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Study Reaction Kinetics of Fuel Model Desulfurization by Electrochemical Oxidation Technique

Israa Mohammed [a], ***Hameed Hussein Alwan*** [a]*, ***Ghanim A. N.*** [a]

[a]*University of Babylon , College of engineering , Chemical engineering , Babil , Iraq.*

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ABSTRACT

The model fuel (Heptane contained 2500 ppm from DBT) was desulfurized electrochemically at a constant current (300 mA), in which the process consists two steps; the first step is electrochemical desulfurization by using an electrochemical cell contains two graphite electrodes immersed in electrochemical cell; the cell contains model fuel, hydrogen peroxide as oxidation agent, 0.106 M is NaCl to enhance electrolyte electrical conductivity. The investigation was at different operation parameters; temperature range (40-50-60 °C), stirring time (10-20-30-40-50) min, while the second step is extraction with acetonitrile. The results show final sulfur concentration decreased when increasing time at the same temperature for example. Kinetics parameters calculation shows that electrochemical desulfurization ECD reaction follows pseudo 1st order reaction, the rates constant of reaction are 0.0175, 0.0191 and, 0.0193 at temperatures 40, 50, and 60 °C, respectively, while activation energy equal 4.433 kJ/mol.

1. Introduction

In general, the main source of air pollution is the combustion of sulfur compounds associated with different petroleum productions when used as fuels because off emissions of sulfur oxides (SOx), which leads to acid rain and foggy weather, on the other hand, I may cause catalyst poisoning, affects product quality, equipment corrosion and unwanted odors for that. Sulfur compounds should be removed from petroleum products Tang et al. [1]. Thus there a hard environmental consideration for allowable sulfur content with fuel were applied in developed countries, for example, China, in 2014, the maximum sulfur content allowed in fuel was set to be less than 10 ppm [1]. In the United States, the gas contains between 50 to 500 ppm, while Iraqi gas oil contains 10,000 ppm Ho et al. [2]

There are many techniques used to remove sulfur compounds in the oil refining industry, but the common commercial method is the hydrodesulphurization method HDS is a chemical process that works with high pressure and temperature in addition to the presence of an amount of expensive catalyst and huge amount of hydrogen Alwan et al. [3] , HDS method characterized by its high energy consumption Mehri et al. [4] , due to the high operating conditions and is ineffective in removing some compounds sulfur, such as benzothiophenes BT, and Dibenzothiophene DBT [5, 6], therefore, new methods have been suggested by researchers, such as oxidation, extraction, extraction, and biological sulfur removal [1].

The ECD process, which operates under moderate operating conditions such as air pressure and a normal temperature of less than 80 °C, was discovered and the cost of operation and investment was reduced due to its lack of need for hydrogen in comparison with the HDS method Zhang et al. [7] , and and can be easily remove (BT, DBT, etc.). ECD process

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* *Corresponding author.*
E-mail address: hameed@uobabylon.edu.iq (hameed Hussein Alwan)

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requires oxidizing agents such as hydrogen peroxide, oxygen ,ozone , proxy acid, and ionic liquid to increase the polarity of the sulfur compounds as a result of donating them with oxygen atoms to facilitate the removal of sulfur compounds later by distillation, adsorption or extraction Campos ‑ Martin et al. [8].The ECD consists two steps ; the first step is oxidation sulfur compounds by oxidant agent to formulae have high polarity Tang et al. [9] and the second step is extraction the oxidized sulfur compounds by solvent such as acetonitrile [1].

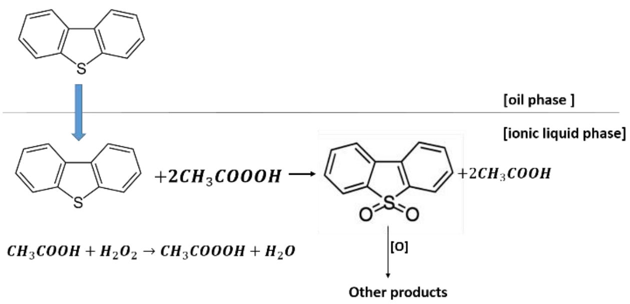

Figure 1-oxidation DBT by used per acetic acid in ionic liquid phase [10].

To enhance the reaction rate between compounds founded in different phases (immiscible liquids) and transfer materials from one phase to another phase can be added small amount of phase transfer catalyst PTC. For example, when mixing hydrogen peroxide with acetic acid(CH3COO), it will give per acetic acid (CH3COOOH) which is a strong oxidant. DBT can be oxidize to DBTO2 when used per acetic acid (CH3COOH) in ionic liquid as shown in **Fig. 1** [10, 11].

In this work, ECD for model fuel (heptane contains 2500 ppm DBT) by H_2O_2 at different reaction temperature and time, followed by extraction with acetonitrile. The study was done to investigate the impact of temperature and time in desulfurization. The reaction kinetic parameters were estimated rate constant, reaction order) at studied temperature as well as the activation energy.

2. Materials and method

2.1. Materials

Model fuel prepared (Heptane contained 2500 ppm from DBT) used as feedstock, Analytical grade chemicals are used; hydroxide peroxide H2O2, sodium chloride NaCl, glacial acetic acid CH3COOH, Acetonitrile CH3CN. All the reagents and solvents used in this study obtained from Sigma-Aldrich with their standard purity.

2.2. Experiment method

Electrochemical desulfurization ECD done at two steps in which the electrochemical cell apparatus in **Fig. 2** ; first step is oxidation, the electrochemical oxidative experiments were carried out in electrolysis cell have two electrodes made from graphite at distance 2 cm, while electrolyte is contains0.106 M NaCl solution as supporting electrolyte to enhance electrical conductivity for electrolyte , 5ml of hydrogen peroxide as oxidant agent and 2.5 ml of 10% acetic acid solution as phase transfer catalyst . 47 ml of fuel model was added to the cell, the electrolyte mixture was heated at constant temperature (40 ,50 and ,60 °C). The power supply was switch on to start oxidation reaction and the power supply was switch off at different time.

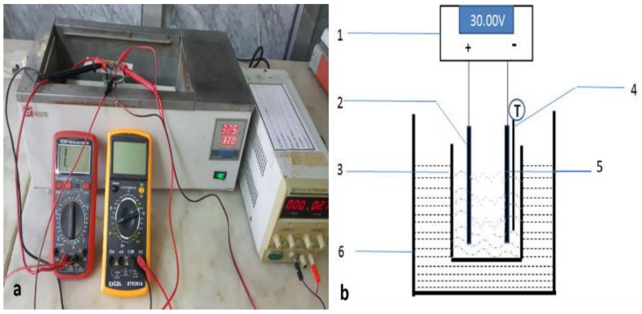

Figure 2- (a) Electrochemical desulfurization experimental apparatus, and (b) Electrochemical desulfurization experimental sketch (1-power supply, 2-anode, 3-electochemical cell, 4-thermostatic sensor, 5-cathode, 6-water bath).

Table 1 Showed selected factors for experimental fuel model. The fuel model and electrolyte are layered. Second step is solvent extraction for removing oxidation products by adding 2.5 ml of acetonitrile to 5 ml of desulfurized fuel model.

Table 1. Values of variables used for desulfurization experiments

Run	Factors	
	Temperature (0 C)	Time (min)
1	40	10
2	40	40
3	40	50
4	50	30
5	50	40
6	50	50
7	60	10
8	60	20
9	60	30
10	60	40

The final sulfur concentration was measured after electrochemical-extraction desulfurization by using Sulfur meter model RX-620SA/TANKA SCINTIFIC.

3. Result and Discussion

Table 2. results for desulfurization experiments

Run	Time	Temperature	Final sulfur content (ppm)
1	10	40	1977
2	40	40	1202
3	50	40	1074
4	30	50	1552
5	40	50	1051
6	50	50	980
7	10	60	1875
8	20	60	1550
9	30	60	1344
10	40	60	1275

3.1. Impact time on sulfur content

As seen in **Table 2**, which listed the desulfurization experiments at different time and temperature with kept NaCl concentration constant, the impact of time on sulfur removing was shown in **Fig. 3**, the final sulfur concentration was decreased with time increasing and this is agreeing with many literatures [3, 4, 9] . Increasing time meaning increasing contact time between reactants. As seen in **Fig. 3**, the final sulfur

concentration is decreasing with temperature but with increasing time the it was started to increasing such as shown at 4o °C and this is may be because off heptane vaporization with increasing time and temperature or this is coming by decreasing in electrolyte conductivity due to releasing heat by oxidation reaction which detain desulfurization reaction as well as electrolysis of water may cause oxygen evolution was lead to energy losses Tang et al. [9] .

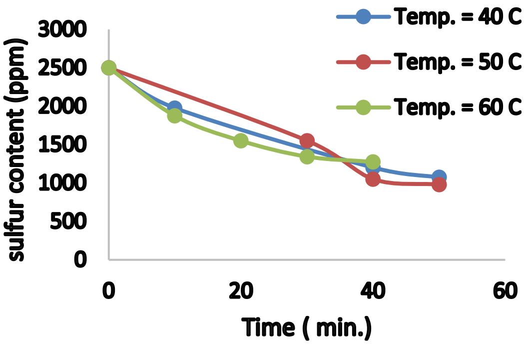

Figure 3- Effect of time on sulfur removal at different temperature in fuel model

3.2 Oxidation Desulfurization Reaction Kinetics

Kinetics reaction for ECD studies at different temperatures against time using NaCl concentration 0.106 M. The total sulfur content measured with time (10,20,30,40 and ,50) minutes at temperatures (40, 50 and, 60) ° C. The reaction is represented as follow:

$$\mathrm{DBT} + \mathrm{H_2O_2} \rightarrow \mathrm{Prodect} \qquad (1)$$

$$-\frac{\mathrm{d[Cs]}}{\mathrm{dt}} = \mathrm{k}\ [\mathrm{H_2O_2}]^{\mathrm{m}}\ [\mathrm{C_s}]^{\mathrm{n}} \qquad (2)$$

Where [CS] is DBT concentration, k is reaction rate constant, t is time, n and m are the reaction rate order in respect to DBT and H2O2 concentration respectively.

By assume the H2O2 term dependent can be neglected due to excess amount Bej et al. [12] . Many workers have been stated that oxidation reaction follows pseudo 1st order reaction, thus Equation (2) can be written for n = 1 as:

$$-\frac{\mathrm{d[C_S]}}{\mathrm{dt}} = \mathrm{k[Cs]} \qquad (3)$$

Where k is apparent rate constant, Equation (3) can be integrated between two limits:

$t = 0 \rightarrow Cs = C_0$,

$t = t \rightarrow Cs = Cf$

$$\ln\left(\frac{C_0}{C_f}\right) = -kt \qquad (4)$$

Where k is the reaction rate constant [min -1] and Cs, Cf, and Co are concentration of sulfur, final concentration of sulfur and initial concentration of sulfur respectively [mol/L].

When plotting $-\ln\left(\frac{C_0}{C_f}\right)$ with time at different temperatures gives linear equation with high R^2 which approves the above assumption of kinetics , The reaction rate constant can be calculated from the slopes of straight lines as showed in **Fig. 4**. The reaction constant and R2 increases with increasing the temperature of the ECD reaction because it strongly temperature dependent [13] , as seen in **Table 3**.

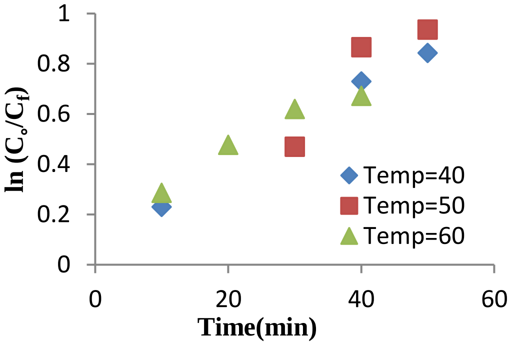

Figure 4- The relation between of ln (C0/Cf) and time at studied temperature.

Table 3. Reaction rate constant is calculate based on power law model at different temperature.

Temp. (°C)	k (min -1)	R2
40	0.0175	0.9771
50	0.0191	0.8308
60	0.0193	0.6779

According to Arrhenius equation estimated the activation energies (Ea) for ECD reaction $k = k_0\ exp\ (-E_a\ /\ R\ T\ )$ From slop of draw (ln k) against (1/T) from **Fig. 5** was calculated the activation energy Ea is equal 4.433 kJ / mole.

In addition to the above kinetics analysis, here Levenberg –Marquardt algorithm was used to estimate kinetics parameters for more accurate calculation, the Levenberg – Marquardt algorithm is a statistical technique which combination between Gauss –Newton and gradient descent methods to solve nonlinear regression by fitting actual experimental results Urych et al. [14] . The kinetics factors were estimated by minimize error between actual results and predicated results with using Levenberg-Marquardt algorithm Trejo et al. [15]

Assume that ECO reaction is nth order and interference hydrogen peroxide concentration effect on reaction; so the equation of reaction rate can be represented as followed:

$$\frac{dC}{dt} = -k[C_{DBT}]^n[C_P]^m \qquad (5)$$

Where [CDBT] and [CP] are DBT and hydrogen peroxide concentration respectively, while n, and m are the reaction order with respect to DBT and hydrogen peroxide respectively. The equation can be integrated to get the following:

$$[C_{DBT}]_f^{1-n} - [C_{DBT}]_0^{1-n} = (n-1)k[C_p]^m t \qquad (6)$$

Where [CDBT]f, and [CDBT] 0 are DBT concentration in product and feed respectively.
Substitute reaction rate constant (k) by using Arrhenius formula which lead to the following:

$$[C_{DBT}]_f^{1-n} - [C_{DBT}]_0^{1-n} = (n-1)k_0\, exp\left(-\frac{E}{RT}\right)[C_p]^m t \qquad (7)$$

Where: K0 is per exponential for equation of Arrhenius,
E activation energy in (J/mol)

R is universal gas constant (8.314 J/mol K)

T is reaction temperature in (K).

t is reaction time.

Equation (7) became:

$$[C_{DBT}]_f = [(n-1)k_o[C_p]^m t\,\exp\left(-\frac{E}{RT}\right) + [C_{DBT}]_0^{1-n}]^{\left(\frac{1}{1-n}\right)} \qquad (8)$$

The actual experimental result for DBT oxidation reaction were fitted with the equation and analyzed as nonlinear regression by aim of STATISTAICA software version 5, as seen the equation, it has four parameters (n, m, k0 and E).

The kinetics parameters values were obtained from nonlinear regression by SPSS software were: n = 0.78, m= -4.59, k0=582.6 and Ea =7.448
For comparison with some previous different oxidation reactions processes for DBT by chemical catalytic reaction and electrochemical reaction were listed in **Table 4**.

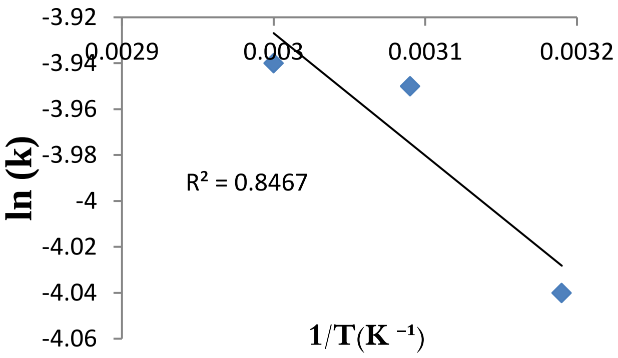

Figure 5- Effect of temperature on reaction rate constant

Table 4. Activation energy for Dibenzothiophene for various oxidation reaction

Kind of reaction	catalyst	activation energy kJ /mol	reference
Chemical	H3P W12 O40	45.9	[16]
Chemical	H3P Mo12 O40	29.0	[16]
Chemical	H3 Si W12 O40	28.3	[16]
Chemical	HPW/aEVM	30.3	[17]
Chemical	Fe2O3/Graphene	36.26	[3]
Electrochemical	-	6.9783 (emulsion electrolyte)	[18]
Electrochemical	-	9.1826 (non-emulsion electrolyte)	[18]
Electrochemical	-	4.433 *	This work
Electrochemical	-	7.448 **	This work

(*) calculated by power law and, (**) calculated by Levenberg-Marquardt algorithm**.**

4. Conclusion

This study showed that the electrochemical oxidation desulfurization of the model fuel the concentration of DBT was decreased with increased time at a constant amount of NaCl and the same temperature. The ECD reaction kinetics show that is obeyed the first-order reaction for desulfurization of DBT by oxidation with H2O2 and reaction rate values 0.0175, 0.0191, and 0.093 at 40, 50, and 60 °C respectively. The ECD reaction show activation energy equal to 4.433 kJ/mol. Levenberg-Marquardt algorithm using is present good agreement for the experimental results in with reaction is obeys (0.78) order and activation energy is 7.448 kJ / moles.

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