Enhancement of Light Naphtha Quality and Environment using New Synthetic Nano-catalyst for Oxidative Desulfurization: Experiments and Process Modeling

Aysar T. Jarullah [1,2], Ghazwan S. Ahmed [1], Ban A. Al-Tabbakh[3],
Iqbal M. Mujtaba[4,5]
[1]Chemical Engineering Department, College of Engineering, Tikrit University, IRAQ
[2] Email: A.T.Jarullah@tu.edu.iq
[3]Petroleum Research & Development Center, The Iraqi Ministry of Oil /Baghdad, IRAQ
[4] Chemical Engineering Department, Faculty of Engineering & Informatics, University of Bradford,
Bradford BD7 1DP, UK. [5] Email: I.M.Mujtaba@bradford.ac.uk

Abstract

Batch oxidative desulfurization (ODS) process is investigated here for the removal sulfur compound from light naphtha using homemade new nano-catalyst. The catalyst is made of manganese dioxide supported on zeolite nanoparticles which shows an excellent catalytic performance with good impregnation, high activity, good pore size distribution and larger surface area. Different reaction temperature, time and initial sulfur concentration are used to have a deeper insight of the process. The experimental results reveal that the conversion of sulfur compound is increased by increasing the initial sulfur concentration, the reaction temperature and batch time.

A mathematical model of the process is developed and validated using the experimental data within gPROMS software with high accuracy. The validated model (errors less than 5% between experimental and predicted results) is then utilized to obtain the optimal operation conditions of the process giving maximum conversion of sulfur (higher than 99%) resulting in an environmentally friendly fuel.

Key words

Oxidative desulfurization, Environment friendly fuel, Manganese dioxide, Batch reactor, Kinetic parameters estimation.

1- Introduction

The growing demand for cleaner production and progressively increasingly stringent legislations on sulfur concentration in transportation fuels has made desulfurization most significant issue in petroleum industries. Generally, the sulfur issue has become more serious problem, especially for car fuels as the requested sulfur concentration has got an order of magnitude lower, whereas the sulfur concentrations of crude oils are getting higher. Petroleum products contain several sulfur compounds such as mercaptans, thiophenes, sulfides and disulfides which are undesirable due to several industrial and environmental disadvantages like odor, corrosive nature causing acid rain. Several techniques are used for sulfur removal but the promising one is the oxidative desulfurization (ODS) because it operates at safe operating condition and low cost. Oxidative desulfurization process is a method that carries out in two steps to produce fuels with very low sulfur content. The sulfur components found in fuels mainly thiophenes are oxidized into corresponding sulphones and sulphoxides and then these compounds formed can easily be extracted via adsorption or extraction process owing to their high polarity. In ODS process the operating conditions used is low temperature (less than 373 K) and low pressure (1 bar) and without hydrogen [1-6]. ODS process is conducted using different oxidants agent such as air, hydrogen peroxide, oxygen and ozone. Air is used due to its availability, low cost and no environmental effluent [7-9]. The most important issue in ODS process is the catalyst that should be selected for sulfur compounds. The supported transition metal oxides having high reactivity toward sulfur compounds and the extent of reaction will be determined by the type of metal oxide as well as having high activity and availability [9, 10]. Manganese metal can show higher activity from some of other metals toward oxidation of sulfur compound in addition to its ability for adsorption [12,13]. As well as, nano-catalyst has recently got large attention due to its higher activities in comparison with bulk material [12].

Therefore, the main focus of the present work is to prepare a new catalyst based on manganese dioxide supported on zeolite nano-particles and using it to remove most of the sulfur compound from light naphtha by oxidative method in a batch reactor thus producing an environmentally benign fuel. Note, loading of manganese dioxide on zeolite Nano-particles has not been reported in the public domain and therefore it is regarded a new homemade synthetic nano-catalyst. Also, employing such new synthetic nano-catalyst for sulfur removal via ODS process with air as an oxidant is also new. Table 1 summarizes the importance of this study compared to other studies available in the public domain.

Table 1: This study compared to other studies including HDS or other ODS

Parameter	**Other studies**	**This study**
Catalyst	Traditional	New
Reactor	TBR, Three phase	Batch
Oxidant	H_2O_2,TBHP, O_2,Ozone, H_2SO4, NO_3, …etc	Air
Conditions	Sever	Moderate
Construction cost	High cost	Low cost
Structure	Particles	Nano
Active metals	Pd, Ad, Cu, Co, Mo, others	MnO_2
Pollution	Pollutes air by H_2S	Environmental friendly
Support	Al_2O_3, Titania, Silica, Zirconia, others	Homemade HY-Zeolite
Order of reactions	Usually are kept constant (assumed first or second order)	Have been estimated based on experiments with minimum errors
Kinetic parameters	They are kept constant	Have estimated based on experiments
Estimation of kinetic parameters	Numerical methods	Advanced optimization technique
Physical properties	Usually are kept constant	Have been estimated as a function of operating conditions
Effectiveness factor	Usually ignored	Has taken into accounts

The other aim of this work is to a create a high fidelity mathematical model of the process which can be used to obtain further and deeper insight of the process via simulation and optimization. A model is of no use if it does not represent the real process. Therefore, parameter estimation technique is used to obtain optimal kinetic parameters of the process, The technique is based on minimizing the difference between the experimental data and the model predictions while optimizing the unknown model parameters. The actual experimental data are utilized to firstly find the optimal kinetic parameters (via optimization technique) that can be applied confidently to reactor design, operation and control for removing of sulfur compounds selectively from light naphtha with high efficiency by oxidation reactions process in batch reactor using homemade nano-catalyst (manganese oxide/ zeolite nanoparticle) based on air as an oxidant. Finally, the model will be used to get the free-sulfur content of such process via optimization process.

2-Experimental Work

2.1-Materials

Ethyl mercaptan (obtained from BDH Chemicals Ltd) is used to evaluate the reactivity of sulfur components by ODS process and dissolved in the oil feedstock with several concentrations based on the following reasons:

1- To mimic actual light naphtha found in refineries.
2- To test the performance of the new nano-catalyst prepared.
3- To study the kinetic of mercaptans catalytic oxidation because the kinetic model of ethyl mercaptan oxidation as sulfur compound, which is commonly presented in light naphtha, is still unknown.
4- To take into considerations the effect of initial concentration of sulfur, which is essential for optimization of design parameters, operating conditions and catalyst performance.
5- To obtain a complete kinetic model for sulfur removal that can be confidently used to reactor design, operation and control based on the new nano-catalyst prepared here.
6- To reduce the content of Ethyl Mercaptan found in light naphtha owing to the huge problems of such component

The main properties of ethyl mercaptan are listed in Table 2. HY-Zeolite nanoparticle has been used as a carrier to prepare the catalyst. The main specifications are shown in Table 3. Light naphtha (total sulfur content = 0.2 ppm) was obtained from KAR refinery/Erbil-Iraq was used as a liquid feedstock in this study. The physical properties of the light naphtha are illustrated in Table 4.

Table 2: Physical properties of ethyl mercaptan

Properties	Description
Molecular formula	C_2H_5SH
Molecular weight	62.13
Physical form	Liquid
Specific gravity at 20 ^oC	0.837
Boiling point (^oC)	36

Table 3: HY-Zeolite nanoparticle specifications

Specification	Zeolite nanoparticle
Surface area(m^2/g)	612.83
Pore size (nm)	2.394
Bulk density(g/cm^3)	0.548
Particle shape	Sphere
Pore volume(cm^3/g)	0.36678

Table 4: Properties of light naphtha feedstock

Physical property	Values
Density at 15 ºC, g/cm^3	0.6568
Vapor pressure at 37.8 ºC (Kpa)	69
Octane number, Motor	71.3
Octane number, Research	79.5
Total aromatic components (%)	8.5
Total sulfur content (ppm)	0.2
Distillation	(ºC)
Initial boiling point (ºC)	41
10% recovered, vol% (ºC)	49
50% recovered, vol% (ºC)	56
90% recovered, vol% (ºC)	88
Final boiling point (ºC)	99

Light naphtha is a major source for car fuel (gasoline) and it is regarded one of the highest fuel in the world. Where, in the conventional process the light naphtha is obtained by atmospheric distillation column and the next destination is the hydrotreating process then the reforming unit and the final ultimate product is the gasoline. Therefore, choosing the light naphtha as a fuel (car fuel) using ODS process instead of hydrotreating process via utilizing the new homemade nano-catalyst is not a simple task in view of the intricate chemical and physical changes that are undergone in the feed together with transport phenomena.

Active components which were used in this study is manganese acetate with purity 99% (was purchase from Sigma Aldrich). Air is used as an oxidizing agent.

2.2 Catalyst preparation

The preparation steps for manganese oxide over zeolite nanoparticle (5% MnO_2/ zeolite nanoparticle) are described as follows:

Dissolution process is conducted by dissolving 1.45 g of manganese acetate ($Mn(CH_3COO)_2.4H_2O$) in 60 ml of deionized H_2O (has got by ***Samarra Company***-Iraq), while the solution is stirred by magnetic stirrer for 60 min at room temperature to insure solubility of the salt. 10 g of zeolite nanoparticles have placed in the beaker and the prepared solution will be added to zeolite with stirring for 1 h via magnetic stirrer at room temperature to get homogeneous solution of impregnated zeolite. The impregnated solution is then put in crucible and placed in the furnace for drying and calcination steps. The steps of drying and calcination are started by raising the temperature to 120°C for 2 h, then to 250°C for 2 h, at 400°C for 1h and then to 580°C for 2h. The calcination process is conducted at low flow of air. The flow chart and catalyst preparation steps are shown in Figures 1 and 2.

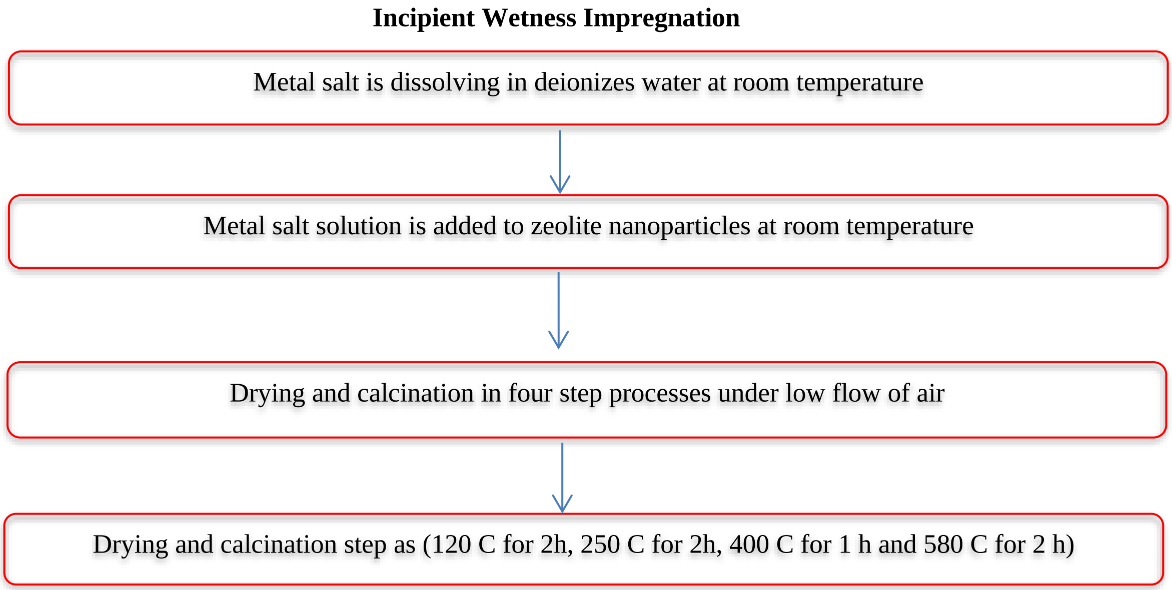

Figure 1: Flow chart of catalyst preparation

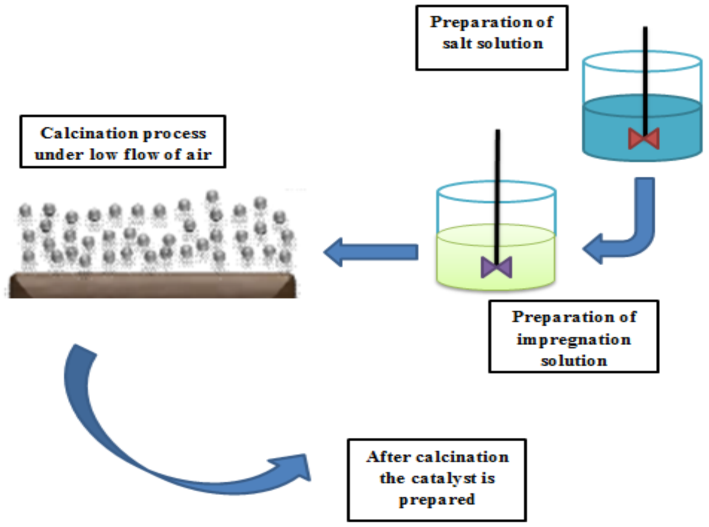

Figure 2: Preparation of catalyst steps by IWI method

2.3 Characterization of the prepared catalysts

The prepared homemade catalyst has been tested in the Petroleum Research & Development Center - the Iraqi Ministry of Oil - Baghdad to measure the main specifications, mainly pore volume, pore size, surface area and particle diameter that are showed in Table 5.

Table 5: The properties of the prepared catalyst

Characteristic	**Zeolite nanoparticle**	**Catalyst**
Calcination temperature, K	-	853
Pore size, nm	2.394	2.5452
Bulk density, g/cm^3	0.548	0.57
Pore volume, cm^3/g	0.36678	0.362011
Surface area, m^2/g	612.83	568.91
Active phase, MnO_2 , %	-	5

2.4 Oxidative desulfurization reactor

2.4.1 Batch reactor

The oxidation reaction of sulfur compound is conducted in a batch reactor. Three necks round bottom flask of 250 ml was used for such reaction. The first neck is connected to a vertical condenser to condense the vapor of naphtha by leaving the air only. The second neck is used as air inlet and is connected to compressor and the air will reach to bottom of flask by glass tube while the third neck used to measure the temperature in the flask by inserting a thermometer to the solution inside the flask and to withdraw the sample when the reaction time is approached. The heating and mixing of batch reactor are carried out by heating magnetic stirrer. The process diagram is shown in Figure 3.

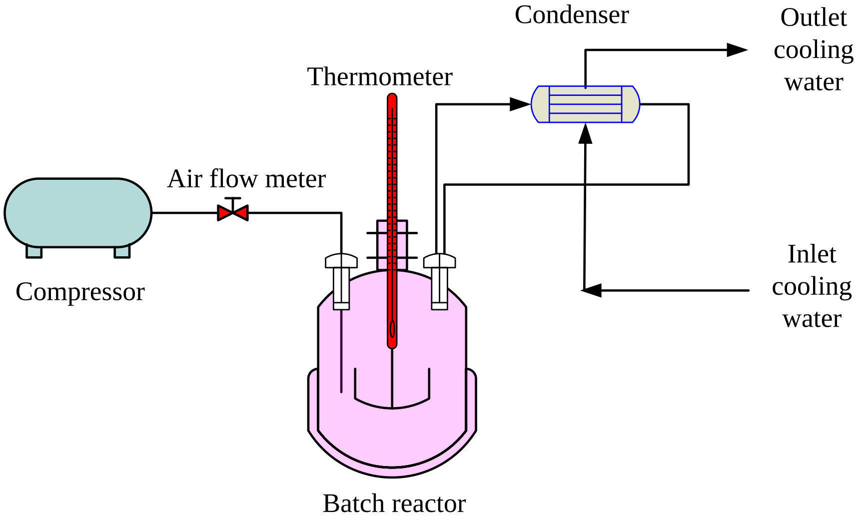

Figure 3: Schematic diagram of ODS batch reactor

2.4.2 The ODS reaction

The proposed mechanism of sulfur compound oxidization in the presence of a heterogeneous catalyst in the desulfurization process is described as follows: Ethyl mercaptan is oxidized to disulfide in the presence of 5% MnO_2/ zeolite nanoparticles catalyst. Firstly, oxygen of air attacks to metal oxide and peroxo species is produced. The peroxo species attacks the sulfur atom of ethyl mercaptan that oxidizes sulfur atoms to the disulfide and primary form of metal oxide is obtained. The produced disulfide can be easily removed by extraction with a polar solvent and the total reaction is as follows:

$$2RSH + O_2 \xrightarrow{\qquad\qquad} 2RSSR + H_2O$$

The chemical formula of the compounds in the ODS reaction in this study can be written as:

$$2C_2H_5SH + 0.5O_2 \xrightarrow{\qquad\qquad} C_2H_5\text{-}S\text{-}S\text{-}C_2H_5 + H_2O$$

2.5 - Experimental testing

2.5.1 Operating conditions

In this study, the experimental work includes different experiments of ODS process utilizing the following operating conditions:

- Type of catalyst: (5% MnO_2/ zeolite nanoparticles).
- The reaction temperature: 303 K, 313 K, 323 K.
- The contact time: 20 min, 30 min, 40 min.
- Initial sulfur concentration: 150 ppm, 200 ppm, 250 ppm.
- The air flow rate: (20-25) L/h
- Pressure: 1.103 bar

The experimental data points were selected based on the maximum and the minimum point and between them with taking into accounts the safe and moderate conditions.

2.5.2 Experimental steps for ODS reactions

The feedstock is prepared by adding ethyl mercaptan to light naphtha with a specified initial concentration. Following steps are performed in each run of the experiment:

80 ml of oil feedstock is charged to the flask with a specified initial concentration. The flask is placed on the heating magnetic stirrer and connected to the tube of air and the condenser. Note, it is ensured that the cooling water flows throughout the condenser to prevent any vaporization of light naphtha. A thermometer is inserted of the purpose of measuring the reaction temperature. When the required temperature is achieved, 0.8 g of the prepared catalyst is added to the reactor. When required reaction time is arrived, the sample is withdrawn via the thermometer hole. At the end of the run, the heating magnetic stirrer is stopped and the remaining materials should be removed. The reactor is cleaned before the next run.

2.6 Analysis of liquid samples

The total sulfur concentration in the oil feedstock and products are measured in the laboratory. Total sulfur concentration has analyzed via X-ray fluorescence following the ASTM-D4294 method. All analytical techniques that have been utilized for the properties of the feedstock and the products were accurate, fast and repeatable. Product analysis has been repeated twice for each sample at each operating condition to ensure the accuracy of the results. Average results have been taken into accounts for each run with maximum deviation of 0.5% among all runs.

3-Mathematical model of the ODS process

Mathematical model should be used extensively due to being essential for understanding or controlling a system. Process model is commonly used in the optimization of chemical process due to it permit of estimation the optimum operating conditions of the process without any change on the actual process[14]. Mathematical model is a set of equations contain several variables to describe the behavior of the system and the variables have relationships among them. The fast computer and advanced solver for solution method is used for whole process was enabled [15].

The following assumptions are taken into account in this study for ODS processes in batch reactor:

- Isothermal and constant pressure operation of the reactor.
- The gaseous reactant present in large excess.
- Ideal mixing inside the reactor to get uniform concentration and temperature throughout the reaction volume.

3.1 Mass balance equation

The general mass balance equation for catalytic batch reactor related to the sulfur component inside reactor at any period of time (dt) is written as follow:

[input]=[output]+[consumption by reaction]+[accumulation] (1)

Input of sulfur, mass/time = 0.

Output of sulfur, mass/time = 0.

Consumption of sulfur by reaction, mass = - (r_{RS})V dt.

Accumulation of sulfur, mass = V $\frac{dC_{RS}}{dt}$ dt.

Introducing these terms into equation (1) will give:

$$0 = 0 + (- r_{RS})\ V\ dt + V\ \frac{dC_{RS}}{dt}\ dt \qquad (2)$$

Then

$$- (-r_{RS}) = \frac{dC_{RS}}{dt} \qquad (3)$$

So:

$$dt = \frac{-dC_{RS}}{(-r_{RS})} \qquad (4)$$

Where:

at t = 0 $C_{RS} = C_{RSO}$

t = t $C_{RS} = C_{RS}$

Thus:

$$\int_0^t dt = \int_{\mathrm{CRSO}}^{\mathrm{CRS}} \frac{-dC_{RS}}{(-r_{RS})} \qquad (5)$$

Finally, the design correlation for the ideal batch reactor is written in terms of batch time to be

$$t = \int_{\mathrm{CRSO}}^{\mathrm{CRS}} \frac{-dC_{RS}}{(-r_{RS})} \qquad (6)$$

This equation can be integrated to estimate the concentration of sulfur compound in catalytic reactor, but ($-r_{RS}$) is certainly depended on the concentration of sulfur.

3.2 Chemical reaction rate

The mechanism and the kinetic of catalytic air oxidation of sulfur are complex including several steps to reach the end of reaction. The complexity of the chemical reaction rate equation should be taken into account in the form of n^{th} order kinetics.

$$(-r_{RS}) = k_{app}\ C_{RS}^{n} \qquad (7)$$

The apparent kinetic constant is related to intrinsic kinetic constant by internal diffusion which is represented by the catalyst effectiveness factor (η_O) as follows [16]:

$$k_{app} = \eta_O \, k_{in} \tag{8}$$

By substituting equations presented above in equation (1) and integrating this equation, the final expression of the catalytic oxidation reaction of sulfur with n^th order kinetic is obtained as follows:

$$C_{RS} = [C_{RSO}{}^{(1-n)} + (n-1).t.k_{app}]^{(\frac{1}{(1-n)})} \tag{9}$$

3.3 Reactor performance

In order to account other physical effects, equation (1) is rewritten as (using η_O, k_{in} instead of k_{app}) [16]:

$$C_{RS} = [C_{RSO}{}^{(1-n)} + (n-1).t.k_{in}.\eta_o]^{(\frac{1}{(1-n)})} \tag{10}$$

Reaction rate constant for ODS reaction (K_{in}) can be estimated for each reaction utilizing the Arrhenius equation as follows:

$$k_{in} = K_0 \, e^{-\frac{EA}{RT}} \tag{11}$$

K_0 is the frequency or pre-exponential factor and (EA) is the activation energy of the reaction. This term fits experiment well over wide temperature ranges and is highly proposed from different standpoints as being a very good approximation to the actual temperature dependency. The chemical reaction rate can be expressed as:

$$C_{RS} = [C_{RSO}{}^{(1-n)} + (n-1).t.K_0 \, e^{-\frac{EA}{RT}}.\eta_o]^{(\frac{1}{(1-n)})} \tag{12}$$

The oxidation process of sulfur compound includes several parameters such as oil viscosity, effectiveness factor, diffusivities and others. Such parameters will be calculated by employing the following equations.

3.3.1 Effectiveness factor (η_O)

Effectiveness factor (η_O) is a function of Thiele modulus (Φ) and is estimated calculated by the following correlation which is valid for sphere particle [16,17]:

$$\eta_O = \frac{3(\Phi\coth(\Phi)-1)}{\Phi^2} \quad (13)$$

While, Thiele modulus for nth order irreversible reaction is determined by the following generalized equation [16,17]:

$$\Phi = \frac{V_p}{S_p}\sqrt{\frac{(n+1)}{2}\,\frac{K_{in}{C_{RS}}^{(n-1)}\rho_p}{D_{ei}}} \quad (14)$$

3.3.2 Surface (S_p) and external volume (V_p) of the catalyst

The external surface and external volume of the catalyst can be calculated according to shape of the particle: So that, for sphere particle:

$$V_p = \frac{4}{3}\pi\,(r_p)^3 \quad (15)$$

$$S_p = 4\pi\,(r_p)^2 \quad (16)$$

3.3.3 The effective diffusivity (D_{ei})

Effective diffusivity represents the structure of the catalyst (porosity and tortuosity) by taking the pore network inside particle into account as follows [16,18]:

$$D_{ei} = \frac{\epsilon_B}{\tau}\,\frac{1}{\frac{1}{D_{mi}}+\frac{1}{D_{ki}}} \quad (17)$$

Where, the catalyst porosity (ϵ_B) is calculated using the next two equations based on experimental data:

$$\epsilon_B = \rho_p V_g \quad (18)$$

$$\rho_p = \frac{\rho_B}{1-\epsilon_B} \quad (19)$$

The tortuosity factor (τ) of the pore network have the value of 2 to 7 [19]. Based on the literatures, τ has reported to be 4 [16,19].

D_{ei} through the catalyst particle contains two types of diffusivity, molecular diffusivity D_{mi} and Knudsen diffusivity D_{ki}.

The molecular diffusivity is calculated by **Tyn-Calus** equation's [20, 21]:

$$D_{mi} = 8.93 * 10^{-8}\ \frac{\upsilon_L^{0.267}\ T}{\upsilon_{RS}^{0.433}\ \mu_L} \tag{20}$$

The Knudsen diffusivity is calculated as follows [15,17]:

$$D_{ki} = 9700 r_g (\frac{T}{M_i})^{0.5} \tag{21}$$

3.3.4 Viscosity

The viscosity of light naphtha is estimated by using the following equation as follows [22]:

$$\mu_L = 3.141 * 10^{10}(T - 460)^{-3.444}[log_{10}API]^{a} \tag{22}$$

$$a = 10.313\ [\ log_{10}(T - 460)] - 36.447 \tag{23}$$

The (API) is estimated from this equation.

$$\text{API} = \frac{141.5}{sp.gr_{15.6}} - 131.5 \tag{24}$$

3.3.5 Molar volume

The molar volume of model sulfur compound is estimated by the following correlation [23]:

$$\upsilon_{RS} = 0.285(\upsilon_{cRS})^{1.048} \tag{25}$$

The critical volume of liquid (light naphtha) is determined by a **Riazi-Daubert** equation's [25]:

$$\upsilon_L = 0.285\ (\upsilon_{cL})^{1.048} \tag{26}$$

$$\upsilon_{cL} = (7.5214 * 10^{-3}(T_{meABP})^{0.2896}(\rho_{L,15.6})^{-0.7666})M_L \tag{27}$$

The mathematical model equations presented in this section for ODS reaction have coded and simultaneously solved utilizing gPROMS (**g**eneral **P**rocess **M**odeling **S**ystem) package.

4- Kinetic parameter estimation technique

The tricky point in the improvement of the model based on experiments is parameter estimation. The optimal values of the kinetic parameters have evaluated by minimizing the error between the experimental data and the predicted values by the mathematical model [24, 25].

Two approaches are employed here to achieve the best values of the kinetic parameters depending on the sulfur content in the ODS process at different operating conditions. These approaches are [23, 24] are given below:

First: Linear regression: it determines the reaction order (n) and reaction rate constant (k), then using Arrhenius equation with linear regression to evaluate the activation energy (E) and pre-exponential factor (K_o).

Second: Non-linear regression: which simultaneously evaluates the reaction order (n), activation energy (E) and the pre-exponential factor (K_o) directly.

For the purpose of estimating the best value of kinetic parameter, the following objective function was minimized as shown below:

$$SSE = \sum_{n=1}^{Nt} (C_{RS}^{exp} - C_{RS}^{pred})^2 \tag{28}$$

In equation 26, Nt, C_{RS}^{exp} and C_{RS}^{pred} represent the numbers of runs, the experimental concentration and predicted concentration by model of sulfur respectively.

4.1 Optimization problem formulation for parameter estimation

The model kinetic parameters for ODS process have been obtained via optimization technique with gPROMS software based on two approaches to estimate the kinetic parameters.

a) **First approach (Linear regression):**

The formulation of optimization problem for parameter estimation of ODS process in first approach is presented as follows:

Given	The reactor configuration, the catalyst and the process conditions
Obtain	The reaction order (n) and reaction rate constant (k) at each temperature are optimized and then calculation the activation energy and pre-exponential factor by linear regression to Arrhenius equation.
So as to minimize	The sum of squared error (SSE)
Subjected to	Constraints and linear bounds on all optimization variables of the process

Mathematically utilizing linear regression, the optimization problem is stated as follow:

Min. SSE

n^j , K_i^j , (i=1-3)

st. $f(t, x(t), \dot{x}(t), u(t), v)=0$

$$C_L \leq C \leq C_U$$

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

$$K_{iL}^j \leq K_i^j \leq K_{iU}^j$$

b) **Second approach (Non-linear regression):**

The problem is stated as follow:

Given	The reactor configuration, the catalyst and the process conditions
Obtain	The reaction order (n), activation energy (E) and pre-exponential factor (K_o) are simultaneously estimated.
So as to minimize	The sum of squared error (SSE)
Subjected to	Constraints and linear bounds on all optimization variables of the process

Mathematically, the problem is stated as follow:

Min. SSE

n, E, K_o

st. $f(t, x(t), \dot{x}(t), u(t), v)=0$

$$C_L \leq C \leq C_U$$

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

$$E_L^j \leq E^j \leq E_U^j$$

$$K_{oL}^j \leq K_o^j \leq K_{oU}^j$$

Where: $f(t, x(t), \dot{x}(t), u(t), v)=0$: represent the process model that presented previously. t= is the reaction time. X(t)= represent the set of all algebraic and differential variables. U(t)= is the decision variable. $\dot{x}(t)$ = represent the derivative of differential variables with respect to time. V= is the design variable. C, C^L, C^U = concentration, lower and upper bounds of concentration. L,U = are lower and upper bounds.

The method of optimization solution by gPROMS is performed by two steps that can be presented as follows [25,26]:

- First: implements a simulation including all the equality constraints represented by **(f)** function and satisfying the inequality constraints.
- Second: implements the optimization process (the data of the decision variables like the kinetic parameters that can be updated).

5. Results and Discussions

5.1 Experimental section

The experiments have been conducted in batch reactor by using manganese oxide over nanoparticle of zeolite prepared experimentally as catalyst. The influence of reaction temperature, reaction time and initial concentration of sulfur compound are described as follows.

5.1.1 Effect of reaction temperature

The influence of temperature on the conversion of oxidation reactions of sulfur compound is studied at 303 K, 313 K and 323 K at different batch time (20 min, 30 min and 40 min). From Figures 4 and 5, it can be observed the conversion of sulfur compound has decreased by increasing the reaction temperature. Where, the conversion increases from 68.65% to 89.23% when the reaction temperature increase from 303 °K to 323 °K at 40 min and 250 ppm. Such behavior can be attributed to the following reasons:

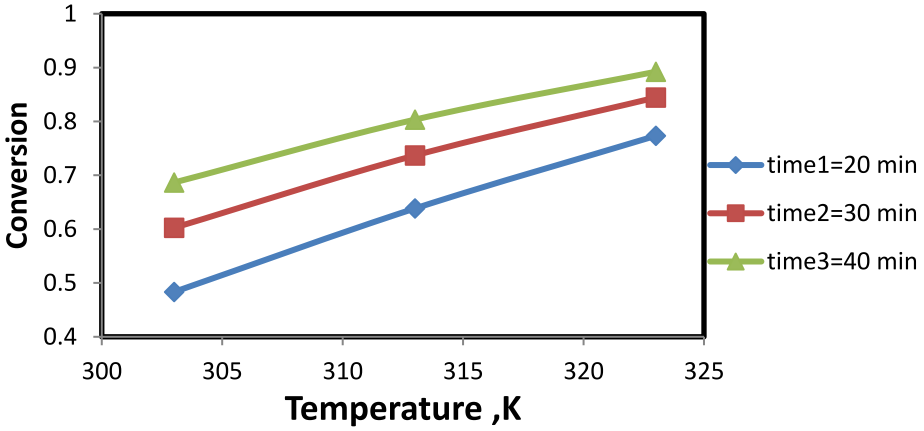

Figure 4: Effect of temperature on the process conversion of sulfur compound for initial mercaptan concentration=250 ppm at different batch time

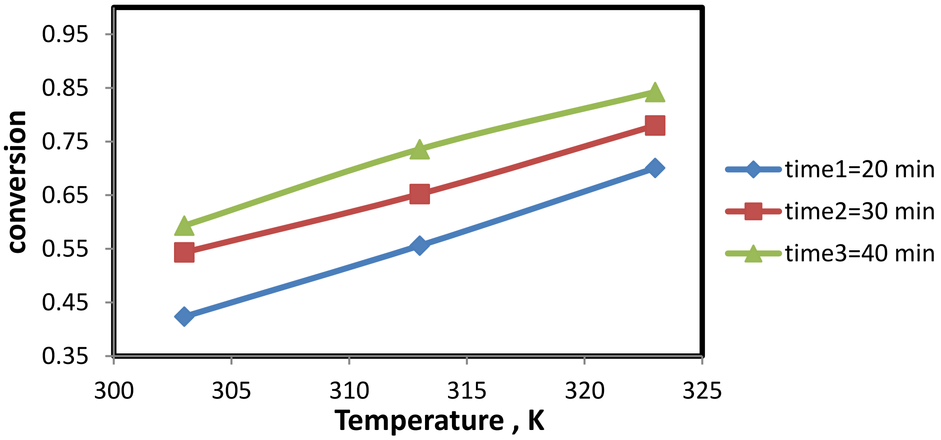

Figure 5: Effect of temperature on the process conversion of sulfur compound for initial mercaptan concentration=150 ppm at different batch time

- Increasing the temperature means that the number of molecules involving in the ODS reaction will increase due to increase the activation energy. Besides, the diffusion and osmoses inside the pores of the catalyst will increase with temperature [27]. Also, temperature rising will have influence on a high impact physical properties. Diffusivity and Henry's constant will increase while surface tension and viscosity will be decreased. Thus, raising the temperature promoted beside the contact batch time the absorption rate of molecular air into light naphtha and the diffusing rate of sulfur compound beside the rate of dissolving air into the catalyst pores for reaching the active sites, where ODS reaction takes place [28,29].
- The phase change from liquid to vapor of sulfur compound will take place when the temperature increase upon to 313 ^{o}K and 323 ^{o}K (boiling point of ethyl mercaptan is 309 ^{o}K). Thus, the conversion of sulfur compound increases because molecules in vapor phase having high diffusion rate into the catalyst pores [30].

5.1.2 Effect of reaction time

The influence of batch time on the conversion of sulfur compound via oxidation reaction was studied at 20 min, 30 min and 40 min, which are shown in Figure 4 and 5.

The conversion increased from 77.32% to 89.23% when the batch reaction time increased from 20 min to 40 min at 323K and 250 ppm. It can be noticed that such increasing in the batch reaction time giving higher conversion due to increase the contact time among the reactants giving longer contact with the active site of the catalyst [10].

Experimentally, the best batch time giving the highest conversion is reported to be at 40 min at higher temperature (323 K) and initial sulfur concentration at 250 ppm.

5.1.3 Influence of initial sulfur concentration

The impact of initial concentration of sulfur compound in light naphtha has investigated at 150 ppm, 200 ppm and 250 ppm as shown in Figure 6.

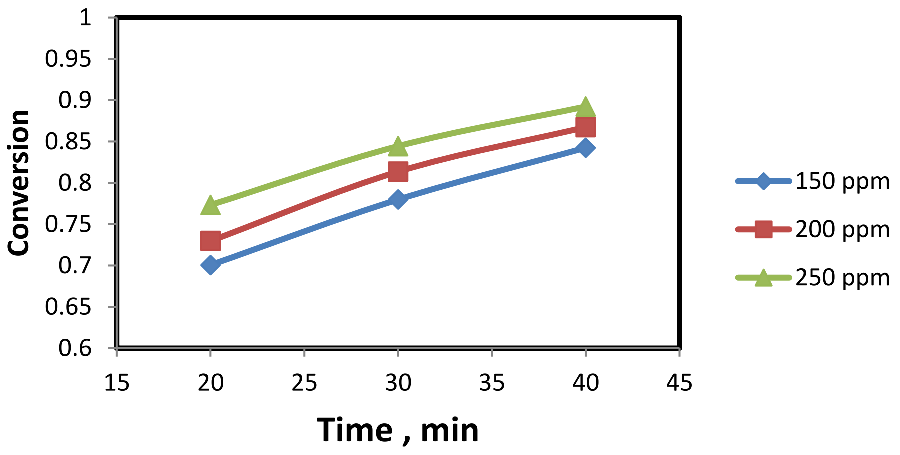

Figure 6: Effect of initial sulfur concentration on oxidation reaction at T = 323 ºK

From Figure 6, it can be noted that the conversion of sulfur compound has decreased upon decreasing the initial sulfur concentration. Where, the conversion of sulfur compound decreased from 89.23% to 84.24% when sulfur concentration decreases from 250 ppm to 150 ppm at 323 K and 40 min as illustrated in Figure 6. Such behavior is attributed to fact that a decreasing in the initial concentration of sulfur compound, the chemical reaction rate will be decreased. However, existing a large amount of sulfur compounds in the liquid leads to increase the number of molecules interaction on the active sites of catalyst. It has also been noted that there is no irreversible adsorption between oxidized mercaptan (disulfide) and active site (responsible of oxidation reaction) of the catalyst due to the weak interaction among them where adsorbed mercaptan are oxidized then the high polar products will be desorbed from the active sites. The experimental results referred to the conversion of sulfur compound increased by increasing the initial sulfur concentration (direct proportion). Such behavior is due to the extent of manganese oxide over the surface of zeolite in addition to zeolite Nano-particle which is characterized as a good adsorbent for sulfur compound [31]. Thus, they have high capability for adsorption/oxidation of sulfur compound at low and high initial concentration of sulfur compound.

5.2 Kinetic parameters estimation

The appropriate values of the kinetic parameters have been calculated, where the errors between the experimental data and the predicted data have minimized through mathematical model. So, the predicted data generated by the model should match as closely as possible to experimental data [32]. The optimal values of the kinetic parameters in this study are achieved by using two approaches (linear and nonlinear) depending on the sulfur content in the ODS process at different operating conditions using mathematical model. The constant parameters utilized in the model are shown in Table 6 below. The measured data points used to estimate the parameters were 29 points for each approach (linear and non-linear) based on experimental data (3 reaction temperatures,.3 batch times and 3 initial sulfur concentrations).

Table 6: Values of constant parameters used in ODS model

Parameter	Symbol	Unit	Value
Initial concentration	Co1, Co2, Co3	Wt%	Co1=0.015, Co2=0.02 Co3=0.025
Temperature	T1, T2, T3	^oK	T1=303, T2=313, T3=323
Batch Time	Tim1,Tim2, Tim3	Min	Tim1=20, Tim2= 30, Tim3=40
Gas constant	R	J/mol. ^oK	8.314
Density of light naphtha at 15^{o}C	ρ_l	g/cm^3	0.6568
Mean average boiling point	T_{meABP}	^oR	608
Acceleration gravity	g	m/sec^2	9.81
Specific surface area of particle	Sg	cm^2/g	Sg_{Mn} =5689134
Volume of catalyst particle	Vp	cm^3	Vp_{Mn} =2.6057*10^{-15}
External surface area of particle	Sp	cm^2	Sp_{Mn} =0.9156*10^{-9}
Bulk density	ρ_B	g/cm^3	=0.57$\rho_{B,Mn}$
Pore volume per unit mass of catalyst	Vg	cm^3/g	Vg_{Mn}= 0.362011
Molecular weight of light naphtha	Mw_L	g/gmol	91.04
Molecular weight of ethyl mercaptan	Mwi	g/gmol	62.134
Mean pore radius	r_g	Nm	$r_{g,Mn}$ =1.2726
Critical volume of ethyl mercaptan	$V_{C,RS}$	$cm^3/gmol$	207

5.2.1 Linear approach

The optimal values of the kinetic parameters generated by 1st approach (Linear regression) give an absolute error less than 5% as presented in Table 7 below:

Table 7: Optimal kinetic model parameters obtained by optimization process by first approach

Parameter	Initial Value	Optimal Value	Unit
n	1.5432	1.60382	-
k1	0.5893	0.393942	$(wt)^{-0.60382}$. min^{-1}
k2	0.8031	0.617125	$(wt)^{-0.60382}$. min^{-1}
k3	1.2765	1.0749	$(wt)^{-0.60382}$. min^{-1}
SSE	-	$1.107179*10^{-6}$	-

- **Activation energy (E)**

Activation energy has been calculated by plotting (lnk) versus (1/T) based on linearization of Arrhenius equation to get straight line with a slope of (-E/R) as shown in Figure 7. Linearization of equation 11 (Arrhenius equation) gives the following equation:

$$lnk = lnk_o - \frac{E}{R}.\frac{1}{T} \quad (29)$$

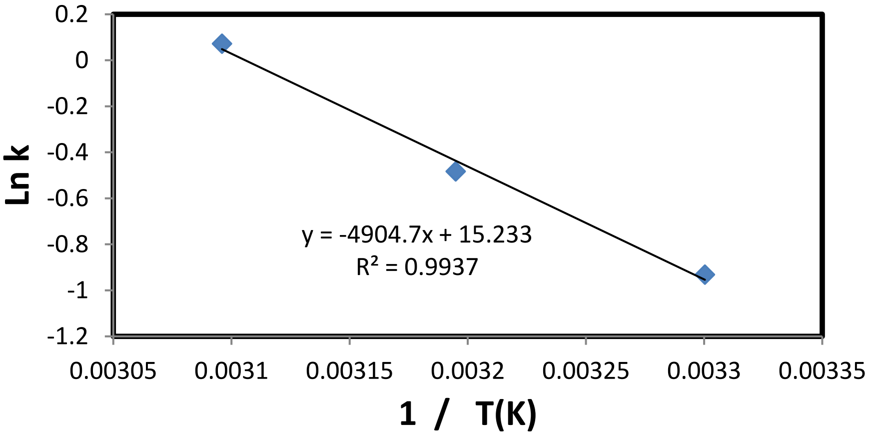

Figure 7: lnk versus 1/T for kinetic parameters of the oxidation process

From this figure, the activation energy has been estimated to be 40.777 kJ/mol is and pre-exponential factor is $4.1267*10^6$

5.2.2 Non-linear approach

In this approach, the reaction order, activation energy and pre-exponential factor have simultaneously been calculated as presented in Table 8 below:

Table 8: Optimal kinetic parameters obtained via optimization process by second approach

Parameter	Initial Value	Optimal Value	Unit
n	2.001	1.59761	-
E	47.80	40.6435	kJ/mol
k_o	$2.23*10^7$	$3.8991*10^6$	$(wt)^{-0.59761} . min^{-1}$
SSE	-	$8.808*10^{-7}$	-

5.3 Experimental and simulation results

After estimating the optimal kinetic parameters, the oxidation process is simulated by gPROMS software. The experimental and predicted results by gPROMS program are presented in Tables 9 to 14 below at different operating conditions for both approaches.

Table 9: Experimental and simulation results using linear approach at T=303 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	88.33	41.11	86.46	42.36	2.16
150	30	71.42	52.38	68.48	54.34	4.30
150	40	59.17	60.55	61.01	59.32	3.01
200	20	108.30	45.84	107.58	46.21	0.67
200	30	85.33	57.33	81.28	59.36	4.99
200	40	69.29	65.35	68.52	65.74	1.12
250	20	125.93	49.62	129.18	48.32	2.51
250	30	97.16	61.13	99.38	60.24	2.23
250	40	77.64	68.94	78.37	68.65	0.92

Table 10: Experimental and simulation results using linear approach at T=313 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	69.57	53.61	66.59	55.60	4.48
150	30	52.47	65.01	52.18	65.21	0.57
150	40	41.24	72.50	39.63	73.58	4.07
200	20	82.87	58.56	78.96	60.52	4.96
200	30	60.74	69.62	59.90	70.05	1.42
200	40	46.77	76.61	45.62	77.19	2.52
250	20	94.13	62.34	90.41	63.83	4.12
250	30	67.46	73.01	65.80	73.68	2.53
250	40	51.14	79.54	49.15	80.34	4.06

Table 11: Experimental and simulation results using linear approach at T=323 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	46.50	68.99	44.91	70.06	3.55
150	30	31.99	78.67	33.03	77.98	3.14
150	40	23.58	84.27	23.63	84.24	0.19
200	20	53.25	73.37	54.06	72.97	1.48
200	30	35.61	82.19	37.28	81.36	4.46
200	40	25.77	87.11	26.51	86.74	2.78
250	20	58.66	76.53	56.68	77.32	3.49
250	30	38.40	84.63	38.89	84.44	1.25
250	40	27.41	89.03	26.91	89.23	1.87

Table 12: Experimental and simulation results using nonlinear approach at T=303 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	88.25	41.16	86.46	42.36	2.08
150	30	71.31	52.45	68.48	54.34	4.15
150	40	59.03	60.64	61.01	59.32	3.24
200	20	108.28	45.85	107.58	46.21	0.66
200	30	85.27	57.36	81.28	59.36	4.91
200	40	69.18	65.40	68.52	65.74	0.97
250	20	125.99	49.60	129.18	48.32	2.47
250	30	97.15	61.13	99.38	60.24	2.24
250	40	77.58	68.96	78.37	68.65	0.99

Table 13: Experimental and simulation results using nonlinear approach at T=313 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	66.60	55.59	66.59	55.60	0.02
150	30	49.62	66.91	52.18	65.21	4.89
150	40	38.64	74.23	39.63	73.58	2.48
200	20	79.03	60.48	78.96	60.52	0.10
200	30	57.22	71.38	59.90	70.05	4.47
200	40	43.65	78.17	45.62	77.19	4.31
250	20	89.51	64.19	90.41	63.83	0.99
250	30	63.36	74.65	65.80	73.68	3.71
250	40	47.59	80.96	49.15	80.34	3.16

Table 14: Experimental and simulation results using nonlinear approach at T=323 K

Initial concentration (ppm)	Batch Time (min)	Concentration by simulation (ppm)	Simulation Conversion (%)	Experimental concentration (ppm)	Experimental conversion (%)	Error (%)
150	20	46.53	68.98	44.91	70.06	3.61
150	30	31.96	78.68	33.03	77.98	3.21
150	40	23.52	84.31	23.63	84.24	0.42
200	20	53.34	73.32	54.06	72.97	1.32
200	30	35.62	82.18	37.28	81.36	4.43
200	40	25.73	87.13	26.51	86.74	2.91
250	20	58.81	76.47	56.68	77.32	3.78
250	30	38.44	84.62	38.89	84.44	1.13
250	40	27.39	89.04	26.91	89.23	1.82

From Tables 9 - 11 (for first approach) and Tables 12 – 14 (for second approach), it is noticed that the 2nd strategy (nonlinear) is more accurate depending on the value of the objective function (SSE). Also, the activation energy and pre-exponential factor calculated by linear approach of Arrhenius equation having higher errors than nonlinear approach which is simultaneously estimated (the activation energy and pre-exponential factor). The comparison results between experimental and predicted data using linear approach have showed in Figures 8-13 at several operating conditions.

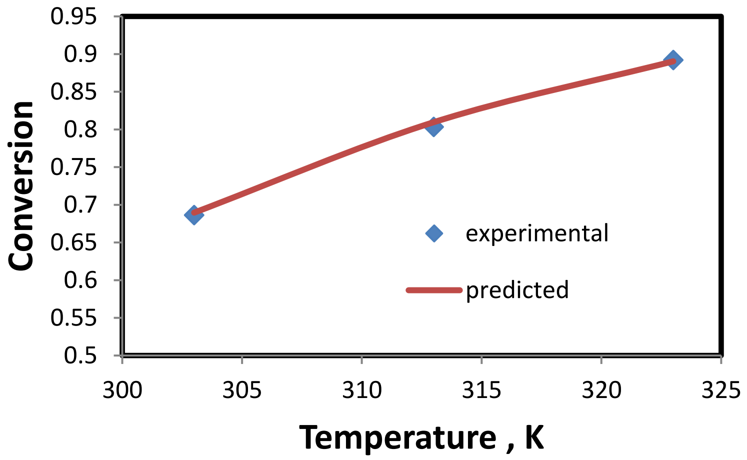

Figure 8: Comparison between experimental and simulated data at initial mercaptan concentration=250 ppm and batch time=40 min

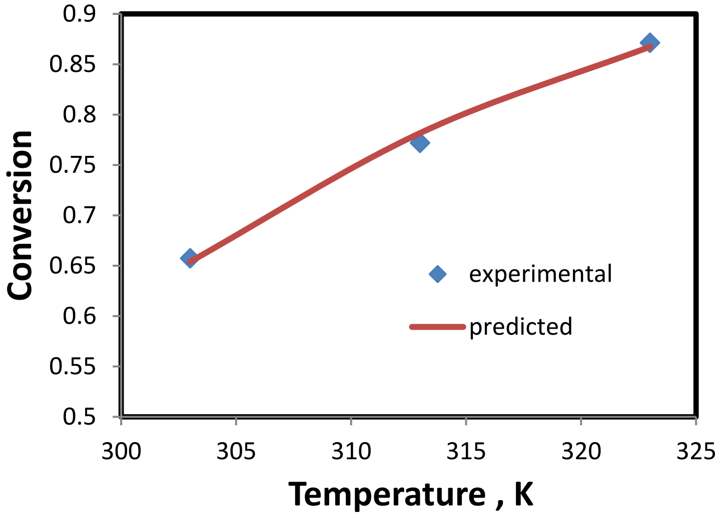

Figure 9: Comparison between experimental and simulated data at initial mercaptan concentration=200 ppm and batch time=40 min

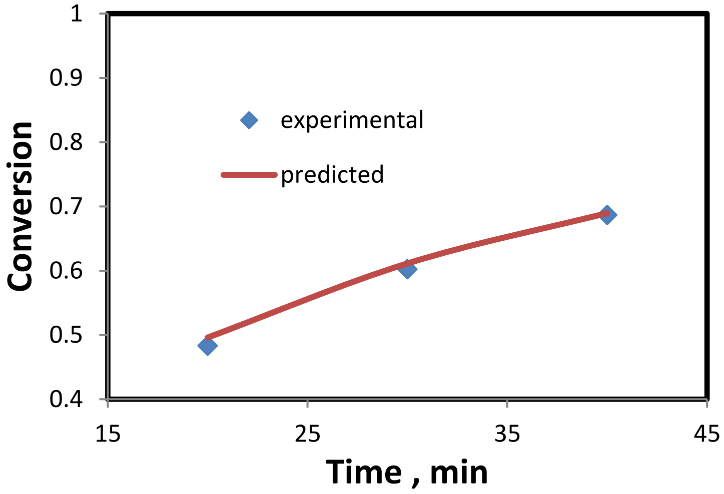

Figure 10: Comparison between experimental and simulated data at initial mercaptan concentration=250 ppm and T=303K

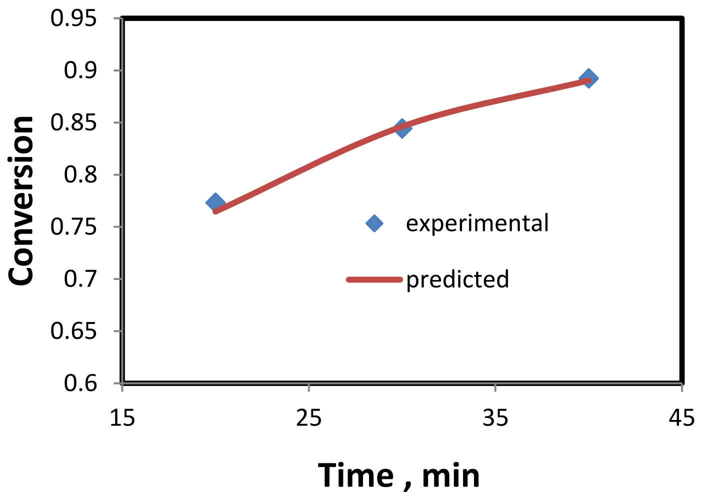

Figure 11: Comparison between experimental and simulated data at initial mercaptan concentration=250 ppm and T=323K

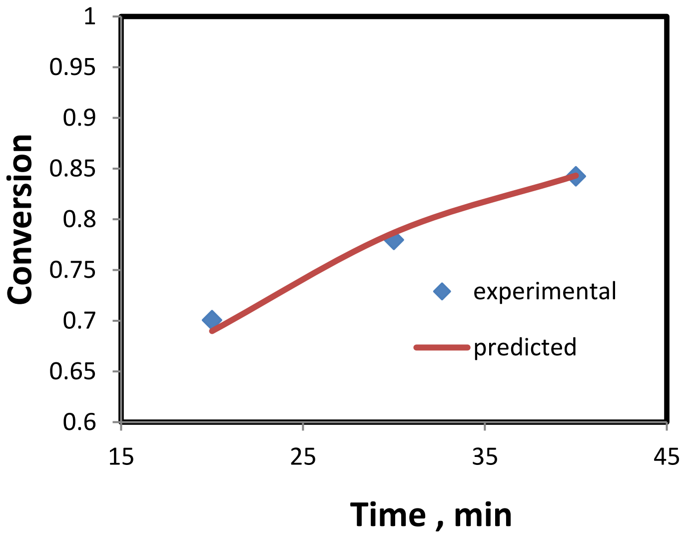

Figure 12: Comparison between experimental and simulated data at initial mercaptan concentration=150 ppm and T=323K

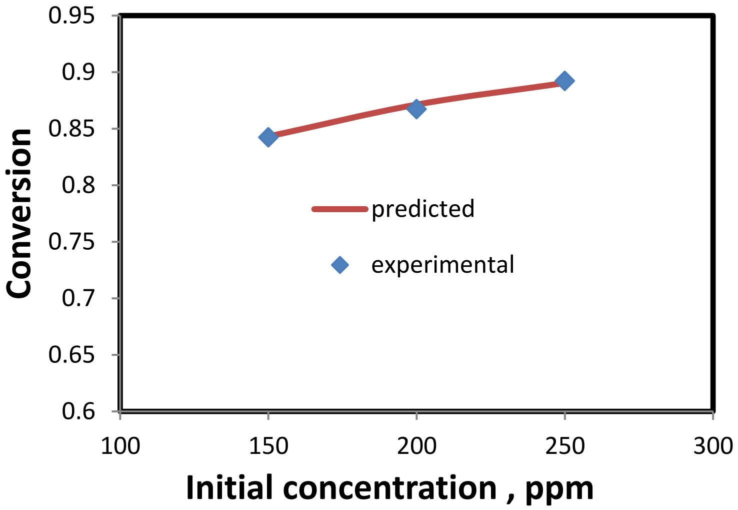

Figure 13: Comparison between experimental and simulated data at T=323K and time= 40 min

From the results shown above, it is observed that the reaction rate of ODS process is increased with increasing the reaction temperature, batch reaction time and initial sulfur concentration.

With the increase in the reaction temperature, the reaction rate will increase owing to increasing rate constant (kinetic constant) resulting in increasing sulfur removal as indicated by Arrhenius equation [4]. Arrhenius equation represents the rate constant as function of temperature of reactants (direct proportion) and activation energy (inverse proportion). In this way, an increase in the batch reaction time, the contact time between reactants on the active sites of catalyst will increase. As well as, the numbers of molecules found on the surface of catalyst are increased as increasing the initial sulfur concentration and as a result the reaction rate will increase. Also, increasing of initial sulfur concentration will create concentration gradient giving more driving force between the bulk solution and surface of catalyst and this plays a significant issue in increasing the reaction rate.

6. Optimal operation conditions for maximum conversion of ODS process (free sulfur content)

6.1 Optimization problem formulation for maximum conversion

After obtaining the optimal kinetic parameter of ODS process based on experiments, the optimal operating conditions to get minimum sulfur content is necessary. Therefore, the formulation of optimization problem for maximum conversion of the process can be stated as follows:

Given	The reactor configuration, the catalyst , the reaction order and activation energy and pre-exponential factor for the reaction
Obtain	The best operating conditions for high conversion
So as to minimize	The product concentration
Subjected to	Process constraints and linear bounds on all optimization variables in the process

Mathematically, the problem can be represented as follows:

Min. C_{RS}

T, time, C_{RSO}

st. $f(t, x(t), \dot{x}(t), u(t), v)=0$

$$(300\text{ K})\ T_L \leq T \leq T_U\ (350\text{ K})$$

$$(10\text{ min})\ time_L \leq time \leq time_U\ (180\text{ min})$$

$$(10\text{ ppm})\ C_{\mathrm{RSO}_L} \leq C_{\mathrm{RSO}} \leq C_{\mathrm{RSO}_U}\ (500\text{ ppm})$$

$$(99\ \%)\ X_{\mathrm{RS}_L} \leq X_{\mathrm{RS}} \leq X_{\mathrm{RS}_U}\ (100\ \%)$$

The optimization solution method is performed by gPROMS software.

6.2 Optimal operating conditions for high fuel quality

After getting the optimal kinetic parameters, such optimal values will be utilized in the kinetic model in order to get the optimal operating conditions to give minimum sulfur content in product (high quality fuel oil). The optimal values for prepared catalyst for this issue are shown in Table 15 below:

Table 15: Optimal operating conditions for ODS process

Parameter	Value	Unit
Co	317.84	ppm
T	327.40	ºK
Batch Time	155.66	min
Conversion	99.05	%

As can be seen from the results reported in Table 15, the optimal reaction temperature, batch reaction time and initial concentration for the purpose of achieving free sulfur content are: 327 K, 155.7 min and 317.8 ppm, respectively. Based on the results, such optimal conditions can be applied with high confidence to achieve the main target of this study employing, the new nano-catalyst which is high fuel quality of gasoline feedstock. As a result, the behavior can match the industrial and environmental regulations.

7. Conclusions

Owing to the environmental with respect to sulfur content (which is regarded the main source of air pollution) and proceeding with the challenges to get an appropriate catalyst of such contamination producing clean fuel, a main thrust for improving of more efficient technologies on new oxidative catalyst is viewed a vital issue in fuel quality development. Using of nano-particles for preparation of catalyst can exhibit high effectiveness in the catalyzed process of the oxidation reaction. The highest conversion of sulfur compound can be achieved over a new homemade nanocatalyst (5% MnO_2/zeolite nanoparticles) under reaction conditions (temperature = 323 K, batch time=40 min and Initial concentration = 250 ppm) using the the air as oxidant giving an excellent ODS reactions and can be utilized confidently to such issue. Mathematical model is developed for the process and validated. Two approaches of optimization techniques can be used (linear and non-linear method) to find the optimal kinetic parameters. It was noted that the second approach (non-linear method) are more accurate compared with first approach utilizing the optimization. The average absolute error among all results was less than 5% at different conditions. The optimal operating conditions to give process conversion above 99% were: temperature =327.4 ^{o}K, batch time=155.66 min and initial concentration = 317.843 ppm. Finally, the homemade new manganese catalyst on nano particle was able to reduce the sulfur content of the fuel significantly thus producing high quality fuel with significantly reduced environmental burden.

Nomenclature

a	Dimensionless
API	American Petroleum Institute
C_{RS}	Mercaptan Concentration, Wt %
C_{RSO}	Initial Concentration of Mercaptan, Wt %
D_{ei}	Effective diffusivity, cm^2/sec
D_{ki}	Knudsen diffusivity, cm^2/sec
D_{mi}	Molecular diffusivity, cm^2/sec
E	Activation Energy, kJ/mol
k	Reaction Rate Constant, $min^{-1}(Wt\%)^{1-n}$
k_{app}	Apparent Rate Constant, $min^{-1}(Wt\%)^{1-n}$
k_{in}	Intrinsic Rate Constant, $min^{-1}(Wt\%)^{1-n}$
k_o	Pre-exponential factor, $min^{-1}(Wt\%)^{1-n}$
M_i	Molecular weight of mercaptan, g/gmol
M_L	Molecular weight of liquid, g/gmol
n	Order of reaction
R	Gas constant, J/mol K
r_g	Pore radius, cm
r_p	Particle radius, cm
S_g	Specific surface area of particle cm^2/g
S_P	External surface area of catalyst particle, cm^2
$Sp.gr_{15.6}$	specific gravity of light naphtha at 15.6^{o}C
T	Absolute temperature, ^{o}K

t	Time, min
T_{meABP}	Mean average boiling point, ^{o}K
V	Volume, cm^3
V_g	Pore volume, cm^3/g
V_P	External Volume of catalyst particle, cm^3
X_{RS}	Conversion of Mercaptan

Greek Symbols

ρ_B	Bulk density, g/cm^3
ρ_P	Particle density, g/cm^3
μ_l	Viscosity of liquid, mPa.sec
η_o	Effectiveness factor
Φ	Thiele modulus
ϵ_B	Porosity
τ	Tortuosity
υ_L	Liquid molar volume, cm^3/mol
υ_{RS}	Mercaptan molar volume, cm^3/mol
υ_{cL}	Critical molar volume of liquid, cm^3/mol
υ_{cRS}	Critical molar volume of mercaptan, cm^3/mol

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