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Modelling and simulating a batch reactor used in kerosene oxidation desulphurization

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Abstract

Petroleum fractions contain harmful sulphur compounds that cause corrosion in engines and emit SO_2, contributing to acid rain. The traditional method of removing sulphur from fuels is catalytic hydrodesulphurisation, but this is expensive This paper presents a maths model for the oxidation desulphurisation of kerosene. The model and simulation process are important as they provide a better understanding of the process. The model was based on experimental results and calculated using gPROMS software. The optimal kinetic parameters were activation energy 19.13650 kJ/mol, pre-exponential factor 2163.56 $(wt)^{-0.66530}$. min^{-1} and reaction order 1.66530. These parameters were used to find conditions for high conversion (≥ 99.9%). These optimum reaction conditions were a reaction temperature of 379.4 ^{o}K and a reaction time of 120 min. A scale-up to a batch reactor was carried out using these optimal parameters and conditions. The results showed that the best reactor size is 1 m diameter.

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 SO_2 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:

$$2R - SH + 2O_2 \rightarrow RSSR + 2H_2O$$

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:

$$\tau = \int_{CRSHO}^{CRSH} \frac{-dC_{RSH}}{-r_{RSH}} \qquad (1)$$

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.

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

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:

$$C_{RSH} = \left[C_{RSHO^{(1-n)}} + (1-n).t.K_{in}.\eta_0\right]^{\left(\frac{1}{1-n}\right)} \qquad (3)$$

The reaction rate constant (kin) can be calculated for ODS reaction by using the Arrhenius equation as follows:

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

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]:

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

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

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

Where:

Φ: Thiele modulus. Vp : Particle volume, m^3.

Sp: External surface area of particle, m^2. De: Effective diffusivity, Cm^2/sec

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

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

Where:

ψ_B: Non-aggregation coefficient. MB: Molecular weight of solvent, g/gmol.

υ_{RSH}: Molar volume of mercaptan, m^3/mol. μ: Viscosity, Pa.s.

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

$$\upsilon_{RSH} = 0.285(\upsilon_{CRSH})^{1.048} \qquad (8)$$

Where:

υ_{CRSH}: Critical molar volume of mercaptan, m^3/mol.

Equations (1) to (8) were coded and solved simultaneously using gPROMS 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 gPROMS software we must reduce the value of sum of square error (SSE) below [7]:

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

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. ºK	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:

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

Energy balance

Reactor:

$$\frac{dT}{dt} = \frac{UA}{\rho_r cp_r\ V}\left(T_J - T\right) + \frac{\Delta Hr_{RSH}V}{\rho_r cp_r\ V} + \frac{\mu N^2 V}{\rho_r cp_r\ V} \qquad (11)$$

Where:

U: Overall heat transfer coefficient, KW/m^2 ºK. ρr: Density of solution in reactor, Kg/m^3.

cp_r : Heat capacity of solution in reactor, kJ/kg ºK. V: Reactor volume, m^3.

N: Impeller speed, RPM. ΔH: Heat of reaction, kJ/mol.

Jacket:

$$\frac{dT}{dt} = \frac{UA}{\rho_r cp_r\ V}\left(T_J - T\right) + \frac{F}{V_j}\left(T_J - T_n\right) \qquad (12)$$

Where:

Tj: Jacket temperature, ºK. Tn: Temperature of input steam, ºK.

F: Steam flow rate, kg/s. V_j: Jacket volume, m^3.

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

$$\mu = 0 \cdot 016T - 3 \cdot 548 \qquad (13)$$

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 minimising the function (SSE) are shown 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 gPROMS software. 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

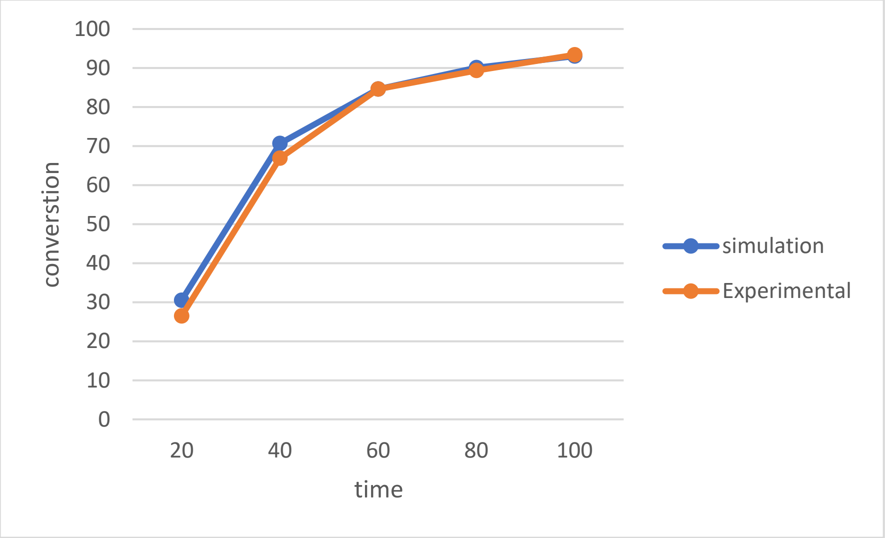

Fig. 1. Comparison between experimental and simulation results at T=300 °K

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.

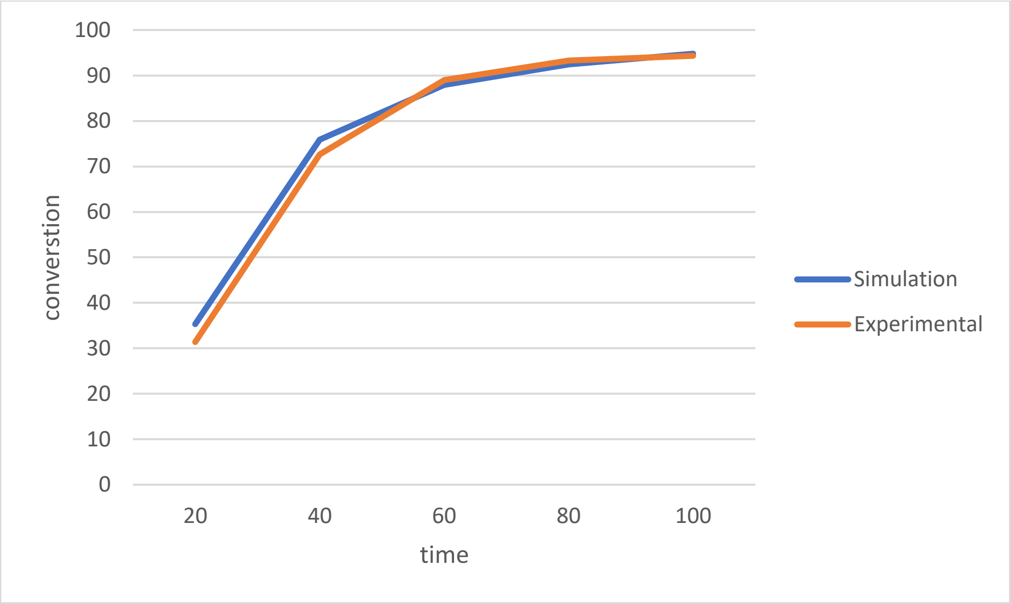

Fig. 2. Comparison between experimental and simulation results at T=310 ^{o}K

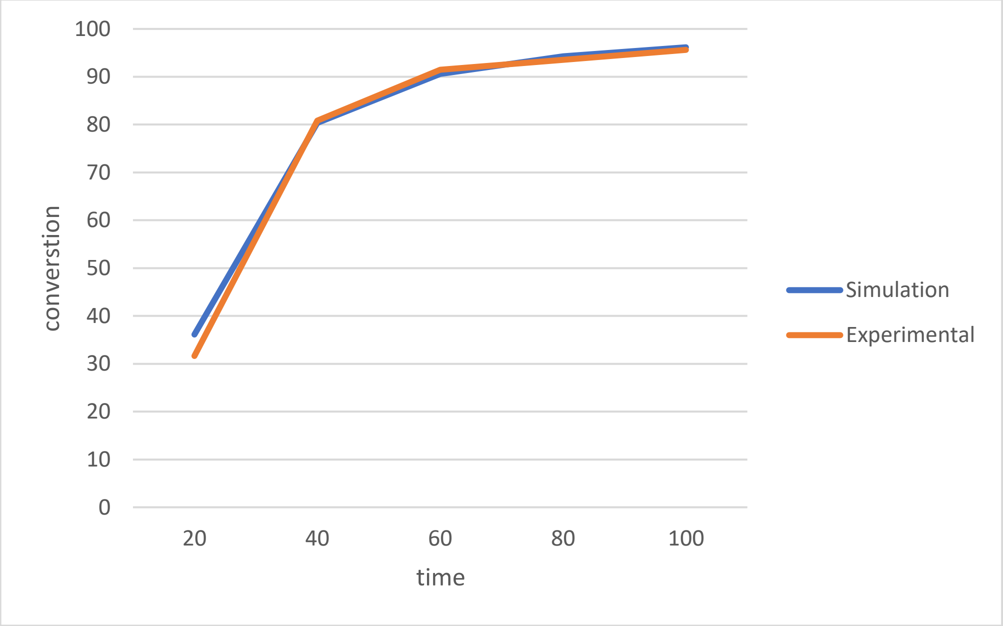

Fig. 3. Comparison between experimental and simulation results at T=320 oK

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 (≥ 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 gPROMS 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

4- Conclusions

1- A mathematical model has been developed to simulate experimental results. The results of applying optimal kinetic parameters in the simulation gives good agreement between predicted and experimental compositions with absolute less than 5% among all results and the model can now be confidently used for reactor design, operation and control and also for predicting the concentration profiles of any component under any conditions.

2- The optimal kinetic parameters and the optimal reaction conditions presented in this study are used to scale up the batch reactor. The results showed that the best reactor size to achieve the high conversion and temperature closest to the optimum value was at reactor diameter of 1 m.

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