

## Kinetics and thermodynamics of the esterification reaction according to the Langmuir-Hinshelwood mechanism

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### ABSTRACT

In this work, kinetics and thermodynamics of esterification reaction were studied. This research investigated the esterification reaction between methanol and acidified oil catalyzed by sulfonated cation exchange resin and proposed a new rate equation for consideration of kinetics of this reaction according to the Langmuir-Hinshelwood mechanism. Thermodynamics and kinetics parameters were calculated according to this equation. The results of this study showed that this new equation was a reasonable equation for kinetics study of the esterification reaction. Also, kinetics parameters were calculated for this reaction. Activation energy and Arrhenius pre-exponential factor were equal to 75.2477 kJ/mol and  $8.9994 \times 10^{13}$  Lit/mol.h respectively.

**Keywords:** Kinetics, Thermodynamics, Esterification, Langmuir-Hinshelwood mechanism.

### 1. Introduction

Because fossil fuels increase greenhouse gases emissions and cause global warming, the use of alternative resources such as biofuels are so important. Biofuels are the fuels produced from renewable sources [1]. There are different sources of oil for biodiesel production such as vegetable oils, animal oils and waste cooking oils [2-4]. The use of waste cooking oils is more economical but these oils create chemical problems [5-7] which are caused by high concentrations of free fatty acids (FFA). High concentrations of FFA in the reaction system create unwanted reactions such as the Saponification reaction [5]. To avoid producing this reaction the chemists use acidic catalysts instead of basic catalysts for biodiesel production [7]. Fatty acids alkyl esters (FAAE) are produced by esterification of free fatty acids by using homogenous and heterogeneous catalysts [8-11]. After using homogenous catalysts in the reaction, these catalysts are removed by washing the products. Under these conditions, the catalysts cannot be used again. On the other hand, the homogenous catalysts can cause corrosion in equipment, piping and facilities and can also produce unwanted products [8].

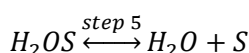
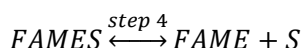
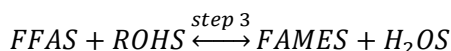
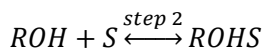
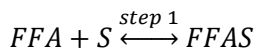
Therefore, the use of heterogeneous catalysts will be economical and chemically useful [12]. In 2016, Corazza et al. studied esterification of long chain fatty acids using montmorillonite K10 as a catalyst which, they concluded, is a high performance catalyst for esterification reaction [8]. In 2009, Li et al. investigated the kinetics of esterification reaction according to the Langmuir-Hinshelwood mechanism; they proposed a new equation for consideration of esterification kinetics. Their study showed that the Langmuir-Hinshelwood mechanism can explain the kinetics behavior of esterification reaction [6]. In 2016, Mikkola et al. examined the kinetics of esterification and transesterification of acid oils to biodiesel using a mesoporous sulfonated carbon catalyst. They calculated rate constants and equilibrium constants for all of the steps in mechanism [13]. In this survey, we proposed a new rate equation according to the Langmuir-Hinshelwood mechanism for esterification reaction and studied the kinetics and thermodynamics of this reaction.

### 2. Mechanism and rate equation

In this research, chemical kinetics of esterification reaction were studied. For this reaction, several rate equations had been proposed; this research proposes a new rate equation for this reaction and thermodynamics

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and kinetics parameters were calculated according to this equation. Langmuir-Hinshelwood mechanism, which was used in this study, consisted of five elementary reactions [6]:



In this mechanism, in the first step, free fatty acids (FFA) are adsorbed on the active sites of catalyst and FFAS are produced. In the second step, alcohol molecules were adsorbed on the active sites of catalyst, producing ROHS. The third step is assumed the rate-controlling step; adsorbed free fatty acids react with adsorbed alcohol molecules and produce adsorbed methyl ester and water molecules on the catalyst surface. In fourth step, desorption process occurs for adsorbed methyl ester on the catalyst surface. Also, in the fifth step, desorption process occurs for adsorbed water on the active sites of the catalyst. The rate equation was built based on below assumptions:

- 1- The rate of the adsorption and the desorption process in this mechanism can be ignored compared to the catalyzed ones.
- 2- All of the active sites on the catalyst surface are same.
- 3- The surface reaction (step 3) is the rate controlling step.
- 4- In derivation of rate equation, we assume that step 3 is an irreversible reaction.

The rate equation for esterification reaction was driven according to the Langmuir-Hinshelwood mechanism. Also, based on this mechanism and the fourth assumption, the surface reaction (step 3) is an irreversible step and also the rate controlling step, so we can write:

$$rate = k_3 \theta_{FFA} \theta_{ROH} \quad (1)$$

In this equation,  $k_3$  is the rate constant for forward step at step 3 in the mechanism. Also,  $\theta_{FFA}$  and  $\theta_{ROH}$  are the coverage fractions of catalyst active sites that have been occupied by free fatty acids and alcohol molecules respectively.

According to the assumption of equilibrium of the step 1 in this mechanism, we can write:

$$k_1 [FFA] \cdot \theta_* = k_{-1} \theta_{FFA} \quad (2)$$

In this equation  $[FFA]$  is concentration of free fatty acids. Also,  $k_1$  and  $k_{-1}$  are rate constants for forward and backward steps at step 1. According to the equation (2), we have:

$$\theta_{FFA} = \frac{k_1}{k_{-1}} [FFA] \theta_* \quad (3)$$

Or:

$$\theta_{FFA} = K_1 [FFA] \theta_* \quad (4)$$

In this equation,  $K_1$  is the equilibrium constant for step 1. Also, for step 2 we can write:

$$k_2 [ROH] \cdot \theta_* = k_{-2} \theta_{ROH} \quad (5)$$

According to equation (5) we can write:

$$\theta_{ROH} = \frac{k_2}{k_{-2}} [ROH] \theta_* \quad (6)$$

Or:

$$\theta_{ROH} = K_2 [ROH] \theta_* \quad (7)$$

Where  $K_2$  is equilibrium constant for step 2. Also, according to the steps 4 and 5 we can write:

$$\theta_{FAME} = \frac{1}{K_4} [FAME] \theta_* \quad (8)$$

And:

$$\theta_{H_2O} = \frac{1}{K_5} [H_2O] \theta_* \quad (9)$$

In equations (8) and (9),  $K_4$  and  $K_5$  are equilibrium constants for steps 4 and 5,  $[FAME]$  and  $[H_2O]$  are concentrations of esters and water,  $\theta_{FAME}$  and  $\theta_{H_2O}$  are the coverage fractions of catalyst active sites that have been occupied by ester and water molecules respectively. In this mechanism, the catalyst active sites have been occupied by alcohol, free fatty acid, water and esters (FAME), thus a relationship between  $\theta_{ROH}$ ,  $\theta_{H_2O}$ ,  $\theta_{FFA}$ ,  $\theta_{FAME}$  and  $\theta_*$  was obtained, where  $\theta_*$  is the empty active sites on catalyst surface. Therefore, we can write:

$$1 = \theta_* + \theta_{ROH} + \theta_{FFA} + \theta_{FAME} + \theta_{H_2O} \quad (10)$$

According to equations (4), (7), (8), (9) and (10), the equation below was written:

$$\theta_* = \frac{1}{1 + K_1 [FFA] + K_2 [ROH] + \frac{1}{K_4} [FAME] + \frac{1}{K_5} [H_2O]} \quad (11)$$

Based on the rate controlling step (step 3) and equations (1), (4), (7) and (11), the following equation was obtained:

$$r = \frac{k_3 K_1 K_2 [FFA] [ROH]}{\left[ 1 + K_1 [FFA] + K_2 [ROH] + \frac{1}{K_4} [FAME] + \frac{1}{K_5} [H_2O] \right]^2} \quad (12)$$

In the next section, this rate equation was evaluated according to the experimental data.

### 3. Results and Discussion

In this section, accuracy of equation (12) was evaluated according to the experimental data. For this purpose, one set of experimental data from the literature has been selected. Lu et al. studied kinetics and thermodynamics of the esterification of acidified oil catalyzed by sulfonated cation exchange resin[14]. In their research work, Lu et al. optimized this reaction at different conditions such as optimization of reaction time, reaction temperature, amount of catalyst and the mass ratio of methanol to acidified oil. The obtained data were used for evaluation of equation (12). These data are indicated at Fig. 1.

Required data were collected from data reported by Lu et al. for fitting to equation (12). The required data were obtained from this method: In step 1, the concentrations of  $CH_3OH$ ,  $FAME$ , and  $H_2O$  were calculated according to the concentration of  $FFA$  and stoichiometry of reaction, so that one molecule of  $FFA$  react with one molecule of alcohol and produce one molecule of water and one molecule of ester. In step 2, A plot of concentration of  $FFA$ ,  $CH_3OH$ ,  $FAME$ , and  $H_2O$  versus time was drawn. In next step, the material concentrations at other times according to the relationship between concentration of this material and time obtained at step 2 were determined. In step 3, On the basis of the plot of  $FFA$  concentration versus time, reaction rate is the slope of the curve in every time, thus the reaction rate according to the relationship between  $FFA$  concentration and time was worked out by equation (13) in every time. The results of the material concentrations and reaction rate were shown at Figs. 2-6.

$$rate = -\frac{d[FFA]}{dt} \quad (13)$$

For example, if the relationship between  $FFA$  concentration and time is as follows:

$$[FFA] = 0.5959 \exp(-0.003 t) \quad (14)$$

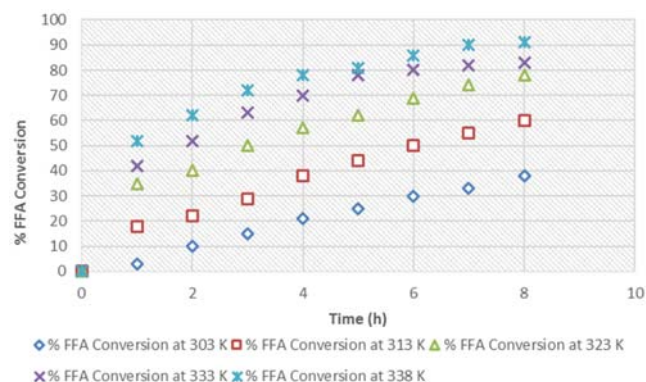


Fig. 1. Plot of FFA conversion (%) versus time at temperatures 303, 313, 323, 333 and 338 K [14].

Using the equation (14) the concentration of the  $FFA$  in every other time was obtained. Also, the slop of this equation is the reaction rate at time of  $t$ . that means:

$$Reaction\ rate = -\frac{d[FFA]}{dt} = 0.003 \times 0.5959 \exp(-0.003 t) \quad (15)$$

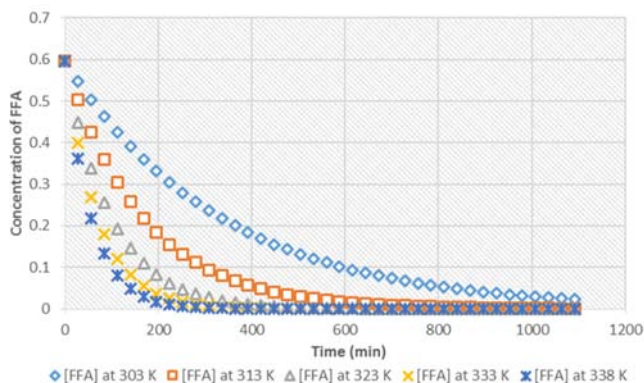


Fig. 2. The results of calculation of FFA concentration according to the method of this study at temperatures of 303, 313, 323, 333 and 338 K.

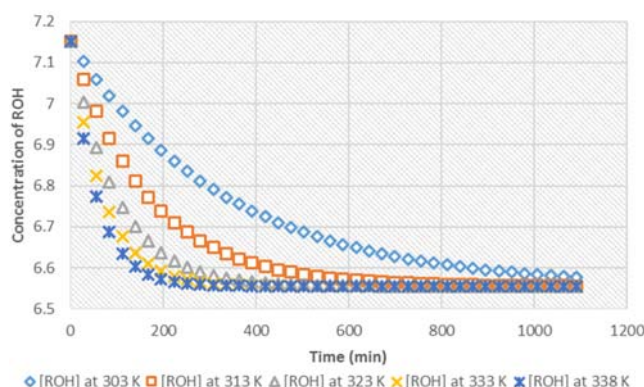


Fig. 3. The results of calculation of methanol concentration according to the method of this study at temperatures of 303, 313, 323, 333 and 338 K.

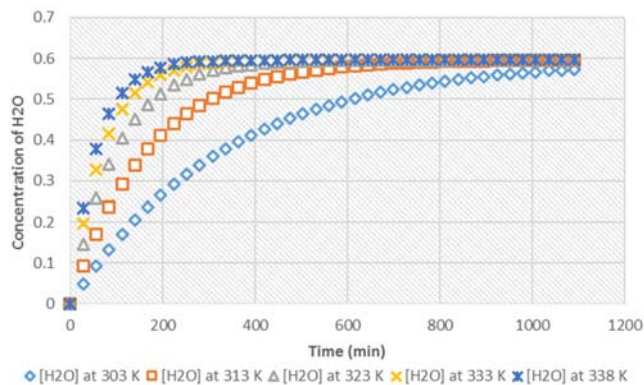
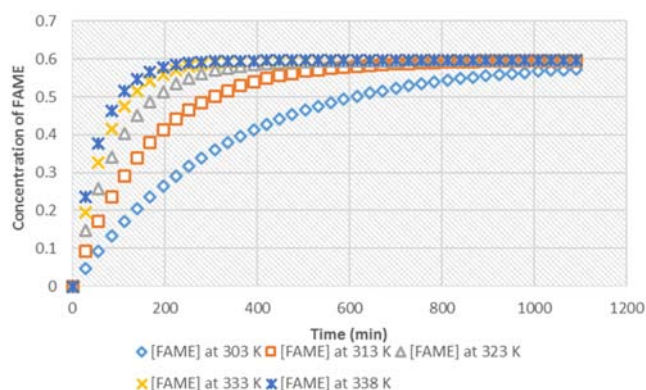
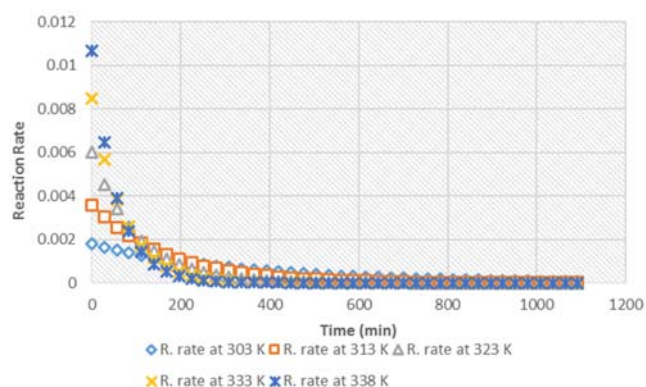


Fig. 4. The results of calculation of water concentration according to the method in this study at temperatures of 303, 313, 323, 333 and 338 K.



**Fig. 5.** The results of calculation of FAME concentration according to the method of this study at temperatures of 303, 313, 323, 333 and 338 K.



**Fig. 6.** The results of calculation of reaction rate according to the method of this study at temperatures of 303, 313, 323, 333 and 338 K.

For example, the *FFA* concentration and reaction rate were determined according to equations (14) and (15) and the results were tabulated in Table 1. For fitting of rate equation with obtained data, the Polymath 6.1 package was employed. The rate equation (equation (12)) was fitted to the obtained data (data set consists of concentration of *FFA*, *CH<sub>3</sub>OH*, *FAME*, and *H<sub>2</sub>O* and reaction rate (according to equation (13)) at times of 0, 28, 56, 84, ..., 424, 452 and 480 minutes and at temperatures of 303, 313, 323, 333 and 338 K).

**Table 1.** The results of *FFA* concentration and reaction rate at 0, 100 and 1000 minutes.

Time (min.)	Concentration of <i>FFA</i> (mol/lit)	Reaction rate (mol/lit.min)
0	0.5959	0.001788
100	0.4415	0.001324
1000	0.0297	0.000089

The results of the fitting are demonstrated at Figs. S1-S5 (See supplementary data). Equilibrium constants for steps 1, 2, 4 and 5 in the mechanism were measured employing equation (12), fitted to obtained data. Also, the forward rate constant for step 3 was achieved. These results are reported in Table 2. In 2012, Zhao et al. developed a rate equation for consideration of chemical kinetics of esterification reaction catalyzed by a cation ion-exchange resin/polyethersulfone hybrid catalytic membrane [17]. They have claimed that this rate equation was driven based on the following assumptions:

- 1- The rate of the non-catalyzed reactions is negligible compared with the catalyzed reactions;
- 2- The catalytic activity of all sites on the catalytic membrane surface is the same.

It is clear that their rate equation has been written according to the overall reaction, this method is wrong because this reaction is not an elementary reaction and reactants react together on the catalyst surface. In other words, the rate equation for kinetics study, must be determined according to a reasonable mechanism. In 2015, Ding et al. applied this method to kinetics study of esterification reaction of acidified oil catalyzed by sulfonated cation exchange resin and they achieved the rate equation on the basis of the overall reaction [18].

In this study a new rate equation was accomplished according to the reasonable mechanism, and this research suggested that this method is better than Zhao and Ding's method.

**Table 2.** Equilibrium constants and rate constant at temperatures of 30, 40, 50, 60 and 65 °C.

Temperature (°C)	$K_1$	$K_2$	$K_4$	$K_5$	$k_3$
30	70.0104	73.0011	19.0003	7.0020	8.0004
40	39.0205	49.0031	25.0024	21.0004	31.0003
50	28.0111	35.0021	29.0010	40.0011	67.0013
60	20.0102	26.0061	33.0009	68.0014	140.0010
65	18.0001	23.0014	36.0000	87.0005	190.0002



In the next step, enthalpy and entropy changes for steps 1, 2, 4 and 5 in the mechanism were measured according to the equilibrium constant that is reported in Table 2. For calculation of enthalpy and entropy changes equation (16) was applied [15]:

$$\ln K_i = -\frac{\Delta H_i^0}{RT} + \frac{\Delta S_i^0}{R} \quad (16)$$

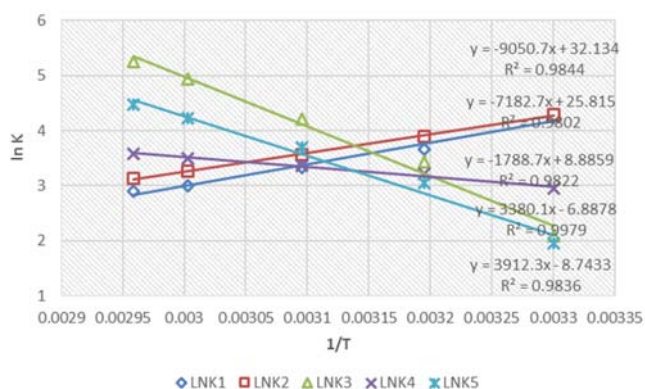
In this equation,  $K_i$  is the equilibrium constant for step  $i$ ,  $\Delta H_i^0$  and  $\Delta S_i^0$  are standard enthalpy and entropy changes respectively for step  $i$ .  $R$  is the gas constant, and  $T$  is the absolute temperature. For calculation of  $\Delta H_i^0$  and  $\Delta S_i^0$ , curve of  $\ln K_i$  versus  $1/T$  should be drawn. Enthalpy and entropy changes ( $\Delta H_i^0$  and  $\Delta S_i^0$ ) have been calculated using the slope and intercept of curves. The results of these calculations are reported in Tables S1-S4 and corresponding plots are shown at Fig. 7. Also, activation energy and Arrhenius pre-exponential factor were calculated through the Arrhenius equation [16]:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (17)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (18)$$

Where ( $k$ ) is the reaction rate constant in rate determining step,  $A$  is the Arrhenius pre-exponential factor and  $E_a$  is the activation energy of the rate determining step,  $R$  is the gas constant and  $T$  is the absolute temperature. For calculation of activation energy and Arrhenius pre-exponential factor, curve of  $\ln k$  versus  $1/T$  should be depicted.

Activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) have been calculated using the slope and intercept of curves. The values of kinetics parameters are reported in Table 3 and the curve of  $\ln k$  versus  $1/T$  is given in Fig. 8.



**Fig. 7.** Plots of  $\ln(K_1)$ ,  $\ln(K_2)$ ,  $\ln(K_4)$  and  $\ln(K_5)$  versus  $1/T$  for calculation of thermodynamics parameters.

In 2015, Banchero studied the kinetics of esterification reaction of free fatty acid catalyzed by  $Nb_2O_5$  catalyst and their results of activation energy and Arrhenius pre-exponential factor for this reaction are in consistent with the results of this work [19].

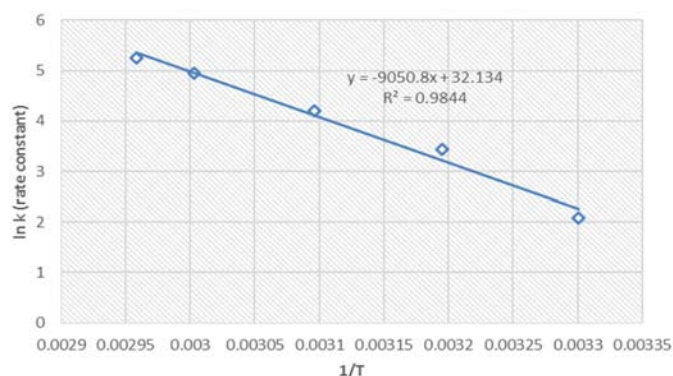
The findings of thermodynamics consideration showed that in step 1 of the mechanism that adsorption of FFA molecules on the catalyst surface is an exothermic reaction and entropy changes of this step is negative and these results for an adsorption step is reasonable. Also, the results of thermodynamics consideration for step 2 is reasonable because this step is an adsorption process too. Two steps, 4 and 5, are desorption processes and the results of thermodynamics consideration revealed that enthalpy and entropy changes are positive and these results are reasonable for a desorption process. According to the kinetics study of this reaction, calculated kinetics parameters for this reaction are reasonable too.

#### 4. Conclusions

In this research work, thermodynamics and kinetics of esterification reaction were examined. Reaction between methanol and acidified oil catalyzed by sulfonated cation exchange resin was studied. A new rate equation for kinetics study of esterification reaction was suggested. For evaluation of this rate equation, data were selected from literature.

**Table 3.** Activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ).

Temp (°C)	$\ln(k_3)$	$E_a$ (kJ/mol)	$A$ (Lit/mol.h)
30	2.0794	75.2477	$8.9994 \times 10^{13}$
40	3.4339		
50	4.2046		
60	4.9416		
65	5.2470		



**Fig. 8.** Plot of  $\ln(k)$  versus  $1/T$  for calculation of kinetics parameters.

The results of this study showed that this rate equation could explain the kinetics behavior of esterification reaction. According to this equation and experimental data, we calculated thermodynamics and kinetics parameters for this reaction. Enthalpy and entropy exchanges for some steps of this mechanism were measured and activation energy and Arrhenius pre-exponential factor for this reaction were determined. Activation energy and Arrhenius pre-exponential factor for this reaction are  $75.2477 \text{ kJ/mol}$  and  $8.9994 \times 10^{13} \text{ Lit/mol.h}$ , respectively.

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