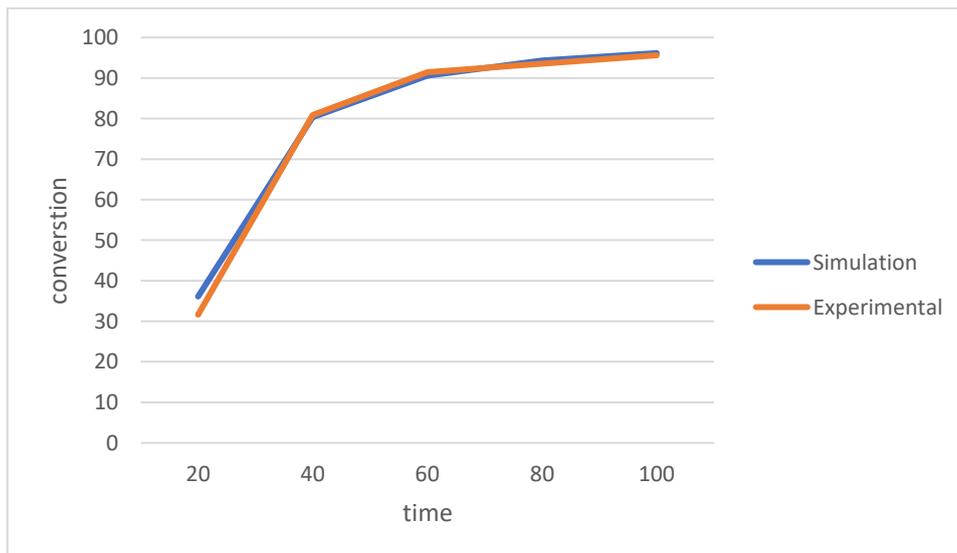


Fig. 3. Comparison between experimental and simulation results at T=320 oK

3.3. Optimal Reaction Conditions

After obtaining the optimal kinetic parameters, these optimal parameters can be used in the model to find the optimal reaction conditions that can be used to obtain a high conversion ($\geq 99\%$) and these conditions are shown in Table 5.

Table 5. Optimal reaction conditions for high conversion

Parameter	Value
Temperature	370 K
Time	120Min
Conversion	99.68%

3.4 Scale up of Batch Reactor

The scale-up of the batch reactor is studied under different reactor sizes to observe the effect of size on concentration and temperature in the model.

The scale up model is used in the MATLAB software to study the output temperature and concentration under different reactor sizes and these values are presented in Tables 6 and 7 below. From these tables, the best value for diameter was at D=1 m due to that when D=1 m, the value of concentration reach to minimum value and the temperature profile were more stable from the other value to diameter, in addition to consider the closest value to the optimum temperature of high conversion. So, from this study for scale up to batch reactor used here the diameter will be m which can be depending on it other dimensions of the reactor.

Table 6. Effect of the reactor size on concentration profile (concentration in ppm).

Time(min)	D=1(m)	D=1.3(m)	D=1.5(m)	D=1.7(m)	D=1.9(m)	D=2(m)
0	190	190	190	190	190	190
10	76.84	82.43	85.79	87.72	90.26	92.45
20	32.32	36.30	38.57	40.35	42.59	44.63
30	18.08	19.69	21.76	22.30	24.71	25.37
40	11.40	12.27	13.84	14.78	15.63	16.79
50	8.99	8.58	9.78	10.31	10.84	11.70
60	7.23	7.00	7.33	7.68	8.03	8.71
70	5.87	5.53	5.76	5.99	6.24	6.80
80	4.92	4.52	4.68	4.84	5.02	5.21
90	3.69	3.78	3.89	4.01	4.15	4.29
100	3.16	2.26	3.31	3.40	3.50	3.60
110	2.72	2.82	2.86	2.92	3.00	3.08
120	2.14	2.47	2.50	2.54	2.61	2.67
130	2.13	2.19	2.20	2.23	2.29	2.34
140	1.91	1.95	1.97	1.98	2.03	2.07
150	1.72	1.75	1.76	1.77	1.81	1.85
160	1.55	1.56	1.57	1.59	1.63	1.66

Table 7. Effect of the reactor size on temperature profile (temperature in K)

Time(min)	D=1(m)	D=1.3(m)	D=1.5(m)	D=1.7(m)	D=1.9(m)	D=2(m)
0	300	300	300	300	300	300
10	352.50	355.37	353.25	350.62	348.36	345.57
20	371.04	370.99	360.22	359.87	357.04	355.64
30	371.65	371.05	365.68	363.63	361.32	364.53
40	372.04	372.12	369.08	368.14	366.57	368.57
50	372.98	373.36	371.09	370.88	370.00	370.93
60	373.44	373.76	371.97	372.27	371.87	372.30
70	373.39	373.71	372.33	372.94	372.89	373.09
80	373.09	373.62	372.43	373.25	373.43	373.88

90	372.76	373.48	372.45	373.37	373.70	374.32
100	372.43	373.30	372.52	373.39	373.83	374.57
110	372.09	373.12	372.61	373.41	373.87	374.70
120	371.76	372.93	372.72	373.47	373.88	374.76
130	371.06	372.74	372.84	373.53	373.91	374.78
140	370.71	372.54	372.95	373.60	373.95	374.79
150	370.35	372.35	373.07	373.68	374.02	374.81
160	370.00	372.15	373.19	373.75	374.07	375.14

3-5 Comparison with Previous Study

The effectiveness in the legitimacy and novelty of the present model was compared with an earlier study on the oxidative desulfurization of kerosene in batch reactor [9]. Comparable deviations between the two models were seen in the kinetic parameters and optimal operation conditions. A different study had been carried out earlier using gPROMS software which had given an activation energy of 18.64 kJ/mol and a reaction order of 1.77, but the present model has given slightly different values as an activation energy of 19.14 kJ/mol and a reaction order of 1.67. Some differences too were identified in the pre-exponential factor. On the optimal conditions of the reaction, this research discovered the milder conditions of 370 K and 120 minutes, as opposed to 379.4 K and 160 minutes in the previous research. Although these are less severe conditions, the current model was able to attain an elevated average conversion rate of sulfur, which was more than 99.9%. Also, the scale-up analysis had the diameter of 1 meter of the reactor as adequate to high performance yet the former study had recommended a bigger dimension of 1.2 meters. Such disparities highlight the enhancement in accuracy and efficiency of the present model that provides more economical and energy-efficient parameters to be used in an industrial setting.

Table 1: Comparison of Key Kinetic Parameters and Operational Conditions

Parameter	Previous Study [1]	current Study
Activation Energy (kJ/mol)	18.64	19.14
Reaction Order	1.77	1.67
Pre-exponential Factor	2201.34 (wt) ^{-0.76636} min ⁻¹	2163.56 (wt) ^{-0.66530} min ⁻¹
Optimal Temperature (K)	379.4	370
Reaction Time (minutes)	160	120
Sulfur Conversion Rate	< 99.9%	> 99.9%
Reactor Diameter (m)	1.2	1

4- Conclusions

this study, a mathematical model was successfully developed to simulate the oxidative desulfurization of kerosene in a batch reactor. The model demonstrated excellent agreement with experimental results, with deviations of less than 5%, confirming its reliability for predicting concentration profiles and guiding reactor design and operation.

A comparative analysis with a previously published study revealed that the current model, implemented using MATLAB, offers improved kinetic parameters and achieves higher sulfur conversion rates under milder operating conditions. These findings highlight the enhanced efficiency and flexibility of the proposed modeling approach.

Furthermore, the scale-up study demonstrated that a reactor diameter of 1.0 m is sufficient to maintain high desulfurization performance, representing a more compact and energy-efficient design

compared to previous recommendations. These results indicate that the proposed model can serve as a practical and effective tool for optimizing batch reactor systems in industrial desulfurization processes.

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