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Research Paper

Kinetic and thermodynamic study of a traditional dye as catalyst for thiol oxidation in sour kerosene

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ABSTRACT

The oxidation process of thiols is industrially used to treat light petroleum products in the presence of a supported catalyst. A low-cost, traditional dye, cobaltous phthalocyanine salt, was used as the active component for catalyst preparation. The supported catalyst was experimentally prepared by impregnation the activated carbon ($d_p = 1.971\text{mm}$) with the uric dye solution in a batch unit. The prepared catalyst was tested for the oxidation of thiols present in row kerosene. All kinetic experiments were carried out at constant pressure concurrent fixed-bed unit. The effect of temperature and LHSV on conversion percent was investigated. Attempts were made to correlate the data with first and second-order reactions, and it was found that the first-order kinetics correlates the data well with an activation energy of 24.48 kJ/mol . This indicates that the synthesized catalyst is effective and necessary for the reaction to proceed at moderate temperatures with a sufficient rate. Also, the change of enthalpy and entropy were found to be equal to 21.94 kJ/mol and 0.153 kJ/molK , respectively, with an average Gibbs free energy change of -24.802 kJ/mol . These values indicate that the reaction is weakly spontaneous and thermodynamically favorable, and could proceed at a suitable rate in the presence of the prepared catalyst. Furthermore, the Thiele modulus and internal effectiveness factor were examined, and it was found that the internal diffusion is the major resistance for the oxidation reaction proceeding, and the oxidation reaction takes place only on the outer layer of the surface of the pellets.

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1. Introduction

Thiols are present in sour crude, but mostly formed by thermal and catalytic decomposition of sulphur compounds, and tend to concentrate in the low-boiling fractions. They impart a foul odour and seriously decrease the octane number and cause metallic corrosion [1, 2]. Removal of thiols by the extraction with alkali reagents has been used for a long time, but the bad economics of such processes set a limit on benefiting from this kind of process. Furthermore, solvent extraction processes are not as cost-effective or efficient as catalytic processes [3]. Refineries currently utilize hydrodesulphurization processes to reduce sulphur levels, but achieving sound desulfurization would require exceedingly severe reaction conditions, a larger reactor, and the cost of additional hydrogen. The catalytic oxidation of sulphur compounds is widely used in petroleum refining processes for the chemical treatment of sour light fractions. This process is typically used for virgin and thermally cracked charge stocks, including jet fuels, kerosene, diesel fuels, and heating oils. Catalytic oxidation offers several advantages, including lower costs, process simplicity, and the ability to produce specific product qualities [4]. This process is usually operated in a fixed-bed reactor at ambient conditions. The reactor contains a bed of activated carbon impregnated with catalyst particles and wetted with alkali solution. Air is injected into the hydrocarbon feedstock in front of the reactor, and in passing through the bed, the sulfur compounds in the feed stream are oxidized to simple separable compounds. The alkali solution is continuously circulated in the reactor to maintain the catalyst bed wet [5]. Cobalt and vanadium phthalocyanine and their sulfonated derivatives, particularly mono and di sulfonated and sulfonamide derivatives, show a catalytic effect in the

treatment of petroleum distillates containing difficult oxidizable thiols. Mantos demonstrated that the transition metal phthalocyanine is a more effective catalyst than other organic chelates for the oxidation [6]. Pereira et al. compared the catalytic activity of the copper, iron, cobalt, nickel, zinc, and vanadium phthalocyanine in the heterogeneous oxidation of cysteine in aqueous solutions and found that only phthalocyanine and tetra sulfonate phthalocyanine of Cobalt and Ferric were catalytically active [7]. Makarov et al. found that the cobalt phthalocyanine is a highly active and stable catalyst for thiols oxidation [8]. Giddaerappa et al. noted that both disodium cobalt di sulfonate phthalocyanine and cobalt poly phthalocyanine catalysts effectively catalyze the oxidation of thiols [9]. The reaction of oxidation is affected by the existence of an alkali solution that works as a reaction medium. The preferred alkali reagents are hydrogen peroxide and sodium or potassium hydroxides [10]. Gupta et al. compared aqueous caustic solution and aqueous ethanol tri methyl ammonium hydroxide when present as a reaction medium in the treatment of kerosene fraction and found that the ethanol tri methyl ammonium hydroxide is more effective than caustic solution [11]. Zuo et al. found that there were unexpected benefits obtained by using tetramethylguanidine as a basic medium because it increases the apparent catalytic activity and thiols conversion [12]. Activated charcoal is a favourable support for the catalyst because of its stability under treatment conditions and capacity for metal phthalocyanine. Moreover, the activated carbon by itself is a catalyst for the oxidation reaction [13]. For the synthesis of supported metallic phthalocyanine catalysts, it is the implementation of the active component adsorption from its solution or dispersion onto a suitable support [14]. The active component solution is drizzled onto the support, or the support is submerged in the solution.

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Nomenclature

A	Factor of collision frequency, $1/h$
C	Concentration of thiol, ppm
C_o	Concentration of thiol at inlet, ppm
d	Diameter of particle, m
D	Diffusion coefficient, m^2/s
d_p	Correlated particle diameter, m
E	Energy of activation, kJ/mol
F	Boltzmann's constant, $1.381 \times 10^{-26} kJ/K$
h	Planck's constant, $6.626 \times 10^{-37} kJ.s$
k	Reaction rate constant, $1/h ppm^{n-1}$
k_T	Coefficient of transmission
l	Length of particle, m
M	Number of experimental data points
n	Order of reaction

R	Gas constant, $8.314 \times 10^{-3} kJ/mol K$
r	Rate of reaction, ppm/s
T	Temperature, K

Greek Symbols

ΔG	Change of Gibbs free energy, $kJ/mol K$
ΔH	Enthalpy change for activation, kJ/mol
$\delta_{j,estm}$	Estimated j point value of an objective function
$\delta_{j,real}$	Real j point value of an objective function
ΔS	Entropy change for activation, $kJ/mol K$
E	Porosity
η	Effectiveness factor
σ	Constriction factor
τ	Tortuosity
Φ	Thiele modulus

Anyway, the surplus solution is removed, and the produced composited material is permitted for drying. Aqueous solutions gave a comparatively poor apportionment of the active component onto the support, and quality assurance is tricky to attain. A methanolic solution has produced a catalytic composite that is extremely active. Methanol has grown more and more unpopular due to its relative cost, toxicity, and difficulty in disposal. Incorporating a strong base results in enhanced solubility in aqueous solution. Szymczak and Michal impregnated cobalt phthalocyanine mono sulfonate on charcoal by solutions containing methanol, ammonium hydroxide, water, or urea and found that the latter composite is the most active and stable [15]. The present study deals with the preparation of a catalyst by impregnation of cobalt phthalocyanine dye onto activated charcoal. Furthermore, the synthesized catalyst was used to oxidize thiols in kerosene and examine the thermodynamics and kinetics of the reaction by investigating the reaction order, activation energy, enthalpy and entropy change, Thiele modulus, and effectiveness factor.

2. Experimental work

It was desired to obtain fundamental information pertinent to the interpretation of the thiols' catalytic oxidation system. Then, using this information to determine the characteristics of the process. So, it was essential to conduct the experiments with well-defined materials. Activated carbon was used as support in the present study. Because it was cylindrical, Eq. 1 was used to determine the correlated particle diameter d_p mathematically from the diameter of the pellet d and its length l of it [16]. The correlated particle diameter was found to be equal to 1.971mm.

$$d_p = \frac{2(d \times l)}{d + 2l} \quad (1)$$

The granular activated carbon was first degassed by a vacuum oven at 373 K and 90 mmHg for 24 hours overnight so as to take off the gases that had already been adsorbed on the surface. Then it was transferred into a desiccator that contains freshly activated silica gel and allowed to cool at ambient temperature. A catalyst deposition experiment was conducted in a batch adsorber by mixing the degassed activated carbon with uric Cobalt phthalocyanine solution (0.5 g catalyst / litre) in a conical flask. The flask was shaken in a water bath shaker overnight at 293 K. After that, the flask content was separated by a filtration unit, which consists of a filtration flask, Buchner funnel, trap, and vacuum pump. The filtrate was analysed with a visible spectrophotometer (Shimadzu, UV-160A), and the quantity of cobalt phthalocyanine deposited on the activated carbon was determined according to the material balance, and the concentration of the active component on the support was determined as 4.23 mg/g. The wet catalyst particles were rinsed with deionised water and dehydrated in a vacuum oven for 4 hours at 383 K and 90 mmHg, to ensure complete vaporization of solvent from pores. Figure 1 shows a scheme of the experimental oxidation appliance. The reactor was a carbon steel tube 1/2-inch Schedule 40) with 234 mm length and 15.8 mm diameter. A gauze plate of very small holes and a coating of glass wool are situated at the upper and lower heads of the packing to catch particles in place and prohibit energy leakage from packed bed terminals. The lines were 1/8 in cupric tubes. An insulation layer of glass wool covers the reactor to make the differences of temperature in the radial orientation as small as feasible. Also, the isolation simulates the adiabatic process that convergent industrial units where reactors with large diameters are utilized. The temperature was measured and recorded by a multi-channel digital recorder at three locations in the bed. The input gases and feed tubes were coiled for approximately 200 cm long and immersed in a water bath to preheat the streams before the reactor inlet.

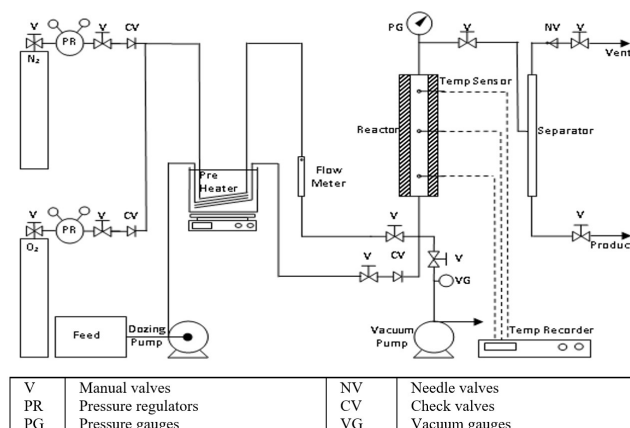


Figure 1. Scheme of the experimental thiols oxidation appliance.

The 20 cm³ of the catalyst was first wetted with a tri-methyl ammonium hydroxide ethanol solution by immersing it in a beaker containing boiling alkali solution for about 5 min. Then, it was filtered from the excess alkali solution and placed in the column. The feed was supplied to the reactor by a calibrated dosing pump, along with a stream of N₂ (79%)/O₂ (21%) that was continuously passed through the apparatus until the entire bed reached the specified temperature. Gas-to-oil volumetric ratio was held constant at 200. The reactor products were separated from the excess gas by passing through a high-efficiency condenser. The condenser coolant is technical ethyl alcohol at a temperature of 253 K, was circulated through a cooling machine. Then the gases were vented to the exterior. Products were collected only after steady-state operation was established, and initial operating products were discarded. The samples were filtered through a rapid filter paper and washed several times with water. The thiols of the feedstock and treated oil were determined by the potentiometric titration method according to a standard method (ASTM: D 3227-83).

3. Results and discussion

The oxidation reaction of thiols in a continuous flow fixed-bed catalytic reactor is a complex process, and many variables affect the process. Throughout this study, the synthesized air pressure and its volumetric flow rate relative to oil were kept constant at 1.2 atm and 200, respectively. The temperature range varied from 298 to 313 K, and the LHSV ranged from 1 to 10 1/h. The effect of temperature and LHSV on the percentage of thiol conversion using supported cobalt phthalocyanine catalyst is shown in Fig. 2. The figure shows that the thiol conversion rises as the temperature of the reaction increases or LHSV decreases. The increase in oxidation at high reaction temperatures because the constant of the reaction rate increasing with temperature according to the Arrhenius equation, and more reactive molecules have been activated enough to react. Also, this phenomenon might be due to the fact that at high temperatures, some of the reactive molecules have much energy to diffuse far in the pores of the catalyst; therefore, more reactive surface will be available for the reaction, and due to the alkaline solution viscosity decreasing as the temperature increases. This improves better distribution of the alkaline solution within the catalyst pores and particles. Furthermore, the unreactive thiols, which most probably belong to high molecular weight ones, become activated enough to react at high temperatures. Meanwhile, the thiols oxidation reaction

is a function of contact time (reciprocal of $LHSV$) between the reacted fluids and the catalyst. $LHSV$ increase will shorten the contact time, leading to a decrease in the reaction conversion.

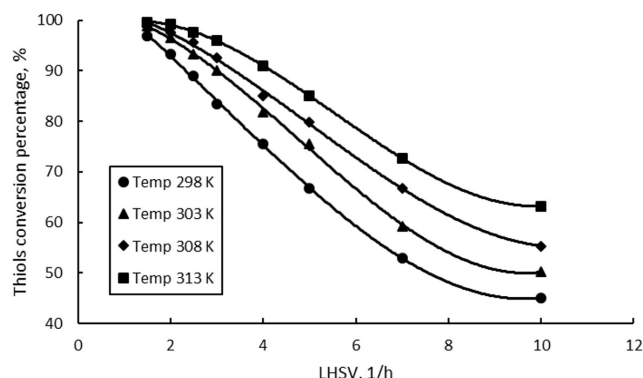


Figure 2. Thiol conversion percentage versus LHSV at various reaction temperatures.

These results are in agreement with those found by Chen et al. [17]. Le, Fabrice, and Abraham considered that the reaction of thiol oxidation is first order relative to both thiol and oxygen concentration [18]. Furthermore, the reaction in this study was considered pseudo-first order relative to thiol concentration only, since in all experiments the oxygen partial pressure was almost constant. By letting r be the rate for the disappearance of thiols and k be the rate of reaction constant, and C be the thiol concentration. The reaction rate correlation for n th order could be written as in Eq. 2.

$$-r = kC^n \quad (2)$$

Where k is the reaction rate constant when the reaction rate is referred to the thiols concentration in the oil phase. The laboratory data obtained for the oxidation of thiols were analysed by the proposed model in Eq. 2. Attempts were made to correlate the data with first and second-order kinetic equations. Figures 3 and 4 show plots between $\ln(C_0/C)$ and $(1/C - 1/C_0)$ versus $1/LHSV$ at different temperatures, respectively. The results from these figures indicate that the first-order kinetic model correlates well with the experimental data. This conclusion is also recognized by observing that the lengths of the error bars in both vertical and horizontal directions for the first-order kinetic model figure are much smaller than those for the second-order kinetic model figure. However, the matching between experimental data and the model equation can be mathematically determined by using a suitable statistical equation. The topical correlation shown in Eq. 3 was utilized in the procedure for minimizing the mean relative error.

$$Error = \frac{1}{M} \sqrt{\sum_{j=1}^M \left| \frac{\delta_{j,real} - \delta_{j,estm}}{\delta_{j,real}} \right|^2} \quad (3)$$

Where M is the experimental data points, $\delta_{j,real}$ and $\delta_{j,estm}$ are the real data point value and estimated data point value of the objective function $\ln(C_0/C)$ and $(1/C - 1/C_0)$, respectively.

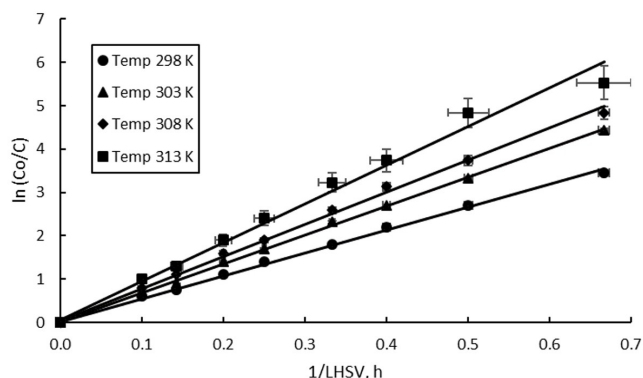


Figure 3. Fitting of thiols oxidation data with a linearized first-order kinetic model at various reaction temperatures.

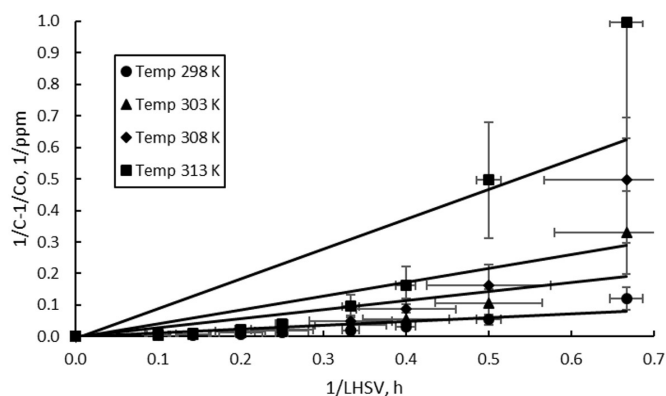


Figure 4. Fitting of thiols oxidation data with a linearized second-order kinetic model at various reaction temperatures.

Table 1 displays the computed rate constants for the two model equations as well as the mean relative error values. It shows that the first order kinetic model correlated the experimental data points with an average mean relative error of 0.59 % whilst 17.40 % for the second order model. Consequently, the preferred fitting was attained with a first-order kinetic model. This result is compatible with the previously mentioned work by Motahari, Mohammad, and Ali [18].

Table 1. Summary of fitting for the first and second order kinetics results.

Temp. (K)	1 st Order		2 nd Order	
	k, (1/h)	Error, (%)	k, (1/ppm h)	Error, (%)
298	5.1521	0.21	0.1548	11.75
303	6.6342	0.13	0.3832	20.64
308	7.2001	0.26	0.5795	20.61
313	8.4769	1.76	1.2659	16.61

The energy of activation determines the quantity of energy that the reactant must have to overcome the barrier of the reaction. The energy of activation for the oxidation of thiols was computed utilizing Arrhenius Eq. 4 that satisfies the relationship between the reaction rate constant and temperature [19].

$$k = Ae^{-E/RT} \quad (4)$$

Where A is the factor of collision frequency, and E is the energy of activation. A diagram of $\ln k$ versus $1/T$ provides a rectum line having a slant equal to E/R , as exhibited in Fig. 5.

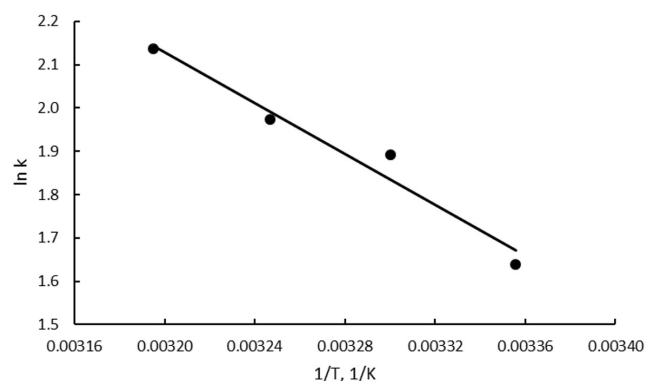


Figure 5. Fitting of thiols oxidation rate constants versus the reciprocal of reaction temperature with the linearized Arrhenius equation.

The energy of activation was calculated using the Arrhenius plot and found to be equal to 24.480 kJ/mol. This value is close to what Akhmadullin et al. found when they used copper oligopyrocatecholate to catalyze the isopropyl thiol oxidation reaction [20]. This relatively low value of the activation energy indicates that the catalyst is very effective and necessary for the reaction to proceed at a sufficient rate, and its presence lowers the activation energy, which could be much higher in the absence of the catalyst. Also, this implies

that the catalytic reaction is fast enough to proceed at moderate temperatures. Furthermore, this low value of activation energy indicates that the catalytic reaction is mass transfer-controlled, and pore diffusion resistance might be the dominant resistance for the reaction. The enthalpy and entropy change of activation for the oxidation reaction were determined by utilizing Eq. 5, which was obtained from the theory of absolute reaction rate [21].

$$\frac{k}{T} = k_T \frac{F}{h} e^{(\Delta S/R)} e^{(-\Delta H/RT)} \quad (5)$$

Where k_T is the coefficient of transmission, F is Boltzmann's constant, h is Planck's constant, ΔS and ΔH are Entropy and Enthalpy change for activation, respectively. A graph of $\ln k/T$ contra $1/T$, as shown in Fig. 6, yields a rectum line having a slope and intersection that leads to the calculation of ΔH and ΔS as 21.940 kJ/mol and 0.153 kJ/molK, respectively.

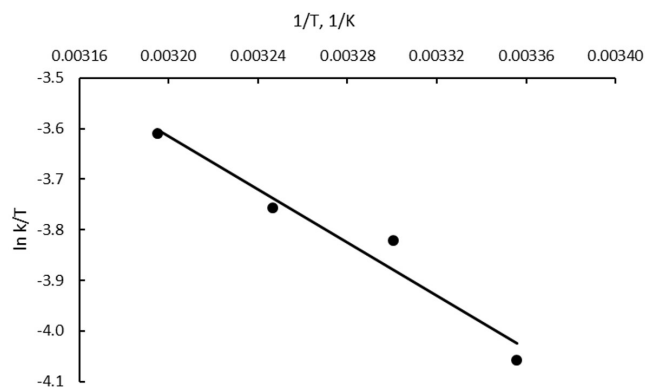


Figure 6. Fitting of $\ln k/T$ for thiols oxidation versus reciprocal of reaction temperature with the linearized form of absolute reaction rate theory.

This low positive amount of the change of enthalpy indicates that the reaction is a slightly endothermic reaction, and temperature increasing shifts the reaction towards products according to Le Chatelier's theory. Therefore, an adiabatic reactor could be quite beneficial if the reactants were preheated to the desired temperature or slightly higher than ambient, since the value of change of enthalpy is not too high. The positive value of the change of entropy indicates that the degree of disorder or the degree of freedom of the products is higher than that of the reactants. So, this state property may improve the turnover frequency of the catalyst if present. But the small value of the change of entropy makes the reaction weak in spontaneity since the change of Gibbs free energy will be slightly negative, as shown in Table 2. The values of Gibbs free energy indicate that the reaction is always spontaneous and thermodynamically favourable at this range of temperatures. Although the Gibbs free energy changes decrease as temperature increases from 298 to 313 K but they are still not too high to proceed with the reaction at a sufficient rate, and an appropriate catalyst must be present. The relative importance of the catalytic rate of reaction and rate of internal diffusion throughout the catalyst pellets could be well characterized by introducing the Thiele modulus [22, 23] as indicated in Eq. 6.

$$\Phi = \frac{d_p}{2} \sqrt{\frac{k\tau}{\varepsilon\sigma D}} \quad (6)$$

Where, Φ is the Thiele modulus, τ is the tortuosity, ε is the porosity, σ is the constriction factor, and D is the coefficient of diffusion, which is taken as the average value of molecular and Knudsen diffusivities. Figure 7 shows a plot of Thiele modulus versus particle diameter at various temperatures. It shows that there is a massive increase in the Thiele modulus as the particle diameter increases. This behaviour suggests that the internal diffusion becomes more and more dominant as the particle diameter increases, and only the outer surface of the particles is active, and much of the catalyst interior surface is underutilized. Also, the very large values of the Thiele modulus indicate that there is a large gap between the reactants' molecular sizes and pore diameter. So, it could be suggested that the surface of the carbon must be modified to optimize pore structure before the impregnation step for the catalyst preparation, or by using very fine particles of activated carbon. But this suggestion must be balanced between mechanical strength and pressure drop versus the effectiveness of the catalyst. The figure also shows that the Thiele modulus decreases with increasing temperature at any fixed particle diameter.

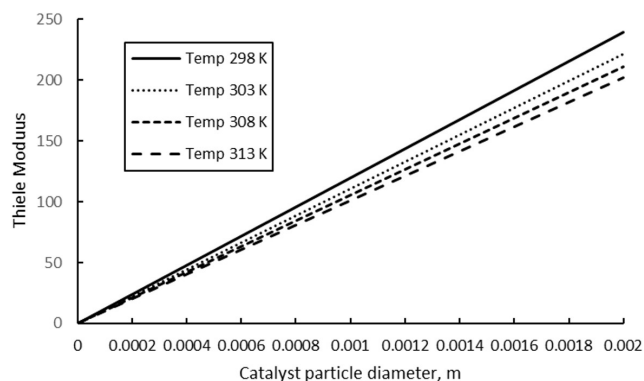


Figure 7. Thiele modulus for thiols oxidation versus catalyst particle diameter at various reaction temperatures.

This is because temperature increase leads to an increase in the reaction rate constant, while the effective diffusivity remains almost constant throughout this range of temperature since it is a weak function of temperature.

Table 2. Change of Gibbs free energy versus temperature for the oxidation reaction.

Temp. (K)	ΔG , KJ/mol
298	- 23.654
303	- 24.419
308	- 25.184
313	- 25.949

Furthermore, the data was correlated by introducing the effectiveness factor as explained by Eq. 7 for better identification of the relative importance between reaction and diffusion rates [24, 25].

$$\eta = \frac{3}{\Phi^2} (\Phi \coth \Phi - 1) \quad (7)$$

Figure 8 shows a plot of the effectiveness factor versus particle diameter at various temperatures. It could be recognized that there is an enormous decrease in the effectiveness factor as particle diameter increases to 0.3 mm, and thereafter it remains decreasing with a slow trend.

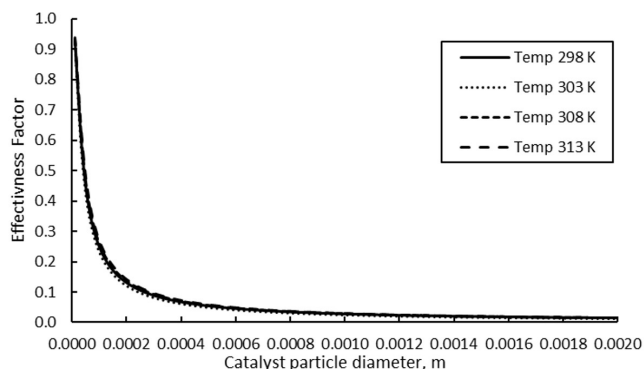


Figure 8. Effectiveness factor for thiols oxidation versus particle diameter at various reaction temperatures.

This phenomenon reinforces the previous conclusion, and it is because the internal diffusion is the major resistance for the oxidation reaction proceeding, and the oxidation reaction takes place only on the outer layer of the surface of the pellets. Also, it could be noted that only about 1.5 % of the catalyst is effectively used, and 98.5 % is unutilized when the particle diameter is 2 mm. The figure shows that there is no discernible impact of temperature on the effectiveness factor values at any specific catalyst particle diameter. This could be explained by the definition of the effectiveness factor, which states that the effectiveness factor is the proportion of the actual reaction rate to that at surface conditions.

In summary, using fine particles is essential to maintain high utilization of the catalyst, and if the use of large particles is necessary for reasons related to pressure drop or reactor design, the surface of the catalyst particles must be treated to reduce the resistance to mass transfer, but also, mechanical properties must be taken into account.

4. Conclusions

- The oxidation of thiols that are present in raw kerosene follows first-order kinetics with respect to thiol concentration in the oil phase.
- The cobaltous phthalocyanine dye is an active catalyst for the oxidation of thiols that are present in sour kerosene because the catalytic reaction has a low activation energy.
- An adiabatic reactor could be quite beneficial for the catalytic oxidation of thiols since the value of the enthalpy change is not too high.
- The high values of the Thiele modulus and low values of the effectiveness factors suggest that the surface of the activated carbon must be modified to optimize pore structure, with the mechanical strength of pellets must be taken into account, or fine particles of activated carbon ($< 0.3\text{mm}$) must be used and pressure drop or reactor design modification must be considered.

Declaration of competing interest

The authors declare no conflicts of interest.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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