

Kinetic Study of Ethyl Mercaptan Oxidation in Presence of Merox Catalyst

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ABSTRACT: *Mercaptans are commonly present in petroleum products. Their foul odor and highly corrosive nature make them the most undesirable sulfur compounds so they should be removed because of environmental issues. Merox process is used for oxidation of mercaptans to disulfide using air in the presence of alkaline solution and Merox catalyst. In this paper, due to lack of information about the kinetic of mercaptan oxidation, the kinetic of conversion of ethyl mercaptan in gasoline and kerosene is studied in order to be able to model and simulate this process. The experiments were carried out in a semi-batch bubble column reactor and it was proved that increasing the temperature, improves the rate of the reaction. The obtained results were analyzed and a correlation for the rate of reaction is suggested. The suggested equation is first-order with respect to mercaptan concentration.*

KEY WORDS: *Merox, Ethyl mercaptan, Phthalocyanine, Catalytic oxidation, Kinetic study.*

INTRODUCTION

Mercaptan oxidation

Mercaptans are the most harmful impurities distributed among petroleum products. They cause foul odor, deterioration of additives in finished products and are corrosive [1]. There are various methods to remove mercaptans but the major one is the catalytic oxidation in the presence of caustic solution and air. Phthalocyanines of the metals like cobalt, iron and manganese, molybdenum and vanadium catalyze the oxidation of mercaptans to disulphides in alkaline medium [1-3]. Among these, cobalt and vanadium phthalocyanines are preferred. As the metal phthalocyanines are not soluble

in aqueous medium, for improved catalytic activity their derivatives like sulphonated and carboxylated metal phthalocyanines are used as catalysts for sweetening of petroleum fractions. The use of cobalt phthalocyanine (CoPc) monosulphonate as the catalyst in the fixed bed sweetening of various petroleum products and cobalt phthalocyanine disulphonated, tetrasulphonate and the mixture thereof as catalysts for liquid-liquid sweetening/alkali regeneration in mercaptan extraction of light petroleum distillates have been reported [4].

Several units are designed for removal of mercaptans in which the most successful one is Merox unit.

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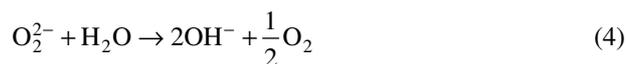
This technology was licensed by UOP Company in 1958 for treating light cuts and middle distillation products [1]. In this unit the gasoline is pre-washed with sodium hydroxide solution and then contacted in the extractor with the alkaline solution. After settling, the gasoline enters the Merox reactor where residual mercaptans are oxidized with air to disulphides in the presence of sodium hydroxide solution and the Merox catalyst. The process combines the extraction of mercaptans with the catalytic conversion of residual mercaptans. This unit uses Merox catalyst consisting of mono and disulphonated phthalocyanines of cobalt and vanadium. These metals are chosen because of their stability and insolubility in organic phase [5]. These reasons make Merox catalysts more suitable than other catalysts for mercaptan removal. Merox unit is used for liquid phase sweetening of petroleum products such as Liquefied Petroleum Gas (LPG), Natural Gas Liquids (NGL), naphtha, gasoline, kerosene, jet fuels, diesel fuels and heating oils. It is also used for sweetening of natural gas and synthesis gas besides other units in the refinery [6].

Knowledge of kinetic study of mercaptans catalytic oxidation is essential for optimization of design parameters, operating conditions and catalyst performance. The kinetic of ethyl mercaptan oxidation, as a sulphur compound that is commonly present in gasoline and other fuels, is still unknown. So the kinetic of ethyl mercaptan oxidation in presence of Merox catalyst has been investigated in this paper.

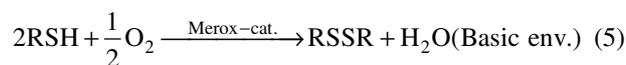
Reaction mechanism

All Merox units are based on catalytic oxidation of mercaptans to disulphides in alkaline environment (basic environment). Generally there is no difference between metal catalysts for reaction of mercaptans and sodium hydroxide except the difference between the activation energy of the reactions [1].

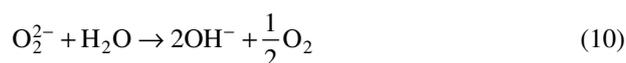
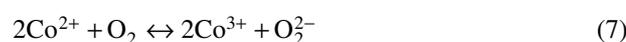
There has not been any effective research for investigating the mechanism of catalytic oxidation of mercaptans but the most reliable mechanism so far was proposed by *Wallace* [7] and *Rollmann* [8]. This mechanism is shown below:



The overall reaction is:



This mechanism indicates that the mercaptide ion is the reactive species which reacts with oxygen to generate free radicals which dimerize to produce disulphides. In conventional systems using transition metal compounds as catalysts, the presence of hydrogen peroxide was not detected and then the mechanism suggested by *Wallace et al.* [9] is:



In these equations, other metals can also be used instead of cobalt, as the catalyst for the oxidation reaction, but previous researchers showed that each metal catalyst has its own optimum operating conditions like pH and temperature [1]. In latter papers, mercaptide ion was proposed to be a ligand and also suggested that disulphide forms directly by the oxidation of the ligand complex. *Leung et al.* [11] proposed to substitute Eq. (8) by these reactions:



Both mechanisms for noncatalytic and catalytic reactions show that the oxidation rate depends on the amount and reactivity of mercaptide ions (RS^-). Thus, factors promoting the formation of mercaptide ion will contribute to improve the overall reaction rate. Both mechanisms show that the rate of reaction increases by increment of sodium hydroxide concentration and it is proved for non-catalytic reactions [5, 14]. In this research various sodium hydroxide concentrations were tested in the presence of catalyst.

EXPERIMENTAL SECTION

Kinetic study of oxidation was accomplished by doing experiments in a reactor designed and built for this project (See Fig. 1). The reactor was filled with 1000 mL of kerosene containing 1000 ppm of ethyl mercaptan. In these experiments, air was used as the oxygen source keeping the inlet valve open and the outlet valve closed. After reaching the desired temperature, Merox catalyst dissolved in caustic solution was added, at the same time mixer operating at 1460 rpm was turned on. Time zero was considered to be the time at which Merox catalyst and sodium hydroxide solution was introduced in the reactor. At this initial time a sample of the organic phase was taken for analysis. During the experimental run, the organic phase is sampled (15 to 20 mL for each sample) at certain times then samples were washed by water and the organic phase containing no Merox catalyst or sodium hydroxide was separated and mercaptan concentration (expressed as ppm in weigh of mercaptan sulphur) is determined by potentiometric titration method according to UOP: 163-89 method. In order to verify the achieved results, more than half of the experiments were duplicated casually that led us to the same results. Previous results were confirmed in the analysis section by analyzing each sample two or three times.

Reactor

Experiments were carried out in a semi-batch bubble column reactor made of glass with volume of 3.1 liter and length to diameter ratio of 3 shown in Fig. 1. This reactor could handle the pressure of 3 bars and the temperature of 380 °C and was equipped with a mixer supporting up to 2500 rpm. Organic and aqueous phases were designed to be batch and gas phase to be continuous. Temperature was controlled using a mantle within ± 1 °C of the set temperature.

Materials properties

Merox catalyst

A catalyst named Merox LCPS-30 was used for these experiments. The Merox catalyst is a heterogeneous blue powder (dissolved in water) containing sulphur, cobalt, oxygen, calcium, carbon, nitrogen and sodium. It is possibly a mixture of sulphonated derivatives of cobalt phthalocyanine with sodium and calcium salts. The weight percentages of cobalt in these derivatives are 8.6 and 7.6% respectively, whilst from SEM the richest cobalt regions have 9% of cobalt. The presence of sodium

Table 1: Catalyst LCPS-30 properties.

Physical state	Liquid
Active material	30%wt
Color	Blue
Odor	Ammonia
pH	9
Freezing point	0 °C
Boiling point	>100 °C
Specific gravity	1.15
Solubility	miscible in water, insoluble in hydrocarbon
Stability	stable under normal conditions of use

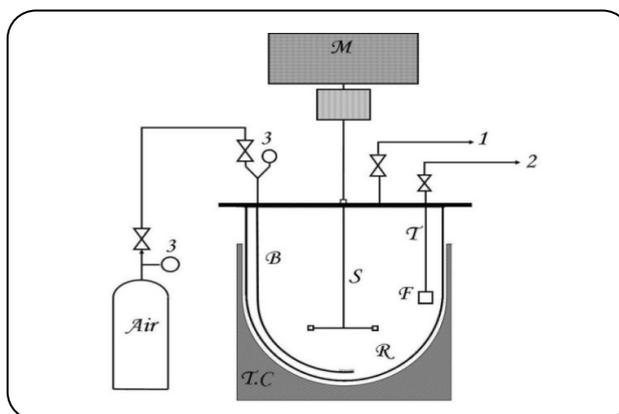


Fig. 1: Reactor equipments; 1: gas outlet, 2: sampling output, 3: barometer, B: air inlet, T&F: sampling tube and baffle, M: mixer, S: shaft R: reactor, T.C: mantle (temperature controller).

in the catalyst formulation can enhance the activity and stability of the catalyst [10, 15]. The catalyst properties are listed in Table 1.

Organic solvent

Gasoline and kerosene obtained from Isfahan Refinery were used as the organic solvents. The concentration of sulphur compounds in both solvents was less than 1 ppm. Solvent properties are listed in Table 2.

Other materials such as potassium iodide, acetic acid and hydrochloric acid obtained from Merck ® Company were used specially in mercaptan analysis procedure.

Analysis system

After each experiment, all samples were washed by water in order to remove catalyst from the organic solvent

Table 2: Kerosene properties.

I.B.P	150°C
Recovered @ 185°C	50 %
Recovered @ 200°C	70 %
Recovered @ 210°C	90 %
Recovered @ 235°C	95 %
F.B.P	275°C
Density @ 15°C	813.5 Kg/m ³

then samples were settled for a while so that the organic and aqueous phases could become completely separated. The organic phase was analyzed using potentiometric titration method UOP: 163-89. This analysis method can determine the mercaptan contained in gasoline, kerosene, aviation fuels and distilled fuels having a concentration of 0.0003 wt% to 0.01 wt% within ± 1 ppm of the actual concentration. In this method other sulphur compounds such as disulphides and sulphides cannot affect the result. The whole analysis package containing titration equipments, potentiometer and electrodes were purchased from PetroTest ® Company. Further information is available in the company's website [16].

Experimental parameters

In order to compare the effect of each parameter, a reference condition close to industrial ones was chosen. The reference condition is listed in Table 3.

The most objective parameters are temperature, pressure, phase volume ratio, sodium hydroxide concentration, solvent, and mixer rotational speed.

RESULTS AND DISCUSSION

Rate constant and order of reaction

The order of reaction in respect to ethyl mercaptan concentration was determined using integration method for the reference experiment. As was mentioned in the past researches, three models were proposed for the estimation of the order of reaction in respect to mercaptan concentration:

A: zero-order:

Reaction rate equation for the zero-order:

$$-r = \frac{-dC_{\text{mer}}}{dt} = k \quad (13)$$

Table 3: Reference condition.

Solvent	Kerosene
Merox catalyst weight	10 mg
Aqueous phase volume	10 cc
Organic phase volume	1 lit
Temperature	28 °C
mixer rotational speed	1460 rpm
Sodium hydroxide concentration	2.5 Molar

On rearrangement,

$$-dC_{\text{mer}} = kdt \quad (14)$$

Integration,

$$\int -dC_{\text{mer}} = k \int dt \quad (15)$$

Hence,

$$C_0 - C_{\text{mer}} = kt \quad (16)$$

And the final form will be

$$1 - \left(\frac{C_{\text{mer}}}{C_0} \right) = \left(\frac{k}{C_0} \right) t = k't \quad (17)$$

So plotting dimensionless mercaptan concentration against time will give us a linear curve with the slope of "k/C₀" if the rate equation is zero-order.

B: first-order:

Reaction rate equation for the first-order:

$$-r = \frac{-dC_{\text{mer}}}{dt} = kC_{\text{mer}} \quad (18)$$

On rearrangement,

$$\frac{-dC_{\text{mer}}}{C_{\text{mer}}} = kdt \quad (19)$$

Integration,

$$\int \frac{-dC_{\text{mer}}}{C_{\text{mer}}} = k \int dt \quad (20)$$

Hence,

$$\text{Ln}(C_0) - \text{Ln}(C_{\text{mer}}) = kt \quad (21)$$

And the final form will be

$$-\text{Ln} \left(\frac{C_{\text{mer}}}{C_0} \right) = \text{Ln} \left(\frac{C_0}{C_{\text{mer}}} \right) = kt \quad (22)$$

Table 4: Order of reaction.

Order	2 nd	1 st	0 th
R ²	0.476	0.994	0.717
Slope	56	-0.679	-0.123

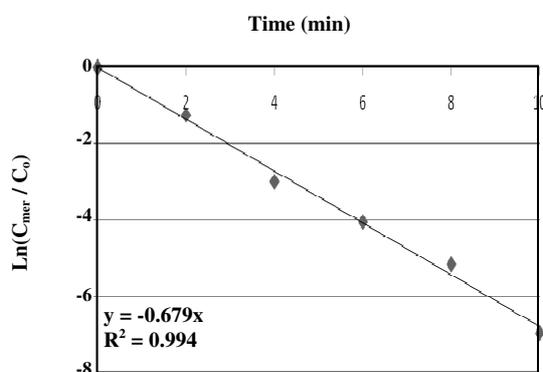


Fig. 2: Integral method for first-order reaction.

Plotting $\text{Ln}(C_0 / C_{\text{mer}})$ against time will give us a linear curve with the slope of “k” if the rate equation is first-order.

C: second-order:

Reaction rate equation for the second-order:

$$-r = \frac{-dC_{\text{mer}}}{dt} = kC_{\text{mer}}^2 \quad (23)$$

On rearrangement,

$$\frac{-dC_{\text{mer}}}{C_{\text{mer}}^2} = kdt \quad (24)$$

Integration,

$$\int \frac{-dC_{\text{mer}}}{C_{\text{mer}}^2} = k \int dt \quad (25)$$

Hence,

$$\frac{1}{C_{\text{mer}}} - \frac{1}{C_0} = kt \quad (26)$$

And the final form will be

$$\left(\frac{C_0}{C_{\text{mer}}} \right) - 1 = kC_0t = k't \quad (27)$$

And plotting (C_0 / C_{mer}) against time will give us a linear curve with the slope of “ kC_0 ” if the rate equation is the second-order.

Using equations 17, 22 and 27 the data was plotted for each guess. Slopes and linearity in the term of R^2 for zero, first and second order guesses are reported in Table 4.

According to Table 4, the best fitted results ($R^2 \sim 1$) are obtained using the first-order reaction equation. In the first-order reactions the slope of “ $\text{Ln}(C_{\text{mer}} / C_0)$ ” Vs. time diagram (See Fig. 2) is “ $-a.k_m$ ” [12].

According to Fig. 2,

$$\text{Slope (with 95\% CI)} = -a \times k_m = -0.679(-0.714, -0.646) \text{ min}^{-1} \quad (28)$$

Hence,

$$a = m / V = 10^{-5} \text{ Kg} / 10^{-3} \text{ m}^3 = 0.01 \text{ Kg} / \text{m}^3 \quad (29)$$

$$k_m \text{ (with 95\% CI)} = 1.131(1.08, 1.19) \text{ m}^3 / \text{Kg}_{\text{cat}} \cdot \text{Sec} \quad (30)$$

Effect of temperature

To investigate the amount of the activation energy and the effect of temperature on the rate of reaction, having all the other parameters fixed, various temperatures were tested. Table 5 indicates the experimental data which are related to the mercaptan concentration in the batch reactor as a function of time at temperatures of 28, 38 and 48°C. Also, Fig. 3 plotted according to these experimental data.

To use the Arrhenius' law and explain the kinetic data, it is necessary to determine the rate of reaction at different temperatures.

Arrhenius' law:

$$k = k_0 e^{\frac{-E}{RT}} \quad (31)$$

So this equation can be written as:

$$\text{Ln}(k_m) = \text{Ln}(k_0) + e^{\frac{-E}{RT}} \quad (32)$$

Hence,

$$\text{Ln}(k_m) = \left(\frac{-E}{R} \right) \times \frac{1}{T} + \text{Ln}(k_0) \quad (33)$$

So using regression method, the values of “ $-E/R$ ” and “ $\text{Ln}(k_0)$ ” are determined by plotting “ $\text{Ln}(k_m)$ ” Vs. “ $1/T$ ” (See Table 6). The plotted line's slope is “ $-E/R$ ” and the intercept is “ $\text{Ln}(k_0)$ ” [13] as it is shown in Fig. 4.

Table 5: Experimental data of C_{mer}/C_0 as a function of time at various temperature.

T (°C)	Time (min)				
	0	2	4	6	8
28	1	0.289795721	0.5	0.017619048	0.005739122
38	1	0.238095238	0.042857143	0.006666667	0.001904762
48	1	0.132380952	0.37142857	0.008571429	0.000952381

Table 6: Relation between rate constant and temperature.

T (°C)	28	38	48
Slope	0.679	0.801	0.845
K_m (m ³ /kg.sec)	1.131	1.335	1.408
$10^3/T$ (K)	3.321	3.214	3.114
$\ln(k_m)$	0.123	0.288	0.342

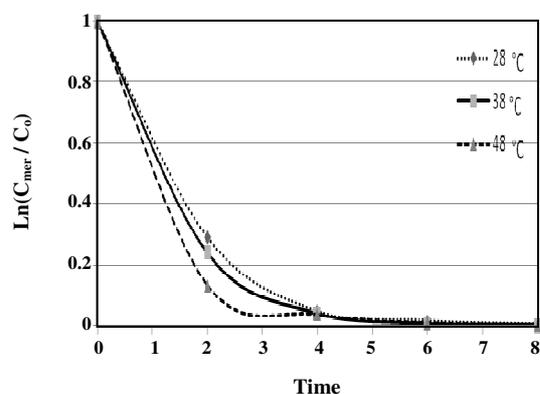


Fig. 3: Effect of temperature over Dimensionless mercaptan concentration as a function of time.

$$k_m = \exp(3.670 - 1063.1/T) = 39.25 \cdot \exp(-1063.1/T) \quad (33)$$

So by fixing all the other parameters, the reaction rate equation can be written as:

$$-r = \exp(3.670 - 1063.1/T) \cdot C_{mer} = 39.25 \cdot \exp(-1063.1/T) \cdot C_{mer} \quad (33)$$

Effect of sodium hydroxide concentration

To achieve the rate of reaction as a function of sodium hydroxide concentration, solutions of 1 and 4.5 Molar of sodium hydroxide were prepared and tested. Fig. 5 was plotted according to experimental data which were shown in Table 7, shows that increasing sodium hydroxide

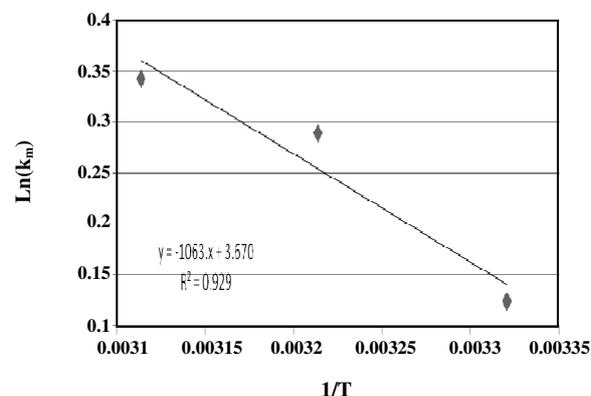


Fig. 4: Arrhenius plot for the catalytic oxidation of ethyl mercaptan in the presence of Merox catalyst.

concentration decreases the rate of the reaction that is in complete paradox with existing chemical mechanisms. There is a possibility that metal phthalocyanines, in addition to cause an increase in the rate of reaction may result in changing the mechanism. Another possibility is the existence of an optimum concentration for sodium hydroxide.

" $T_{1/2}$ " for each experiment was calculated using the rate of reaction data which were obtained in the experiment (See Table 8). Afterwards, the order of reaction in term of sodium hydroxide concentration was determined by using half lifetime theory method [1].

General reaction rate equation

$$-r = \frac{-dC_b}{dt} = kC_b^n \quad (35)$$

Table 7: Experimental data for C_{mer}/C_0 as a function of time at various sodium hydroxide concentrations.

C_{NaOH} (M)	Time (min)					
	0	2	4	6	8	10
1	1	0.199333333	0.020666667	0.002	0.00066667	0
2.5	1	0.289795721	0.5	0.017619048	0.005739122	0.000952381
4.5	1	0.462962963	0.203703704	0.066666667	0.020370370	0.009259259

Table 8: Relation between rate constant and sodium hydroxide concentration.

C_b (M)	1	2.5	4.5
$T_{1/2}$ (sec)	43.57	61.22	90.03
$\text{Log}(T_{1/2})$	1.639	1.786	1.954
$\text{Log}(C_b)$	0	0.40	0.65

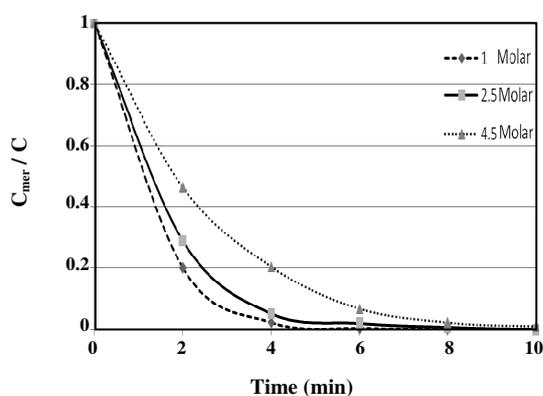


Fig. 5: Effect of sodium hydroxide concentrations over dimensionless mercaptan concentration as a function of time.

After integration,

$$C_b^{1-n} - C_0^{1-n} = k(n-1) \times t \quad (36)$$

So " $T_{1/2}$ " can be derived by substituting C_b by $(C_0 / 2)$:

$$T_{1/2} = \frac{(0.5)^{1-n} + 1}{k(n-1)} \times C_b^{1-n} \quad (37)$$

Hence,

$$\text{Log}(T_{1/2}) = (1+n) \times \text{Log}(C_b) + \text{Log} \frac{(0.5)^{1-n} + 1}{k(n-1)} \quad (38)$$

So " $\text{Log}(T_{1/2})$ " must be plotted against " $\text{Log}(C_b)$ " (See Fig. 6). This data is listed in Table 6. The line's slope is " $(1+n)$ " and " n " is the order of reaction in term of sodium hydroxide concentration.

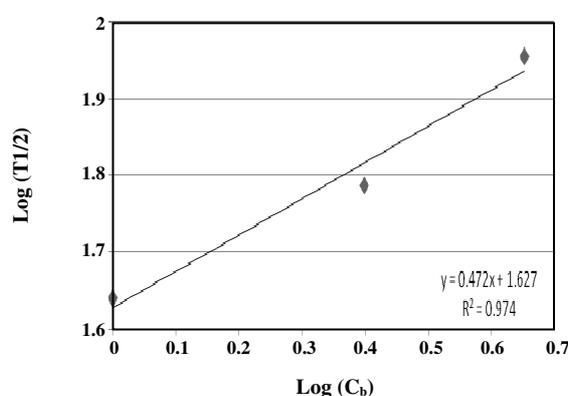


Fig. 6: Fractional lifetime plot for determination of sodium hydroxide concentration effect.

$$\text{Slope} = 0.427 \Rightarrow -0.528 \sim -1/2 \quad (39)$$

Therefore, the order of the reaction rate with respect to sodium hydroxide concentration will be " $-1/2$ ".

Effect of organic to aqueous phase ratio

As another effective parameter, the organic to aqueous phase ratio was considered 100 in the reference experiment and in the next experiments 50 and 200 were also selected for this ratio. Table 9 shows the experimental data of C_{mer}/C_0 as a function of time at various the organic to aqueous phase ratio. These data was plotted in Fig. 7, and subsequently results were mentioned in Table 10.

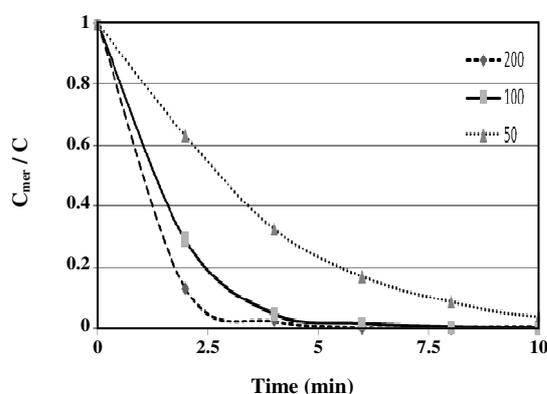
The achieved result can be explained in two ways. As it has been highlighted, ethyl mercaptan oxidation reactions take place in the aqueous phase. Since

Table 9: Experimental data for C_{mer}/C_0 as a function of time at various the organic to aqueous phase ratio.

Ratio	Time (min)					
	0	2	4	6	8	10
200	1	0.133333333	0.025	0.002666667	0.000666667	0.006666667
100	1	0.289795721	0.5	0.017619048	0.005739122	0.000952381
50	1	0.633333333	0.326666667	0.170666667	0.089333333	0.041333333

Table 10: Relation between rate constant and feed ratio.

Phase ratio	200	100	50
$K_m(m^3/(kg.sec))$	1.543	1.131	0.533

**Fig. 7: Effect of various phase ratios over dimensionless mercaptan concentration as a function of time.**

the amount of Mercox catalyst in each experiment is constant (10 mg), decrease in the organic phase is equivalent to increase in Mercox catalyst concentration. Consequently, the ethyl mercaptan chemical oxidation rate change. The second explanation of this behavior relies on hydroxide ion (OH^-) concentration. In regard to the constant sodium hydroxide concentration (2.5M) in these experiments, increase in the aqueous phase comparing to organic phase is equivalent to increase in amount of OH^- and as it was concerned, by increasing the amount of OH^- , ethyl mercaptan oxidation rate reduces.

Effect of Oxygen concentration

In order to illustrate the effect of oxygen concentration on ethyl mercaptan oxidation rate, the pressure of inlet oxygen was doubled while other parameters held constant at their reference values. The obtained results were the same as before. Thus, it can be concluded that inlet

oxygen concentration has no influence on ethyl mercaptan oxidation rate.

Effect of solvent

A set of experiments was carried out in order to investigate the effect of changing the solvent on the ethyl mercaptan oxidation rate. Sulfur-free gasoline was used instead of kerosene to illustrate the effect of solvent. The obtained results were almost the same. Consequently, the content of organic phase does not affect ethyl mercaptan oxidation rate. *Yabroff* also expressed the same conclusion in his studies [14]. Feed content may influence of mass transfer between the two phases equations. However, due to high rotational speed of the mixer and subsequent insignificant influence of interphase mass transfer on reaction rate, the effect of organic phase content is not noticeable.

Effect of mixer rotational speed

Theoretically, inter-phase mass resistance reduces by increasing the mixer rotational speed. By decreasing the rotational speed to 1200 rpm and holding other factors constant at their reference values; the influence of rotational speed on ethyl mercaptan oxidation rate was investigated. As it was expected, the results were the same as reference experiments. Although decrease in the rotational speed may cause a greater mass transfer resistance between the two phases, speed used in the experiments was high enough to neglect the effect of interphase mass transfer resistance. Hence, mixer rotational speed variations in the range used in this work, do not have a noticeable effect on ethyl mercaptan oxidation reactions.

CONCLUSIONS

The kinetics of liquid phase oxidation of ethyl mercaptan in the presence of Merox catalyst has been investigated and the equation proposed for constant phase ratio is suggested as follows:

$$r = -V_{\text{org}} / m_{\text{cat}} \frac{dC_{\text{mer}}}{dt} = \quad (40)$$

$$k'_0 \times e^{\left(\frac{-E}{RT}\right)} \times C_{\text{mer}}^n \times C_b^m \times C_{\text{O}_2}^k$$

Using fractional life and integral method for determining the kinetic and the order of reaction, the values of 0, 1 and -1/2 are respectively suggested for k, n and m. so the above equation is revised as follows:

$$r = -V_{\text{org}} / m_{\text{cat}} \frac{dC_{\text{mer}}}{dt} = k'_0 \times e^{\left(\frac{-E}{RT}\right)} \times \frac{C_{\text{mer}}}{\sqrt{C_b}} \quad (41)$$

The other parameters for the organic to aqueous phase ratio of 100 were determined using Arrhenius' law:

$$k'_0 = 62 \text{m}^3 \cdot \text{M}^{0.5} / \text{sec} \cdot \text{kg}_{\text{cat}} \quad (42)$$

$$E/R = -1063.1 \text{K}^{-1} \quad (43)$$

The conclusion made from obtained results from these experiments could be summarized as follows: The amount of dissolved oxygen (gas phase) has no effect on the rate of reaction. The nature of organic phase (mercaptan polluted solvent) has no effect on the rate of reaction. Effect of the pressure was investigated by doubling the oxygen stream's pressure but no change in the rate of reaction was observed, also changing the mixer's speed from 1460 to 1200 did not affect the rate of the reaction but effect of these two factors can be checked in next researches by doing experiments at higher pressure and less mixer speeds.

Nomenclature

Symbols

A	Merox catalyst weight per volume of organic phase , kg/L
C	Concentration, mol/L
CoPC	Cobalt phthalocyanine
E	Activation energy , erg
F.B.P.	Final boiling point
I.B.P.	Initial boiling point
K	Rate constant, mol.m ³ /sec.Kg _{cat}

k ₀	Arrhenius' constant, mol.m ³ /sec.Kg _{cat}
k' ₀	Rate constant , m ³ .M ^{0.5} /sec.Kg _{cat}
M	Merox catalyst weight , kg
R	Universal gas constant, erg/k
R	Rate of reaction, mol.kg/lit.sec
T	Time , sec
T _{1/2}	Lifetime, sec
V	Organic volume , L
W	Weight , kg

Subscripts

0	Initial
B	Base (sodium hydroxide)
Cat	Catalyst
M	Catalytic reaction
Mer	Mercaptan
Org	Organic phase

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