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Optimal Kinetic Parameters of Trickle bed Reactor for Oxidation of 2-Proplymercaptan in Naphtha

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Abstract

The best kinetic of the reaction are estimated based on experimental data obtained from the literature using parameter estimation technique. The best mathematical model for oxidative 2-proplymercaption via oxygen is taking into account the apparent intrinsic kinetics considering internal diffusion and TBR hydrodynamic effect on the reaction process mainly , catalyst wetting efficiency, catalyst effectiveness factor, Thiele model and the effective diffusivity. The optimal operating condition for oxidative process is carried out utilizing. The optimization technique based upon the minimization of the sum squared error between experimental and predicted composition of naphtha oxidative process to determine the best parameters of kinetics models. The predicted product compositions for oxidation process found to be a good agreement with the experimental data for wide range of operating conditions (2.5-10 hr^{-1}, 75-300 ppm and 293-353K) with minimum error 5% among all results

Keywords: Naphtha oxidation, Trickle bed reactor, Mathematical modeling, Optimization

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Introduction

The deep-ultra-desulfurization of feedstock with low sulfur compounds content has been a major concern in petroleum industries due to in the stringent statutory regulations imposed by the government worldwide [1]. Environmental concerns have driven to remove sulfur compounds containing (mercaptans, sulfide, disulfide and thiophene) from fuel because such compounds lead to produce precursors to acid rain by sulfur oxides and air borne particulate material [2].

The catalysts and other types of oxidizer used in oxidation desulfurization process (ODS) should be very high selective to organic sulfur compounds. Sulfur compounds are known to be slightly more polar than hydrocarbon compounds to prevent the oxidation of olefins or aromatic compounds present in the feedstock [3]. The process of catalytic oxidation desulfurization is commonly used for sulfur removal from fuels [4].

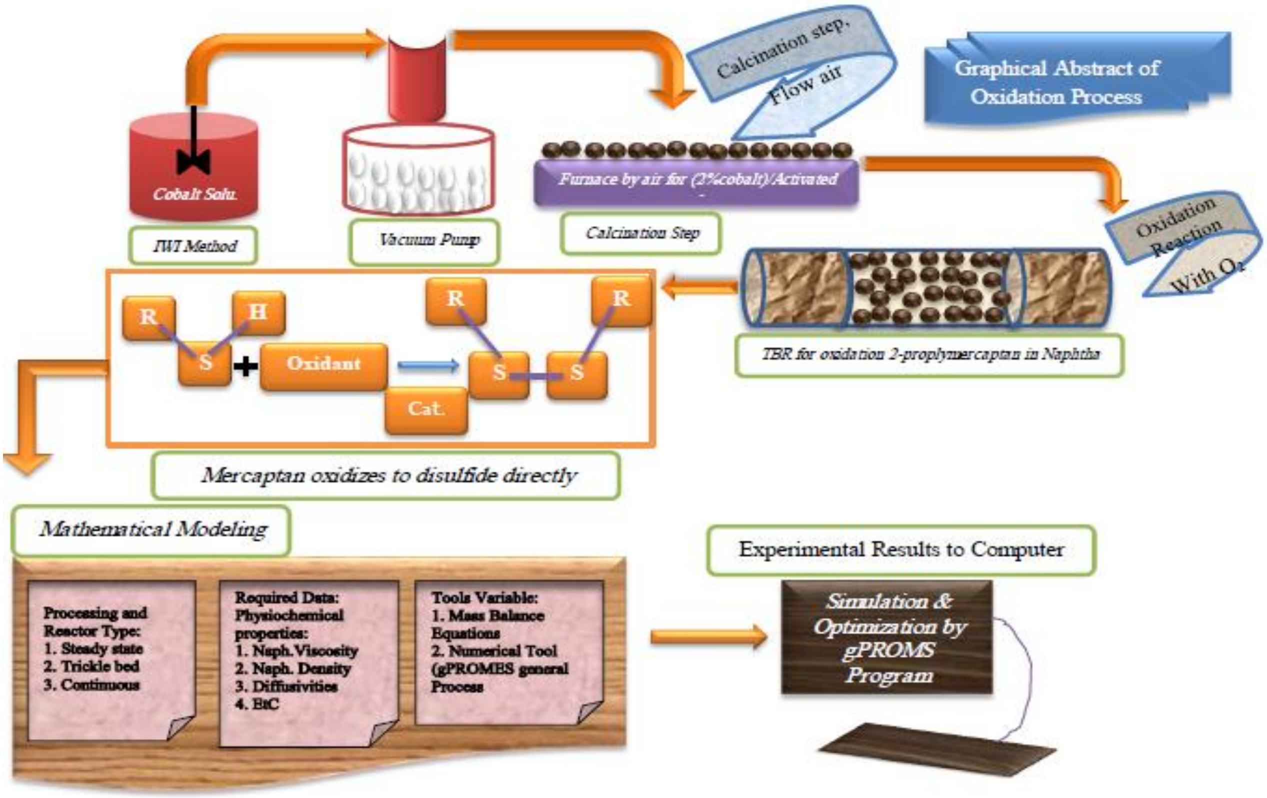
Removing sulfur by oxidation process has received considerable attention owing to the advantages or characteristics of such process. The biggest advantage of this shortage of oxygen-depleting substances is that this process can be carried out under moderate conditions of low temperature and atmospheric pressure. These characteristics distinguish them from the HDS process. Also, the important sulfur compounds tend more reactive to the oxidation process than HDS process. The oxidation process (ODS) is a chemical reaction by catalyst and oxidant leads to form of sulfoxide or sulfones. The oxidized compounds can be removed from oil using non-miscible solvent and choosing the conventional separation method, such as extraction, adsorption or distillation [5].

The oxidants for oxidative desulfurization process (ODS) include nitric acid (HNo_3) [6], hydrogen peroxide (H_2O_2)[7], air[8], oxygen (O_2) [9] and ozone (O_3) [10]. The primary criteria in choosing an appropriate oxidant for ODS process is the active oxygen content as the ratio between the weight of oxygen that can be transfer to sulfur compound, and the molecular weight of oxidant, oxidant cost, selectivity associate to its use in sulfur oxidant, environmental effect (by product), and the necessity to make oxidant recovery and the use of gas oxidant (O_2 and air for example) needs not to make oxidant recovery [11].

There are study on oxidative desulfurization of 2-propelymeracptane. Recently, **Yassin (2010)** [12] developed a mathematical model to investigate theoretical analysis and the performance evaluation for trickle bed reactor process. They compared predictions results with experimental data obtained from trickle bed reactor in oxidation process. They considered a steady state process parametric study and the results showed that an increase in reaction temperature with decreasing in liquid hour space velocity, high conversion was obtained from 2-proplymeracptane oxidative.

However, the model developed by them have described the oxidation process of trickle bed reactor with ignoring most of the parameters affecting the trickle bed reactor, mainly wetting efficiency, internal diffusion and so on. Also, fixed kinetic parameters have been assumed (1st or 2nd order) making the kinetic behavior is not accurate in such oxidation process in addition to the physical properties. Thus, in this study, the optimal kinetic parameters is investigated here in order to obtain the best kinetic parameters of naphtha oxidative with high accuracy and then such optimal parameters can be applied confidently to reactor design operation and conditions.

This study aims to develop a new mathematical modeling of trickle bed reactor for naphtha oxidative process related to 2-proplymercaptan in naphtha. The mathematical modeling has developed based upon the pilot plant experiment with a homemade catalyst (2%Co/AC) for oxidative desulfurization of 2-propelymercaptan in naphtha, under moderate operating conditions using oxygen as the oxidant for 2-proplymercaptan. The gPROMS (general Process Modeling System) Package has been used for modeling, simulation and parameter estimation via optimization. The optimization problem is posed as a nonlinear programming (NLP) and is solved using successive quadratic programming (SQP) method within the gPROMS packing. Graphical abstract as shown in the Figure below.



Experimental Data

The experimental data used in this process has taken from **Yassin (2010)** [12]. **Mathematical Modeling** A heterogeneous one dimensional (axial dispersion) model including a set of mass balances equation as well as kinetics equations is taken is consideration. In the trickle bed reactor, oxidative of RSH-C3 in naphtha by oxygen flow is carried out. The reaction is as follows [14], mercaptan oxidizes to disulfide directly.

$$\text{RSH + Oxidant} \xrightarrow{\qquad\qquad} \text{RSSR}$$

The following assumptions in the mathematical modeling of trickle bed reactor were used in this study:

- ○ The feedstock (naphtha) is saturated with gas inlet (pure oxygen) at all times and gaseous reactant present in large excess.
- ○ The oxidation reaction occurs in axial direction.
- ○ The reaction is assumed to occur only in porous solid.
- ○ Isothermal operation for trickle bed reactor.
- ○ No evaporation or condensation occurs from or into the liquid phase.

• Trickle Bed Reactor with Co-current Gas-Liquid Interface

A trickle bed reactor(TBR) consists of a column that very high(length of TBR), equipped with one or various fixed beds of solid catalysts used in oxidation reaction in the refinery, throughout which gas (Pure O_2) and feedstock liquid (naphtha) move in co-current down flow. Show in the Figure 1. The typical film flow texture found during a trickle-flow regime [40]. In this mode, oxygen is the continuous phase and liquid (naphtha) holdup is lower. This operation is the one most used in practice, since there are less severe limitations in throughput than in counter cur-rent operation.

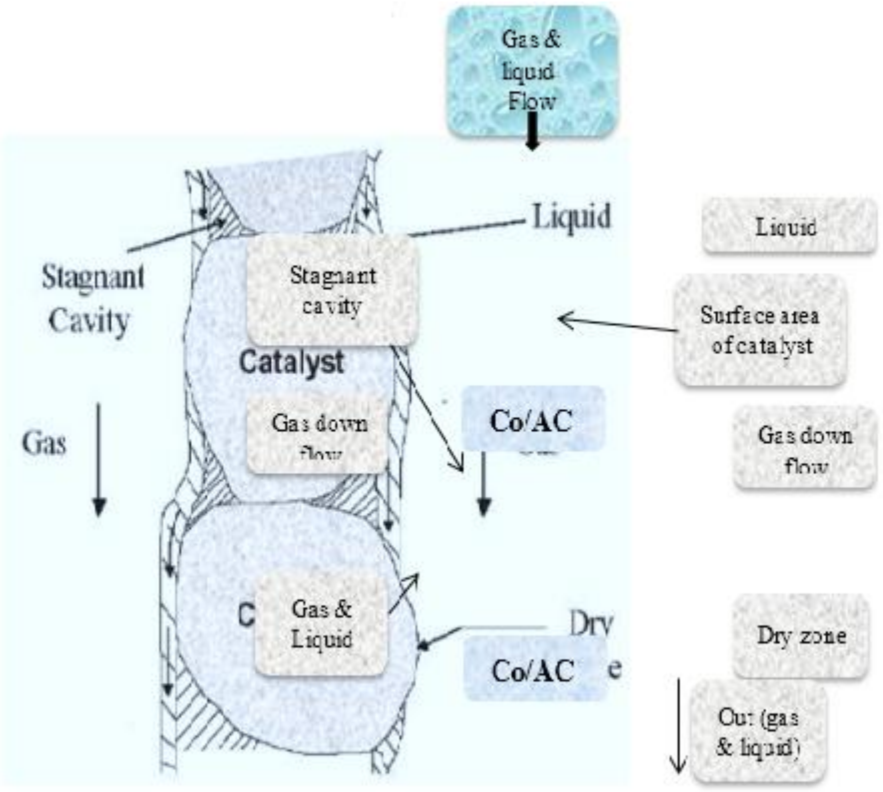


Figure 1: Distribution of feedstock (Naphtha and Oxygen) above the catalyst surface in (TBR).

Mass Balance

The differential equations for oxidation process describing mass balance in the axial direction of a trickle bed reactor are expressed by the following subsections:
The mass balance for catalytic reactor over 2-proplymercaptan compounds entering the trickle bed reactor is follow [15]. Representation of equations in the TBR is show in Figure 2.

$$\Big[\big(Mole\ flux\ of_{(RSH-C3)}, Input * Cross\ section\ area\ of\ reactor\big) - \big(Mole\ flux\ of_{(RSH-C3)}, Output * Cross\ section\ area\ of\ reactor\big) - (Accumulation) - (Generation\ by\ Reaction) = 0\Big] \quad (1)$$

$$\Big[\big(Input\ of\, N_{(RSH-C3)} * A\big) - \big(Output\ of\, N_{(RSH-C3)} * A\big) - \big(Accumulation\ _{(RSH-C3)}\big) - \big(Generation\ by\ Reaction_{(RSH-C3)}\big) = 0\Big] \qquad (2)$$

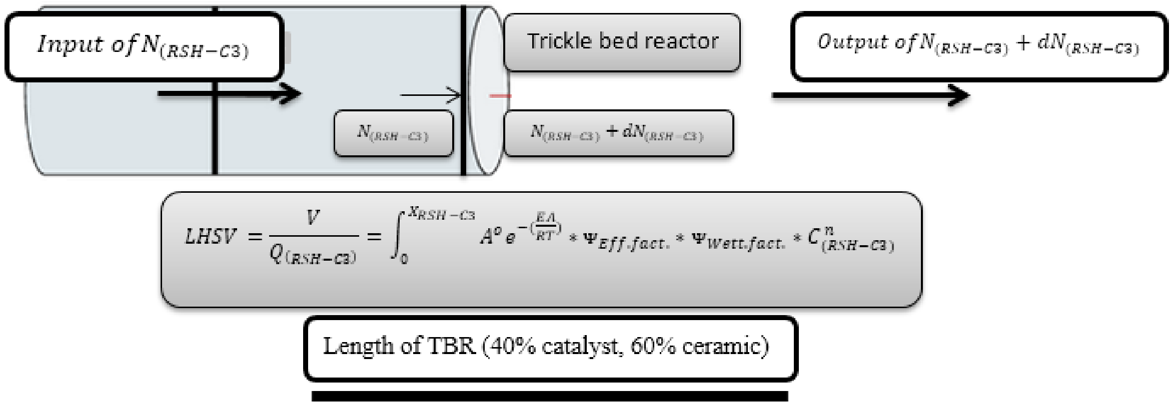


Figure 2. Representation of equations in the Trickle Bed Reactor for oxidation process

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$Input\ of\ N_{(RSH-C3)} * A_{reactor} = C^n_{RSH-C3} Q_{(RSH-C3)}$ (a) $C_{(RSH-C3)} Q_{(RSH-C3)}$ (b)
$Output\ of\ N_{(RSH-C3)} * A_{reactor} =$

$$Generation\ by\ Reaction_{(RSH-C3)} = -R_{(RSH-C3)}dV_{reactor} \qquad (c)$$

$N_A = Mole\ flux\ of\ 2 - RSH$

$A_{reactor} = Cross\ section\ area\ of\ reactor$

$$A_{reactor} = \pi r^2_{reactor} \qquad (d)$$

Accumlution by reaction for mercaptan of oxidation reaction=0

$Substution\ of\ a, b, c\ \&\ d\ in\ equation\ 2\ we\ get,$

$$\left(N_{(RSH-C3)} * \pi r^2_{reactor}\right) - \left(\left(N_{(RSH-C3)} + dN_{(RSH-C3)}\right) * \pi r^2_{reactor}\right) = \left(-R_{(RSH-C3)}dV\right) \qquad (3)$$

$$\left(N_{(RSH-C3)} * \pi r^2_{reactor}\right) - \left(\left(N_{(RSH-C3)} + dN_{(RSH0-C3)}\left(1 - X_{(RSH-C3)}\right)\right) * \pi r^2_{reactor}\right) = \left(-R_{(RSH-C3)}dV\right) \qquad (4)$$

$$\left(N_{(RSH-C3)} * \pi r^2_{reactor}\right) - \left(\left(N_{(RSH-C3)} - N_{(RSH0-C3)}dX_{(RSH-C3)}\right) * \pi r^2_{reactor}\right) = \left(-R_{(RSH-C3)}dV\right) \qquad (5)$$

$$\left(-N_{(RSH0-C3)}dX_{(RSH-C3)}\right)\pi r^2_{reactor} = \left(-R_{(RSH-C3)}dV\right) \qquad (6)$$

- The Chemical Reaction Rate$\left(-R_{(RSH-C3)}\right)$

The chemical reaction rate$\left(-R_{(RSH-C3)}\right)$ and the mechanism of mercaptans oxidation has been reported by some researchers [39], in the presence of an oxidation-reduction catalyst, reactor occurs by an anion-radical mechanism. First forming mercaptide ions

$RSH \rightarrow RSH^{-1} + H^{+1}$

Oxygen can react with the cation by one electron transfer reaction to produce peroxide ion leading to high oxidation state of the cation.

$2M^{+2} + O_2 \rightarrow 2M^{+3} + O_2^{-2}$

Regeneration of the catalyst occurs by one electron transfer reaction between the mercaptide ion and the oxidized cation.

$2RS^{-1} + 2M^{+3} \rightarrow 2M^{+2} + 2RS^{*}$

The resulting thiyl radicals dimerize, and the peroxide ion is destroyed by the next reaction with water.

$2RS^{*} \rightarrow RSSR$

$$O_2^{-2} + H_2O \rightarrow 2OH^{-1} + \frac{1}{2}O_2$$

Finally, hydroxide ions react with proton leading to form water molecule as follows.

$OH^{-1} + H^{+1} \rightarrow H_2O$

The chemical reaction and the mechanism of mercaptans as shows in the Figure 3.

The chemical reaction of oxidation 2-proplymercaptan in naphtha$\left(-R_{(RSH-C3)}\right)$ by oxygen using trickle bed reactor (TBR) may be reasonably taken into consideration assuming n^{th} order kinetics for hydrodynamic processing for all behavior occur in the TBR for oxidation of 2-proplymercaptan using oxygen.

$$-R_{(RSH-C3)} = K_{Hyd.}C^n_{(RSH-C3)} \qquad (7)$$

The hydrodynamic effects and internal diffusion is taken in the reaction based on apparent kinetics as follows [16, 17]:

$K_{Hyd.} = Rate\ constant * Effectivness\ factor * Wetting\ efficiency$

$$K_{Hyd.} = K_{(RSH-C3)} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} \qquad \ldots\ldots (8)$$

Where: $\Psi_{Wett.fact.}$, $\Psi_{Eff.fact.}$ are the catalyst wetting efficiency and effectiveness factor, respectively.

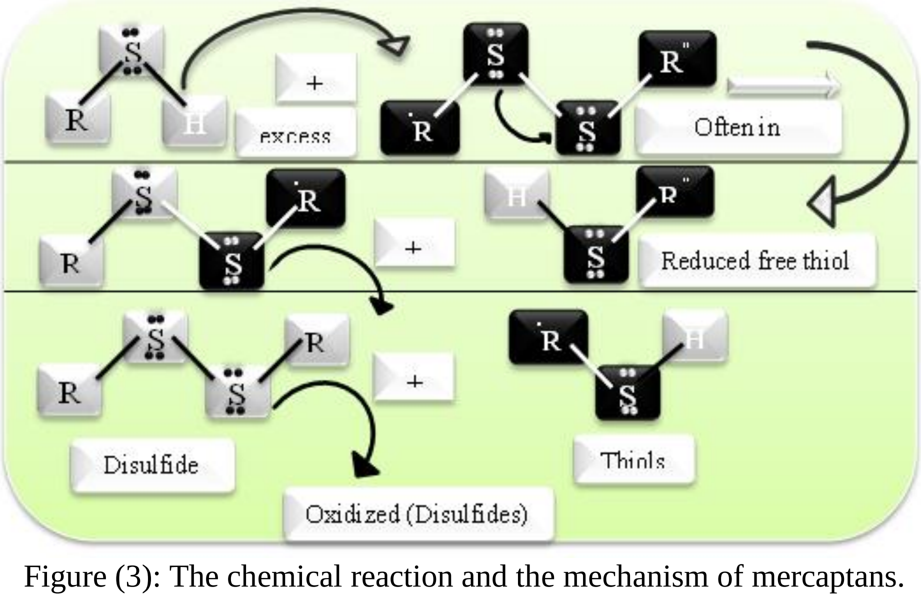


Figure (3): The chemical reaction and the mechanism of mercaptans.

The reaction rate equation for oxidation 2-proplymercaptan is stated as

$$\left(-R_{(RSH-C3)}\right) = K_{(RSH-C3)} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} * C^n_{(RSH-C3)}$$

$$-R_{(RSH-C3)} = -\frac{dC_{(RSH-C3)}}{dt} = K_{(RSH-C3)} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} * C^{n}_{(RSH-C3)} \quad (9)$$

The general behavior can be stated as, higher conversion is achieved at higher temperature due to the fact that at higher temperature, kinetic constant (rate constant) is favorably affected resulting in increasing in 2-proplymercaptan conversion.

Reaction rate constant ($K_{(RSH-C3)}$) can be described by Arrhenius equation as follows [19] :

$$K_{(RSH-C3)} = A^{o} e^{-(\frac{EA}{RT})} \quad …….. (10)$$

Substation equation 10 in equation 9, we get:

The catalytic reaction of 3-proplymercaptan of oxidation by $n^{th} - order$ kinetic substituted equations is integrated and giving the following final expression:

$$(-R_{RSH-C3}) = -\frac{dC_{(RSH-C3)}}{dt} = A^{o} e^{-(\frac{EA}{RT})} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} * C^{n}_{(RSH-C3)} \quad …. (11)$$

$$\tau = \int_{0}^{X_{RSH-C3}} A^{o} e^{-(\frac{EA}{RT})} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} * C^{n}_{(RSH-C3)} \quad ….. (12)$$

The conversion of 2-proplymercaptan to disulfide.

$$X_{RSH-C3} = 1 - \frac{C_{RSH-C3}}{C_{RSHo-C3}} \quad (13)$$

$LHSV$: is the ratio of the hourly volume of oil processed to the volume of the catalyst used in oxidation process.

$$LHSV(hr^{-1}) = \frac{1}{\tau} = \frac{volumetric\ flow\ rate\ to\ the\ reactor\left(\frac{m^{3}}{hr}\right)}{volume\ of\ catalyst(m^{3})} = \frac{Q_{L}}{V} \quad ……. (14)$$

Integration equation becoming:

$$\tau K_{Hyd.} = \frac{Q_{(RSH-C3)}K_{Hyd.}}{V} = \frac{1}{n-1}\left(\frac{1}{C^{n-1}_{(RSHf-C3)}} - \frac{1}{C^{n-1}_{(RSH0-C3)}}\right) \quad (15)$$

$$\tau K_{(RSH-C3)} * \Psi_{Eff.fact.} * \Psi_{Wett.fact.} = \frac{1}{n-1}\left(\frac{1}{C^{n-1}_{(RSHf-C3)}} - \frac{1}{C^{n-1}_{(RSH0-C3)}}\right) \quad (16)$$

$$\frac{K_{(RSH-C3)}\Psi_{Eff.fact.}\Psi_{Wett.fact.}}{LHSV} = \frac{1}{n-1}\left(\frac{1}{C^{n-1}_{(RSHf-C3)}} - \frac{1}{C^{n-1}_{(RSH0-C3)}}\right) \quad (17)$$

- The catalyst wetting efficiency $[\Psi_{Wett.fact.}]$

The catalyst wetting efficiency $\Psi_{Wett.fact.}$ of the external catalyst surface can be calculated based on the atmosphere pressure (in this process at 1 bar) as a function for modified Reynolds number and modified Galileo number using the following correlation [19, 15and 17]:

For Ideal: Complete wetting for catalyst used in the oxidation reaction as show in Figure 4a.

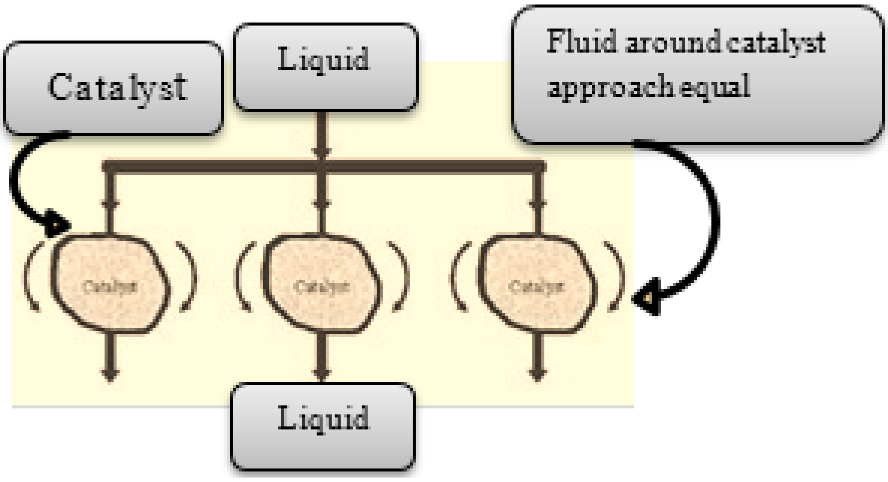


Figure 4a: Wetting efficiency for ideal process.

The wetting efficiency ($\Psi_{Wett.fact.}$) did not complete wetting in the trickle bed reactor (TBR) for non-ideal wetting.

For Non-Ideal: Complete wetting for catalyst used in the oxidation reaction as show in Figure 4b.

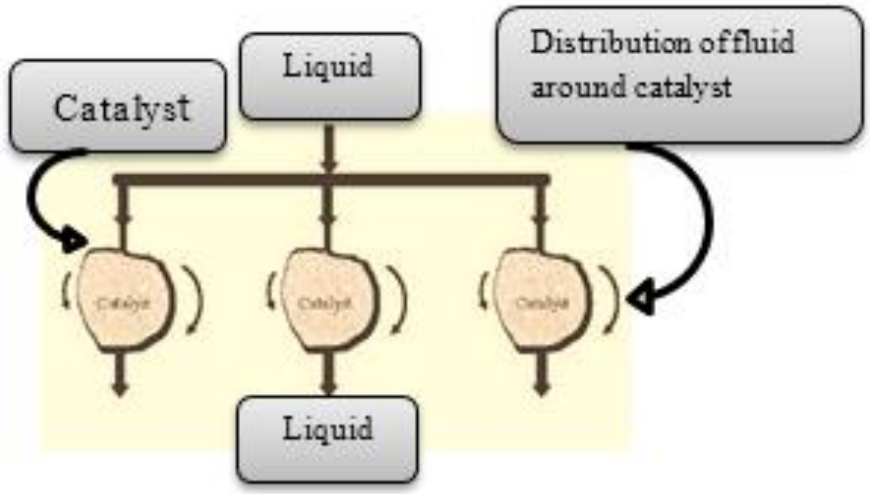


Figure 4b: Wetting efficiency for non-ideal process.

$$\Psi_{Wett.fact.} = 1.617 \left[\frac{\rho_{naphtha} u_{naphtha} D_P}{\mu_{naphtha}(1-\epsilon_{Void})}\right]^{0.146} * \left[\frac{\rho_{naphtha}^2 D_p^3 g \epsilon_{Void}^3}{\mu_{naphtha}^2 (1-\epsilon_{Void})^3}\right]^{-0.071} \quad (18)$$

- The Porosity or void fraction $[\epsilon_{Void}]$

The Porosity or void fraction (ϵ_{Void}) of the catalyst is a measure of the void (i.e. 'empty') spaces in a material, and is a fraction of the volume of voids over the total volume. The catalyst is estimated for undiluted sphere packed catalyst using in the trickle bed reactor from the following equation [20, 21and 22]. The void fraction and porosity in particle is show in Figure 5.

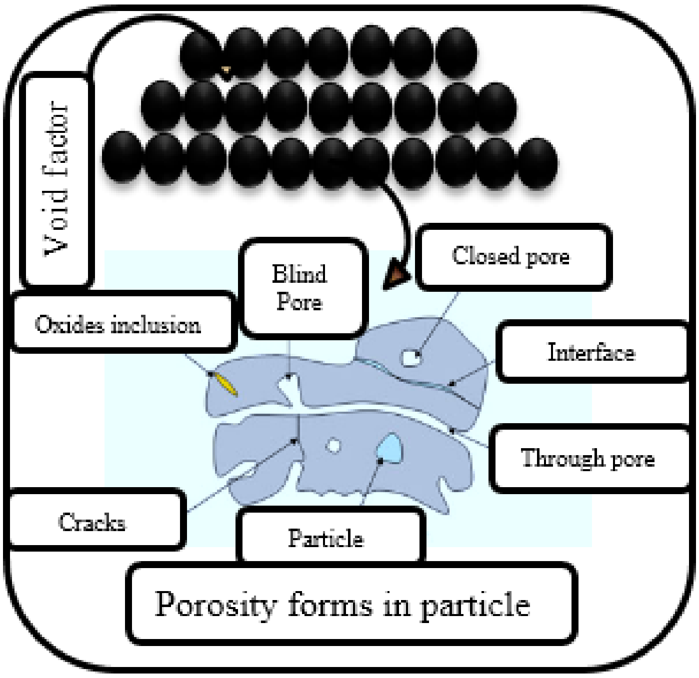


Figure5. Void fraction and porosity forms in packed bed and particle respectively.

$$\epsilon_{Void} = \left[\frac{Volume\ of\ voids\ in\ the\ beds}{total\ volume\ of\ bed}\right] \quad (19a)$$

$$\epsilon_{Void} = 0.453 + 0.037 \left(\frac{D_t - 2D_{pe}}{D_t}\right)^2 \quad (19b)$$

D_{pe}: Equivalent particular diameter, which is defined as the diameter of the sphere that has the same external surface (or volume) as the actual catalyst particle. It is an important particle characteristic that depends on the particle size and shape.

$$\epsilon_{Void} = 0.453 + 0.037\left(\frac{D_t - 2D_p}{D_t}\right)^2 \quad (20)$$

- Density of Naphtha$\left[\rho_{naphtha}\right]$

The density of Naphtha as a function of temperature has been proposed by the following generalized equation to calculate the density of liquids as shown below [23, 24]:

$$\rho_{naphtha} = \left[\frac{P_C * MW_{naphtha}}{RT_C Z_C\left(1+(1-T_r)\right)^{0.285714}}\right] \quad (21)$$

$$Z_C = \frac{P_C V_C}{RT_C} \quad (22)$$

$P_C: Critical\ pressure\ of\ naphtha, psia$

$MW_{naphtha}: Molecular\ weight\ of\ naphtha, \frac{Ib}{Ibmol}$

$R: Gas\ constant, \frac{ft^3 psia}{Ib_{mol} R^o}$

$T_C: Critical\ temperature\ of\ naphtha, R^o$

$Z_C, Critical\ compressibility\ factor, -$

$T_r, Reduced\ temperature, -$

$V_C, Critical\ molar\ volume, \frac{ft^3}{Ib_{mol}}$

- Viscosity of Naphtha$\left[\mu_{naphtha,b}\right]$

The viscosity of naphtha depends mainly on the temperature (inversely proportion), thus, it is particularly desirable to determine liquid viscosities from experimental data when such data exist. Many correlations were used to calculate liquid viscosity and one of the best correlations that have widely been applied in calculating liquid viscosity [24, 25].

$$ln\mu_{naphtha} = \left[\frac{ln\mu_{naphtha,b}}{ln(\alpha * \mu_{naphtha,b})}\right]^{\varphi} ln\left(\alpha * \mu_{naphtha,b}\right) \quad \ldots\ldots (23)$$

$\varphi, Volume\ fraction\ of\ molecule$

$$\varphi = \left(\frac{1-T_r}{1-T_{br}}\right) \quad (24)$$

$$T_r = \left(\frac{T}{T_C}\right) \quad (25)$$

$$T_{br} = \left(\frac{T_b}{T_C}\right) \quad (26)$$

- Effectiveness factor $\left[\Psi_{Eff.fact.}\right]$

The effectiveness factor ($\Psi_{Eff.fact.}$) can be determined as function of Thiele modulus ($\emptyset$) with the following equation valid for sphere particles [26]:

$$\Psi_{Eff.fact.} = \frac{Rate\ of\ reaction\ with\ catalyst\ pore\ diffusion\ resistance}{Rate\ of\ reaction\ with\ surface\ conditions}$$

$$\Psi_{Eff.fact.} = \frac{3}{\emptyset^2}\left[\frac{\emptyset Sinh\emptyset - Cosh\emptyset}{Cosh\emptyset}\right] \quad (27)$$

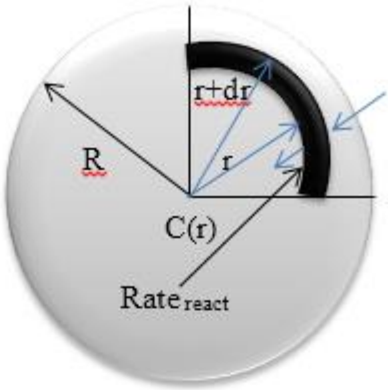
Effectiveness factor as a function of Thiele modulus for different geometries of catalysts are show in semi log flow sheet in the Figure6.

- Thiele Diffusion Modulus$[\emptyset]$

For n^{th} order for oxidation irreversible reaction, the general Thiele Modulus ($\emptyset$) is evaluated using the following relationship [27]:

$$\emptyset = \frac{r_{intrinsic}}{r_{diffusion}}$$

Rate of react is a function of (volume of shell, surface area of pores per volume catalyst and rate per area catalyst). Representation of mathematical model for particle catalyst of Thiele diffusion modulus is show in the below figure.



Where:

$$Volume\ of\ shell = 4\pi r^2 dr$$

$$\emptyset = \frac{V_P}{S_P}\left[\frac{(n+1)K_{Hyd.}(C_{RSH-C3})^{n-1}\rho_{(Co/Ac)}}{2\mathcal{D}_{ei}(1-\epsilon_{Void})}\right]^{1/2} \quad (28)$$

For spherical shape of particle (Co/AC) the surface area (S_P), and external volume (V_P) can be calculated as shown below:

$$S_P = 4\pi\left(R_p\right)^2 \quad (29)$$

$$V_P = \frac{4}{3}\pi\left(R_p\right)^3 \quad (30)$$

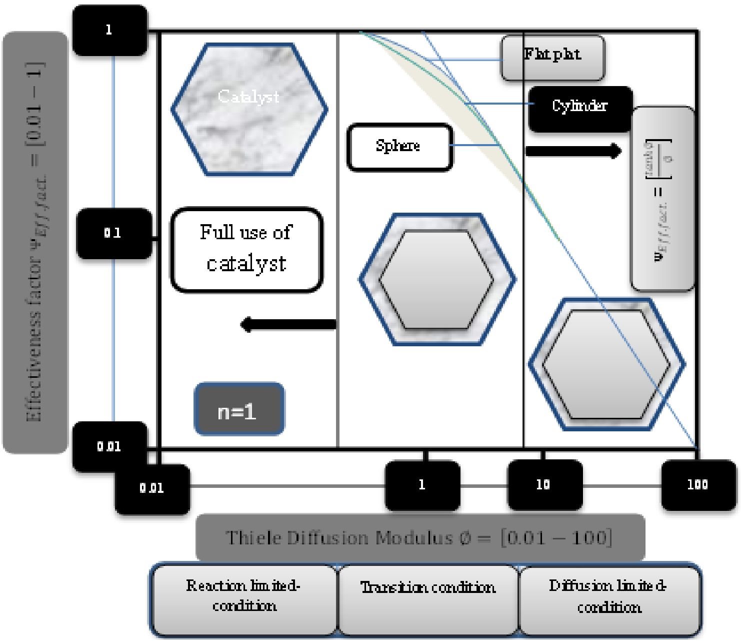


Figure 6: Effectiveness factor as a function of Thiele modulus for different geometries of catalysts.

- Effective diffusivity$[\mathcal{D}_{ei}]$

$\mathcal{D}_{ei}$ Effective diffusivity is the relation between porosity and tortuosity of the pore network inside the particle is taken into account with modeling [28]. As shown in the Figure 7.

$$\mathcal{D}_{ei} = (\mathcal{J} * \epsilon_s)\left[\frac{\mathcal{D}_{mi} * \mathcal{D}_{ki}}{\mathcal{D}_{ki} + \mathcal{D}_{mi}}\right] \qquad (31)$$

Catalyst Porosity(ϵ_s), Catalyst particle porosity can be calculated using simple equation below depending on the particle density and pore volume, Show in Figure8.

$$\epsilon_s = Catalyst\ porosity = \left(\rho_P V_g\right) \qquad (32)$$

The effective diffusivity inside the catalyst particle [29] includes two diffusion contributions: Knudsen diffusivity $[\mathcal{D}_{ki}]$[29] and Molecular diffusivity$[\mathcal{D}_{mi}]$ [30, 31].

$$Rate\ per\ area\ catalyst = K_{Hyd.}C^n(r)$$

Knudsen diffusivity is Known in this equation [15, 17] based on Mean pore radius:

$$\mathcal{D}_{ki} = 9700\left[\frac{2V_g}{S_g}\right]\left[\frac{T}{MW_{Oxgyen}}\right]^{\left(\frac{1}{2}\right)} \qquad (33)$$

Molecular diffusivity:

The Molecular diffusivity of naphtha can be calculated with respect to following equation:

$$\mathcal{D}_{mi} = 8.93 \times 10^{-8}\left[\frac{v_L^{0.267}\,T}{v_{RSH-C3}^{0.433}\mu_{naphtha}}\right] \qquad (34)$$

v_{RSH-C3} Molar volume of 2-proplymercaptan in naphtha, can be calculated by the following equation with respect to correlation [32].

$$v_{RSH-C3} = 0.285 v_{CNaphtha}^{1.048} \qquad (35)$$

The critical specific volume of liquid (naphtha) is estimated by correlation [33].

$$Surface\ area\ of\ particles\ of\ catalyst = 4\pi\left(R_p\right)^2$$

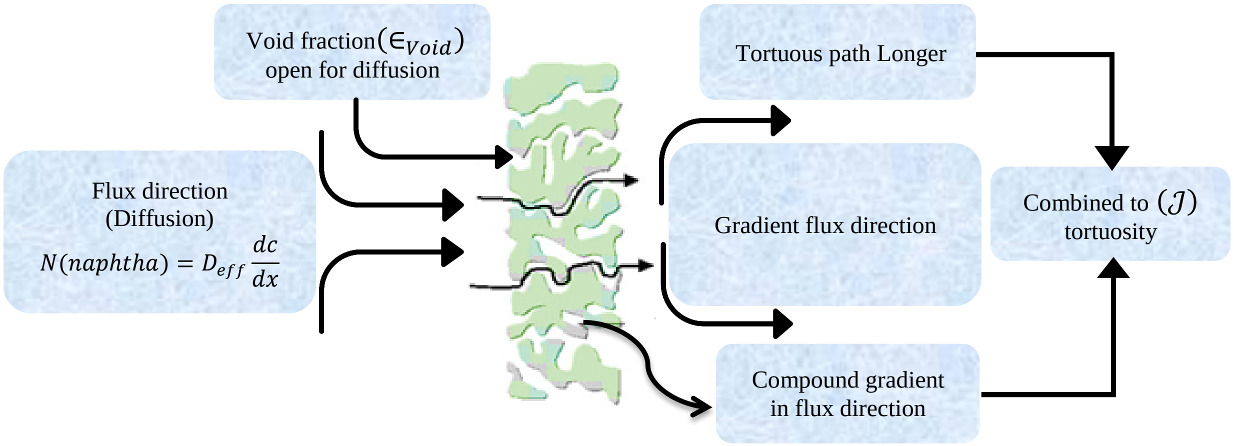


Figure 7: Diffusion in pores of catalyst and presentation of tortuosity factor.

$$v_{cNaphtha} = (7.5214 \times 10^{-3}(T_{meABP})^{0.2896}(\rho_{15.6})^{-0.7666})MW_L \ldots$$

T_{meABP}, Mean average boiling point [33] (36)

$$Mean\ average\ boiling\ point = Volume\ average\ boiling\ point - \Delta$$

$$MABP = VABP - \Delta \tag{37}$$

$$VABP = (T_{10} + T_{30} + T_{50} + T_{70} + T_{90}) \tag{38}$$

$$\Delta = \frac{(T_{90} - T_{10})}{(90-10)} \tag{39}$$

- <u>The tortuosity factor ($\mathcal{J}$)</u>

The tortuosity factor ($\mathcal{J}$) of the pore network, is used in the calculation of $\mathcal{D}_{ei}$ because the pores are not oriented along the normal direction from the surface to the center of the catalyst particle [34] :

$$\mathcal{J} = \frac{2 - \log(\epsilon_S)}{2\epsilon_S} \tag{40}$$

The Trickle Bed Reactor process model for oxidation reaction of naphtha (Equations 1−40) is developed and solved within the gPROMS package. Parameters used in the mathematical model for oxidation reaction are shows in Table1

Table1: Values of constant parameters use in mathematical model.

0	Symbol & Value	Unit
Initial concentration	*C1=300, C2=150, C3=75*	*ppm*
Temperature	*T1=293, T2=313, T3=333, T4=353*	*K*
Liquid hour space velocity	*LHSV1=2.5, LHSV2=3.33, LHSV3=5, LHSV=10*	hr^{-1}
Gas constant	*R=8.314, 0.0823, 10.73*	*J/mol.K*, $atm.lit/.mol.K$, $ft^3.\ Psia/Ibmol.\ R$
Molecular weight of naphtha	MW_L=76.16	*g/gmol*
Molecular weight of oxygen	MW_0=0.21	*g/gmol*
Tube diameter	D_t=1.6	*Cm*
Bulk density	ρ_b=0.46	g/cm^3
Critical specific volume of the 2-proplymercaptan compound	$V_{CRSH\text{-}C3}$=5.0976	ft^3/mol
Velocity of naphtha	u_{L1}=0.02084, u_{L2}=0.02778, u_{L3}=0.04144, u_{L4}=0.08109	*cm/sec*
Acceleration gravity	*g=981*	cm/s^2
Total pore volume	V_g=0.561	cm^3/g
Total geometric of surface area of catalyst particle	S_p=0.0419	cm^2
Total geometric volume of catalyst particle	$V_p = 0.80676 * 10^{-3}$	cm^3
Critical pressure of naphtha	*Pc*	*Psia*
Specific surface area	S_g=2803000	cm^2/g
Diameter of catalyst particle	D_p=0.115	*Cm*
Pressure	*P=14.7*	*Psia*
Mean average boiling point	T_{meABP}=675.55	*R*
Critical temperature of naphtha	T_c	*R*

Estimation of Kinetic Parameters of the Model

For solving the set of ordinary differential equations (ODEs) (for the steady-state regime) or the set of PDEs (for the dynamic regime) presented of oxidation reaction, it is important to estimate a lot of the parameters and chemical properties of the system. Those parameters can be evaluated with existing correlations, whose accuracy is of great importance for the entire state of robustness of the reactor model. Estimation of kinetic parameters is an important and difficult step in the development of models, calculations of unknown kinetic parameters can be achieved by utilizing experimental data. When estimating kinetic parameters of the models, the goal is to calculate appropriate parameter values so that errors between experimental and theoretical data (based on mathematical model) are minimized. The kinetic modeling of oxidation reaction by oxygen process using the following objective function based upon the minimization of the sum of squared errors (SSE) between the experimental concentrations of 2-proplymercaptan ($C_{RSH-C3\ Exp.}$) and predicted ($C_{RSH-C3\ Pred.}$). For parameter estimation, the objective function (OBJ), as given below, was minimized: $\boldsymbol{OBJ = \sum_{n=1} \left(C_{RSH-C3}^{Exp.} C_{RSH-C3}^{Pred.}\right)^2}$ It is known that the predicted conversion of 2-proplymercaptan can be calculated from the following equation:

$$\boldsymbol{X_{RSH-C3} = \frac{C_{RSH0-C3} - C_{RSH-C3}}{C_{RSH0-C3}}}$$

Optimization Problem Formulation for Parameter Estimation

Mathematically, the optimization problem can be described as:

Min *SSE*
N^j, K_i^j, (i=1-4, j=Cobalt/Activated carbon)
St.F (z, x (z), $\underline{x}$ (z), u (z), v) = 0
$C_L \leq C \leq C_U$
$N^j_L \leq N^j \leq N^j_U$
$K_i^j{}_L \leq K_i^j \leq K_i^j{}_U$

F (z, x (z), $\underline{x}$ (z), u (z), v) = 0
Represents the process models presented previously, where z is the independent variable, u(z) is the decision variable, x(z) gives the set of all differential and algebraic variables, $\underline{x}$(z) denotes the derivative of differential variables with respect to length of the bed reactor, and v represents the design variables or the length independent constant parameters.
Where:
C: concentration
C_L and C_U: lower and upper bounds

Results and Discussion

The industrial process can be represented by the mathematical model depending on the results of the experimental process and can represent the process based on the results, where the all design mathematical model can be represented by most of the 27 results of experimental run [15, 17and 24]. The model based on 48 runs results that have been represented via finding the lowest ratio between the theoretical and the experimental about 5% among all the results.

The Best Kinetic Parameter of the Model for oxidation Reaction

The generated kinetic parameters obtained via optimization technique for oxidation reaction process of naphtha are shown below for the oxidation reaction: $(n = 1.14467), (K_1 = 0.72989,\ K_2 = 1.18056,\ K_3 = 1.92782\ and\ K_4 = 2.59994) hr^{-1} wt^{n-1}$. The model kinetic parameters of oxidation reaction have estimated using via gPROMS used for estimating kinetic parameters. According to Arrhenius equation, a plot of (ln*K*) versus (1/*T*(K)) gives a straight line with slope equal to (-EA/R), from which the activation energy is calculated as illustrated in Figure (8). The obtained values of activation energies equal $17.7071 (KJ/mole)$ and the frequency factor value 1062.202. The obtained values are close to those obtained in the literature. Arrhenius equation is shown blow:

$$K_{(RSH-C3)} = A^{o} e^{-(\frac{EA}{RT})} \tag{41}$$

$$lnK_{(RSH-C3)} = lnA^{o} - \frac{EA}{RT} \tag{42}$$

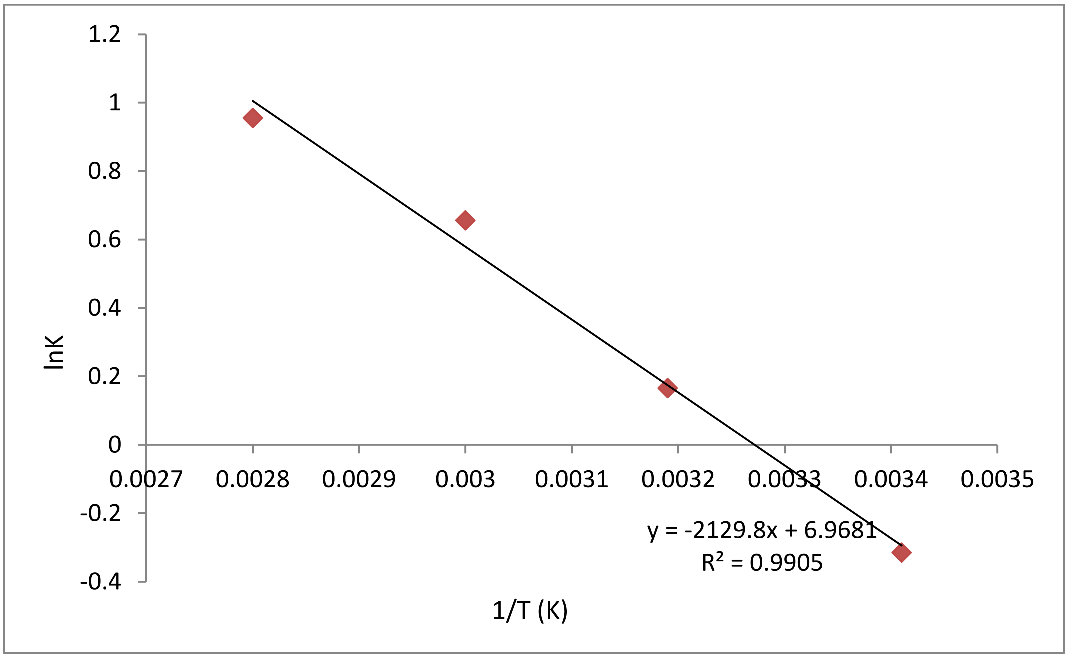


Figure 8: Evaluated value of activation energy for 2-proplymercaptan oxidation

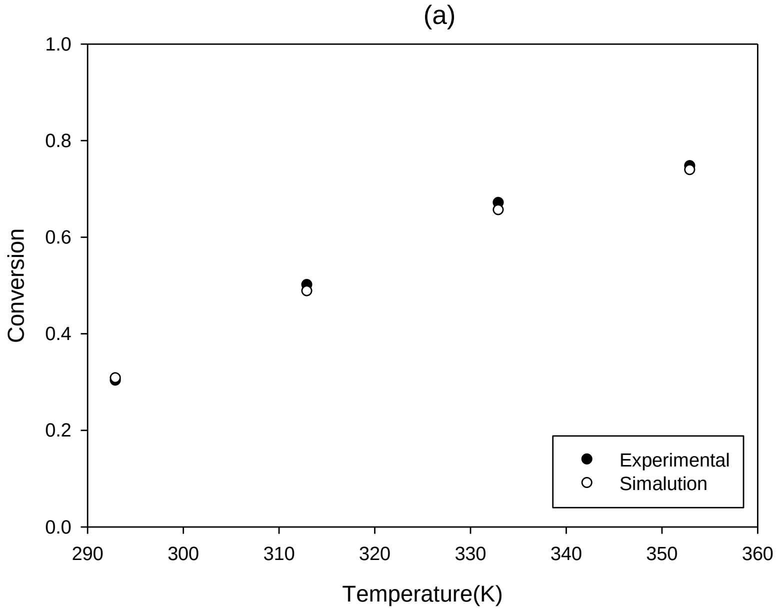
The activation energy of 2-proplymercaptan found in the current work is in agreement with that found in the literature, which is (15.88kJ/mole) using formic acid/H_2O_2 as the phase transfer catalyst[35]. However, **Huang** [36] has found that the activation energy of sulfur is (28.7 kJ/mole) using H_2O_2 as oxidant and poly tetrafluoro ethylene as catalyst system. Also, the solvent used in the process of oxidation reaction can effect on the activation energy, as well as the type of sulfur using in the processing.

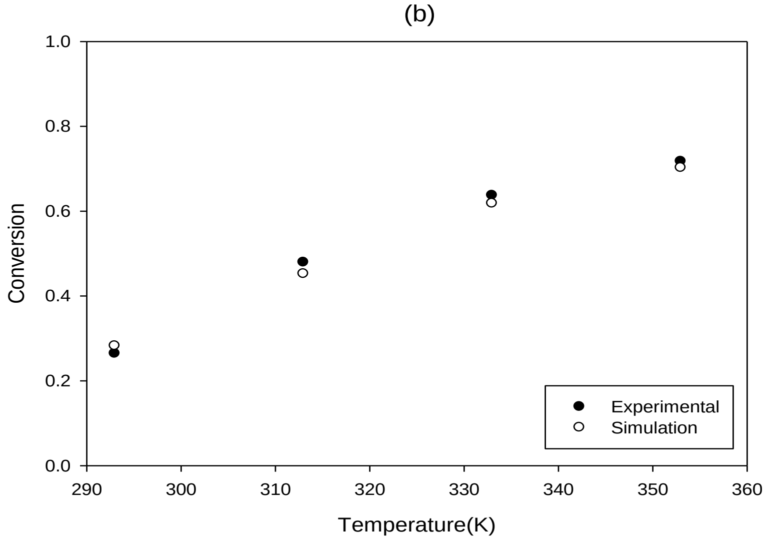
Change of 2-Proplymercaptan Phase

The temperature used in oxidation reaction is increasing from 293 to 353 K, phase changes of in feedstock is found including sulfur content (2-proplymercaptan) from liquid to vapor boiling range of 2-proplymercaptan equal to 326 K, causing the oxidation reaction of 2-proplymercaptan in naphtha to be more active at vapor phase due to high diffusivity rate of molecules inside catalyst pores. While another mercaptan in the feedstock throughout oxidation reaction does not effect on the mercaptan phase through temperature change, where (n-butly mercaptan having boiling point of 373K) this mercaptan does not change the phase when temperature changes from 293 to 353K. This agrees with findings of **Xia** [14], which showed a positive effect of temperature with conversion of OSCs and disagrees with respect to **Gheni** [13] that showed an increase in conversion when the temperature increased from 293 to 313 K.

Effect of Temperature on Oxidation Process

Figure (9) shows the effect of temperature on the oxidation of 2-proplymercaptan at different liquid hour space velocity. The conversion of 2-proplymercaptan is increasing with increasing the temperature from 333 to 353 K at constant liquid hour space velocity of 2.5 hr^{-1} as shown in Figures (9a, 9b, 9c) at LHSV of 2.5 hr^{-1} and different initial concentration of 2-proplymercaptan (a = 300 ppm, b = 150 ppm, c = 75 ppm). It has been observed based on the results obtained that the predicted product conversion showed very good agreement with the experimental data for a wide range of operating conditions. Such behavior (higher conversion) is achieved at higher temperature due to the fact that at high temperature, kinetic constant (reaction rate constant) is favorably affected resulting in increasing in 2-proplymercaptan conversion. The increase in the temperature level will contribute to an increase of magnitudes of some important physical properties (diffusivity and Henrys constant and mainly, decreasing in the viscosity and surface tension). However, the increase in the temperature of the oxidation process will raise the absorption rate of molecular oxygen in the liquid at the diffusion rate of sulfur compound, and the rate dissolved oxygen in the side catalyst, leading to format oxidation reaction[15, 17 and37].





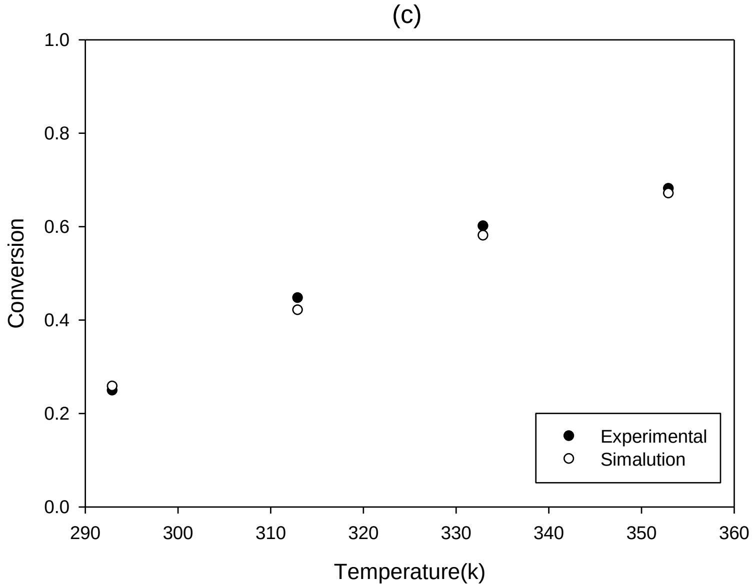


Figure 9: Effect of temperature on 2-proplymercaptan conversion. Reaction conditions (initial 2-proplymercaptan concentration, (a)=300ppm, (b)=150ppm, (c)=75 ppm at 2.5 hr^{-1}).

Impact of Initial 2-Proplymercaptan Concentration on Oxidation Reaction

The impact of initial concentration on the 2-proplymercaptan conversion has studied in the range (300, 150, 75 ppm) with other parameters (LHSV and temperature). The comparison between the experimental data and the predicted data is plotted in the Figure (10) and a good agreement between the experimental results and predicted data have been obtained. In the range of such experiments, sulfur conversion is decreasing as decreased in the inlet sulfur concentration as shows in the Figure (11). It has been noticed that the sulfur conversion decreased from 74.7% to 68.2% at the same operating condition at 353K and 2.5 hr^{-1} for inlet sulfur of 300 to 75, respectively. When decreases the sulfur molecular coverage active site over the catalyst surface leads to decrease the activation of the oxidation reaction [38].

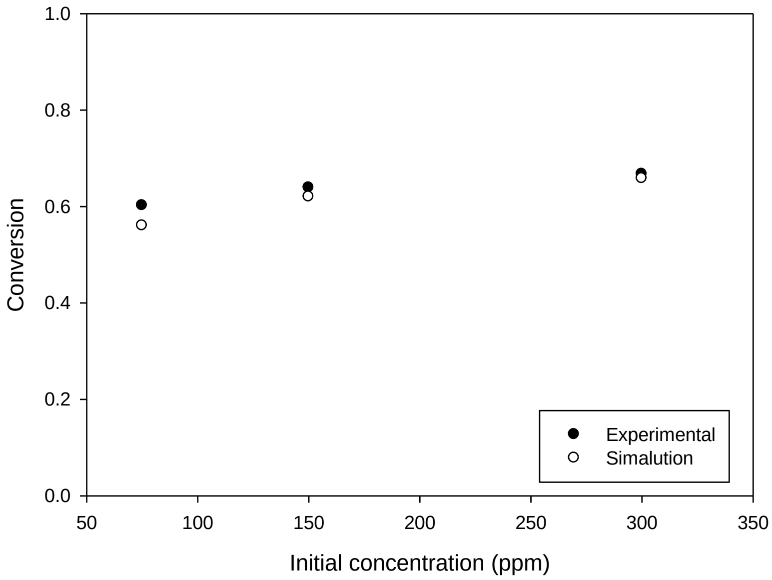


Figure 10: Effect of initial 2-Proplymercaptan concentration on conversion. Reaction conditions (temperature= 353K, liquid hourly space velocity = 2.5hr^{-1}).

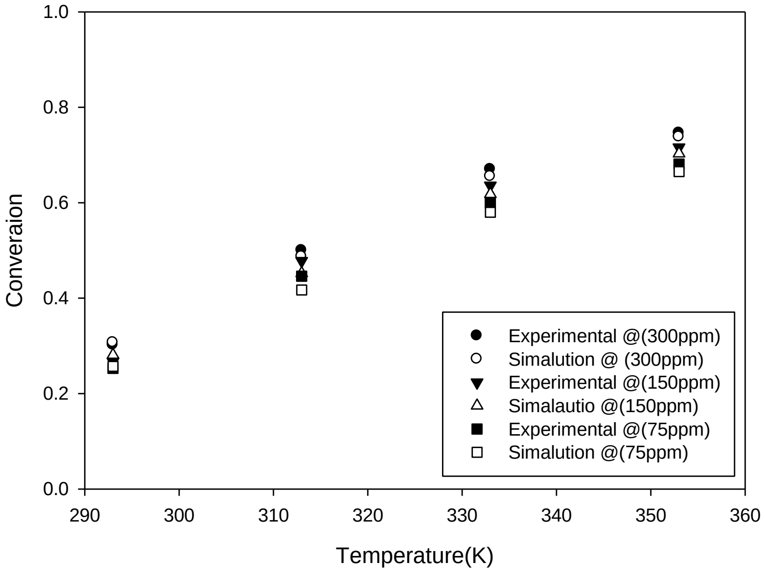
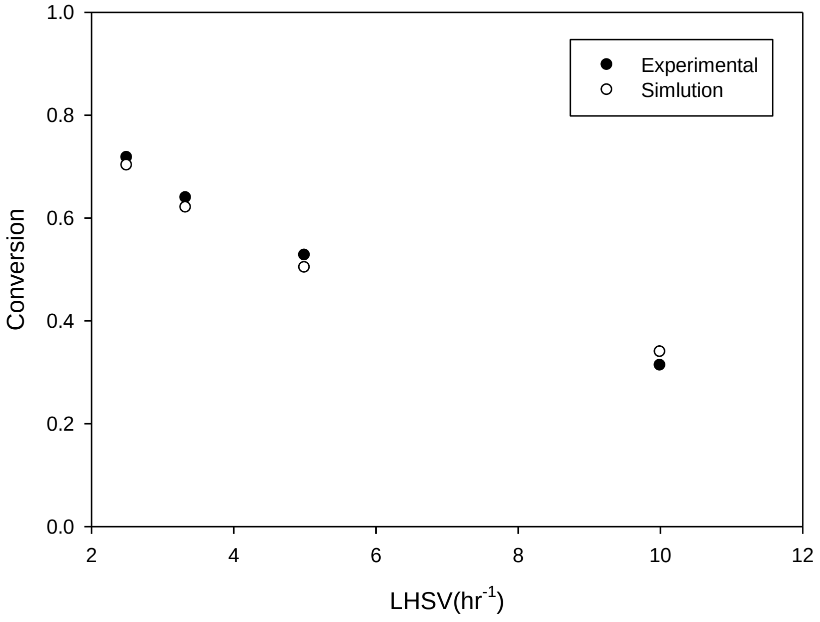


Figure 11: Effect of initial 2- Proplymercaptan concentration on conversion. Reaction conditions (Change of Temperature and constant liquid hour space velocity 2.5hr^{-1}).

Effect of Liquid Hour Space Velocity on Oxidation Process

The effect of liquid hour space velocity on 2-proplymercaptan removal rate was studied in the range (2.5, 3.33, 5, 10 hr^{-1}). The comparison between the experimental and predict results are plotted in Figures (12and13).

As shows in these Figures an increase in liquid hour space velocity or decrease in naphtha volumetric flow rate, cause shorting in contact time between reactant material and catalyst particles [38], Thus, effect the oxidation reaction causes the decrease in 2-proplymercaptan conversion. The increase in liquid hour space velocity can also effect on catalyst wetting radial and axial dispersion and liquid hold up. The conversion of 2-proplymercaptan at 353 K is 73.8% has achieved at 2.5 hr^{-1} , whereas the conversions decreases as increasing in LHSV for 2-proplymercaptan up to 26.7%, 22% , 16%and 8% at LHSV 2.5,3.33, 5 and 10 hr^{-1} respectively, as shows in the Figure(13).



Figures 12: Effect of liquid hourly space velocity on 2-proplymercaptan conversion at constant temperature. Reaction conditions (Temperature 353 K, initial concentration= 300 ppm).

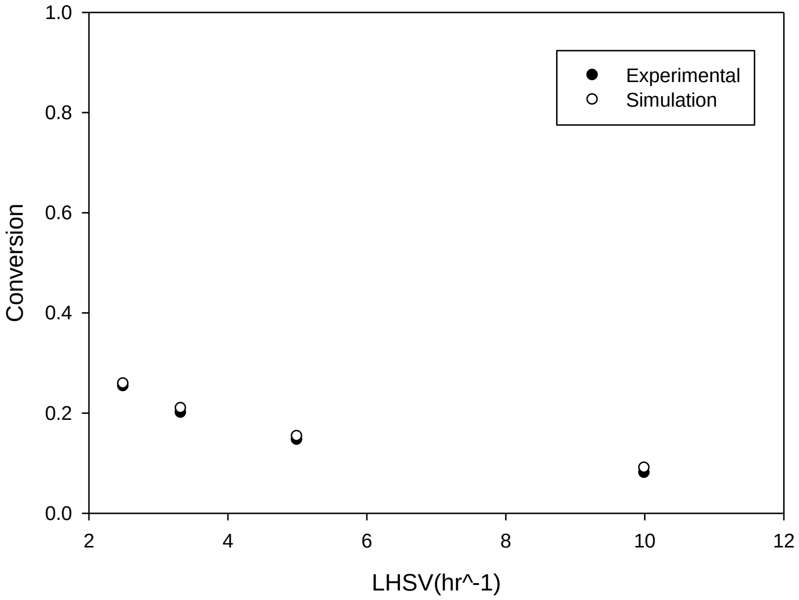


Figure 13: Effect of liquid hourly space velocity on 2-proplymercaptan conversion at constant temperatures. Reaction conditions (Temperature 293 K, initial concentration= 150 ppm).

Comparison between Experimental and Simulation Results

The comparison between the experimental and predicted results is shows in the Figure(14).This Figure shows a good agreement between the experimental and the predicted results that have been simulated (each point represents experimental (X-axis) and simulated (Y-axis) values at the same time with the same operating conditions for each point).

The relation between the experimental and simulated results for 2-proplymercaptan are appeared to be straight line with slope to be 1.0 which indicating very good agreement between the measured and predicted results.

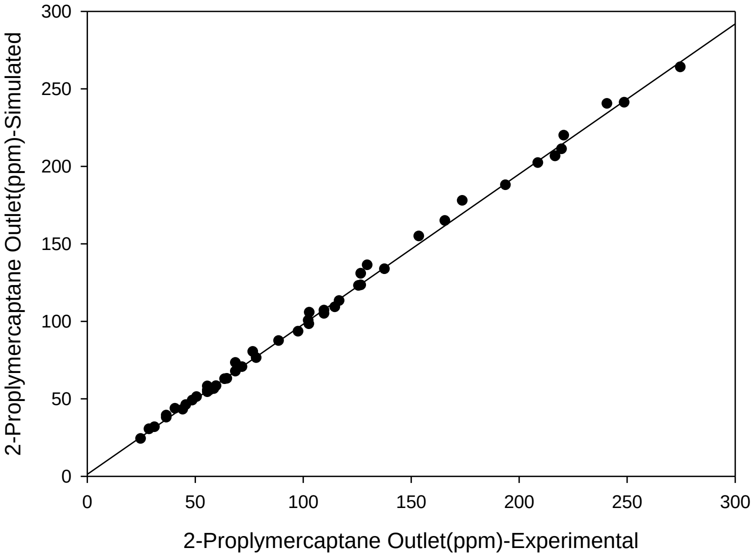


Figure 14: Comparison between the experimental and predicted concentrations of 2-proplymercaptan.

Conclusions

1. Oxidative desulphurization process (ODS) appears to be technically and economically valuable for processing ultra-low sulfur fuel from naphtha feedstock. It can be considered as substitute for hydrodesulphurization process (HDS). Notably, Oxidation process does not require hydrogen for desulphurization, but instead converts the sulfur compounds present in the naphtha to corresponding sulfide that are then extracted from the naphtha. Prospectively, it is expected that capital cost and operating

cost with ODS would be significantly lower than with HDS.

2. It is found that the Non-Linear method, is more accurate based on minimizing the sum of squared error between experimental and predicted results with average absolute error less that 5% among all the results at various of operating conditions (LHSV, temperature and initial concentration of inlet sulfur of 2-proplymercaptan).
3. It is found that the 2-proplymercaptan conversion increased as liquid hour space velocity (LHSV) decreased. While increasing temperature causes increase in 2-proplymercaptan conversion.
4. It was found that the oxidation reaction of 2-proplymercaptan is n^{th} order with respect to 2-proplymercaptan concentration and 1.14467 order with respect to catalyst, the activation energy has been estimated to be17.7071kJ/mole.

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NOMENCLATURES

Symbol	Definition	Unit
$N_{(RSH-C3)}$	$Mole\ flux\ of\ 2-proplymercaptan\ in\ the\ feed$	$\frac{\boldsymbol{mole}}{\boldsymbol{m^2\ time}}$
$A_{reactor}$	$Area\ of\ the\ reactor$	$\boldsymbol{m^2}$
$r_{reactor}$	$Radius\ of\ reactor$	$\boldsymbol{m}$
$Q_{(RSH-C3)}$	$Volumetric\ flow\ of\ liquid\ phase$	$\boldsymbol{Cm^3/time}$
$-R_{RSH-C3}$	$Rate\ of\ reaction\ for\ oxidation\ process$	
V	$Bed\ volume\ of\ particle\ catalyst(Co/AC)$	$\boldsymbol{Cm^2}$
$C(RSH-C3)$	$Concentration\ of\ 2-proplymercaptan$	$\boldsymbol{Cm^3/mole}$
$C(RSH0-C3)$	$Initial\ concentration(inlet\ to\ reactor)$	$\boldsymbol{Cm^3/mole}$
$C(RSHf-C3)$	$Final\ concentration(outlet\ from\ reactor)$	$\boldsymbol{Cm^3/mole}$
$K_{Hyd.}$	$Hydrodynamic\ reaction\ rate\ constant$	$\frac{\boldsymbol{mole}}{\boldsymbol{cm^3sec^{-1}}}$
$K_{(RSH-C3)}$	$Kinetic\ rate\ constant$	$(\boldsymbol{time})^{-1}(\boldsymbol{conc.})^{\boldsymbol{1-n}}$
n	$Order\ of\ reaction\ kinetic$	-
T	$Temperature$	$\boldsymbol{K\ or\ oC}$
R	$Gas\ constant$	$\frac{\boldsymbol{J}}{\boldsymbol{mole.K}},\frac{\boldsymbol{ft^3psia}}{\boldsymbol{Ib_{mol}R^o}}$
EA	$Activation\ energy\ for\ oxidation\ reaction$	$\boldsymbol{kJ/mole}$

A^o	Frequency or pre − exponential factor	$Cm^3/g.sec$
t	Time	hr, min, sec
X_{RSH-C3}	Conversion	-
τ	Residue time	hr
g	Acceleration	cm/sec^2
$u_{Naphtha}$	Velocity of the feedstock (Naphtha)	cm/sec
$\rho_{naphtha}$	Density of naphtha	g/Cm^3
D_t	Tube diameter of TBR	Cm
D_p	Particle diameter	Cm
D_{pe}	Equivalent particle diameter	Cm
P_C	Critical pressure of naphtha	$psia$
$MW_{naphtha}$	Molecular weight of naphtha	$\frac{Ib}{Ibmol}$
T_C	Critical temperature of naphtha	R^o
Z_C	Critical compressibility factor	-
T_r	reduced temperature	-
ppm	Part per million	-
MW_{Oxgyen}	Molecular weight of oxygen	$g/gmole$
$MW_{Naphtha}$	Molecular weight of naphtha	$\frac{Ib}{Ibmol}$
$v_{cNaphtha}$	Critical specific volume of liquid	Cm^3/mole
v_{RSH-C3}	Molar volume of DBT at n.b. temperature	Cm^3/mole
$TmeABP$	Mean average boiling point	R
$\rho_{15.6}$	Density of naphtha at 15.6 oC	g/Cm^3
rg	Mean pore radius	cm
S_P	External surface area of catalyst particle	Cm^2
V_g	Total pore volume	Cm^3/g
$\mathcal{D}_{ki}$	Knudsen diffusivity factor	Cm^2/sec
R_p	Radius of particle for catalyst	Cm
$\mathcal{D}_{ei}$	Effective diffusivity	Cm^2/sec
S_g	Specific surface area of particle catalyst	Cm^2/g
$\mathcal{D}_{mi}$	Molecular diffusivity	Cm^2/sec
V_P	External Volume of catalyst particle (Co/AC)	Cm^3
V_L	Molar volume of liquid at its n.b. temperature	$Cm^3/mole$

GREEK SYMBOLS

Symbol	Definition	Unit
$\Psi_{Wett.fact.}$	External catalyst wetting efficiency	-
$\Psi_{Eff.fact.}$	Effectivness factor	-
τ	Residence time	hr
ϵ_{Void}	Bed void fraction	-
$\mu_{naphtha}$	Dynamic viscosity of liquid phase	$mPas.sec$
α	Constant factor	-
φ	Volume fraction of molecule	-
$\emptyset$	Thiele Modulus	-
$\mathcal{J}$	Tortuosity factor	-
ϵ_s	Catalyst porosity	-