

Thermodynamics Analysis of Glycerol Esterification with Lauric Acid using Zeolite-Y as Catalyst

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ABSTRACT

The glycerol esterification with lauric acid using dealuminated Zeolite-Y as catalyst was studied using stirred batch reactor. The effect of temperature on lauric acid conversion was verified to be influential in this esterification. With the presence of excess glycerol at the reaction, pseudo-second order model is fitted to represent the kinetic model. The activation energy of the esterification reaction with zeolite-Y as a catalyst is obtained to be 32.883 kJ/mol.

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I. INTRODUCTION

Glycerol is a polyalcohol compound with physical properties that is very hygroscopic, colorless, odorless, viscous and a slightly sweet taste, it can be obtained from natural resources or synthesized from petrochemical by-product [1]. Biodiesel and bioethanol production generates glycerol as a by-product, that from economical point of view should be used to produce another product derived from glycerol [2]. Esterification of glycerol is one of the methods to produce a glycerol-product-derivative [3]. Esterification of glycerol with lauric acid produced monolaurin, dilaurin, and trilaurin, where the product of monolaurin or glycerol monolaurate is preferable because of its uses for manufacturing cosmetics, medicines, surfactants, etc [4], [5]. Esterification of glycerol can be conducted at high temperature, but with the help of catalyst, it can lower the reaction temperature needed for reaction to occur [6].

One of the solid catalysts that used for this reaction is zeolite. For the reaction of esterification of glycerol with lauric acid, zeolite-Y had a comparatively higher selectivity to synthesis glycerol monolaurate [7]. Glycerol monolaurate is one of the products of this reaction that is highly desired because of its beneficial properties [8]–[12]. Zeolite-Y is a deposit of minerals that formed from hydrothermal process so that it produced a crystallized aluminosilicate with micropore sizes approximately 0.74 nm [13]. An acidic catalyst is necessary for this reaction to increase the selectivity, for zeolite-Y to increase its acidity is by a process called dealumination [14]. The purpose of this work is to examine the kinetic and thermodynamic parameters of producing monolaurin by esterification of glycerol with lauric acid using zeolite-Y catalyst.

II. MATERIAL AND METHODS

• Materials

Zeolite-Y (Sigma Aldrich Co), glycerin (>99.5%, Merck) and lauric acid (solid, Merck), H₂SO₄ (95-97%, Merck), sodium hydroxide (solid, Merck), isopropyl alcohol (>99.7%), and Phenolphthalein.

• Preparation of zeolite-Y

Zeolite-Y was dealuminated using 8 M H₂SO₄ solution, where for every 10g of zeolite-Y, 100ml is used H₂SO₄ solution. The mixture of zeolite-Y and H₂SO₄ solution stirred and heated to 60°C for 4 hours, after the zeolite-Y separated from the mixture, it's then calcinated in a furnace with the temperature of 500°C for 3 hours.

• Glycerol monolaurate synthesis

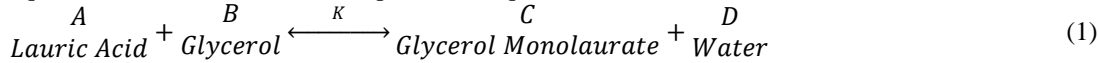
The esterification reaction of glycerol was conducted in a stirred batch reactor, where the dealuminated zeolite-Y catalyst was used at 2wt% from the reactants used. The reactants which is lauric acid and glycerol mixed in the reactor with molar ratio of 1:7.5 respectively. To determine the kinetic and thermodynamic parameters, the temperature is varied at 110, 130, 150, 170°C and with 5 hours of reaction time.

• Product analysis

The percentage of lauric acid before and after the reaction were obtained using a titration method in accordance of AOCS Official Method Ca 5a-40 to determine free fatty acids in the sample, which is the lauric acid.

• **Mathematical model for kinetic and thermodynamic studies**

The reaction of esterification glycerol with lauric acid as shown at eq. (1), from the reaction proposed, the equation of reaction rate can be expressed in eq. (2).



$$-r_a = -\frac{dC_A}{dt} = k_1 C_A^a C_B^b - k_2 C_C^c C_D^d \quad (2)$$

Where as:

C_A = concentration of Lauric Acid

C_B = concentration of Glycerol

C_C = concentration of Glycerol Monolaurate

C_D = concentration of Water

k_1 = kinetic constant for the forward reaction

k_2 = kinetic constant for the backward reaction

a,b,c,d = reaction order

It's proposed for this work the equation for the rate of reaction to be simplified based on the following assumptions:

1. Excess of glycerol was used, thus, the expression for the concentration of glycerol can be treated as a constant.
2. The excess of glycerol push the equilibrium forward, so the reaction can be expressed as irreversible reaction.

Based on those assumption the equation which then become as shown at eq. (3)

$$-r_a = -\frac{dC_A}{dt} = k_1 C_A^a \quad (3)$$

Where $k = k_1 C_B^b \approx \text{Constant}$

Integrating the equation will result in an equation that show the interaction of the concentration of lauric acid with the reaction time, which then by using the experimental result, the kinetic constant can be determined.

To do the thermodynamics analysis, the arrhenius equation can be used to explain the relationship between reaction rate and temperature. The arrhenius equation expressed in eq. (4) usually it's modified by natural logarithm to become the eq. (5) so that from the plot of reaction rate constant obtained from the the calculation from experimental result we can get the value of the arrhenius constant and energy activation.

$$k = A e^{\frac{-E_a}{RT}} \quad (4)$$

$$\ln k = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln A \quad (5)$$

Where:

k = reaction rate constant

R = ideal gas constant

A = arrhenius constant

E_a = activation energy

T = absolut temperature (K)

III. RESULTS

The conversion profile of lauric acid from the result of the experiment is displayed in Fig.1. The increase of reaction temperature significantly increasing the conversion of lauric acid. The conversion at 110°C is 28%, while at 130°C is 50%, and at 150 and 170°C it is 67% and 84%, for 5 hours of reaction time. These results suggested the high catalyzing potential of the mesoporous catalyst in the reaction. This figure also suggested that in increasing the temperature, enhancing the interaction between the reactant molecule and the active sites of the catalyst[15]. The presence of acid sites in the zeolite-Y catalyst also helped in increasing the conversion.

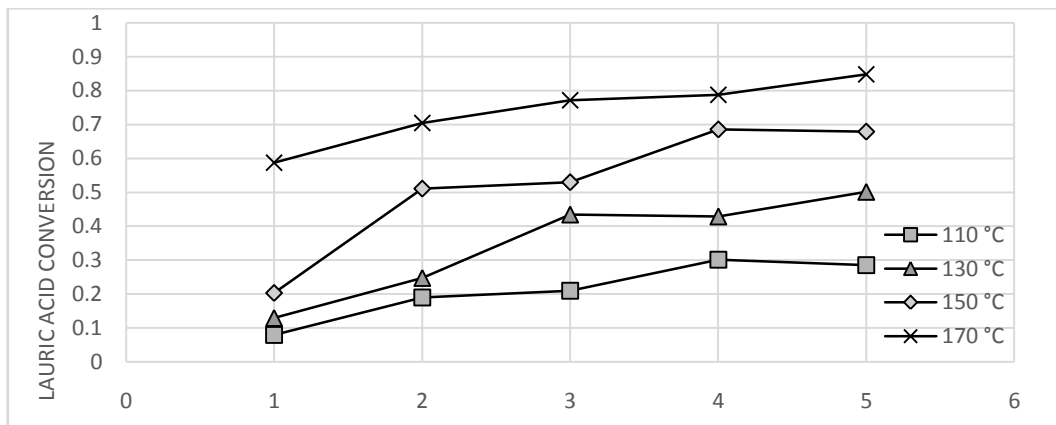
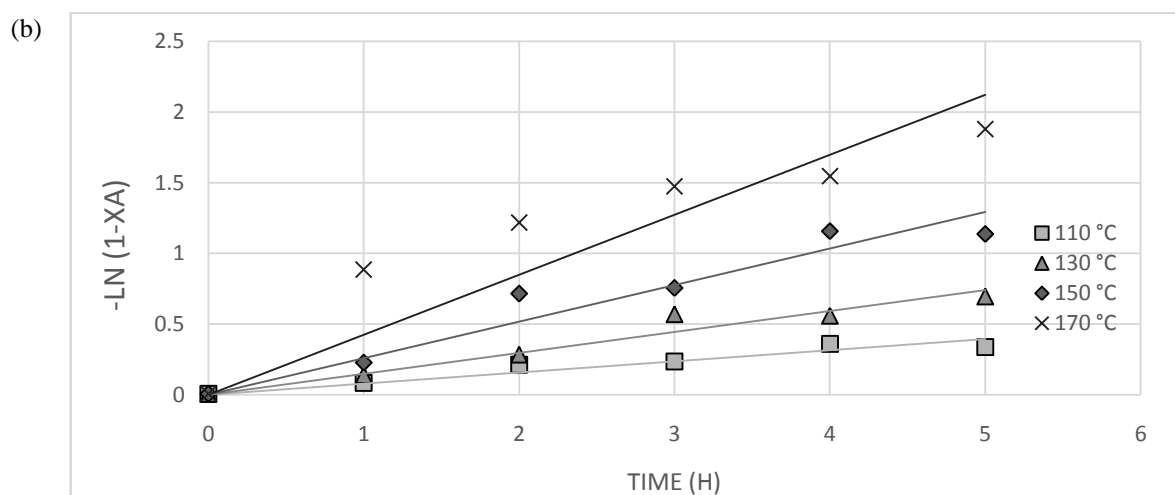
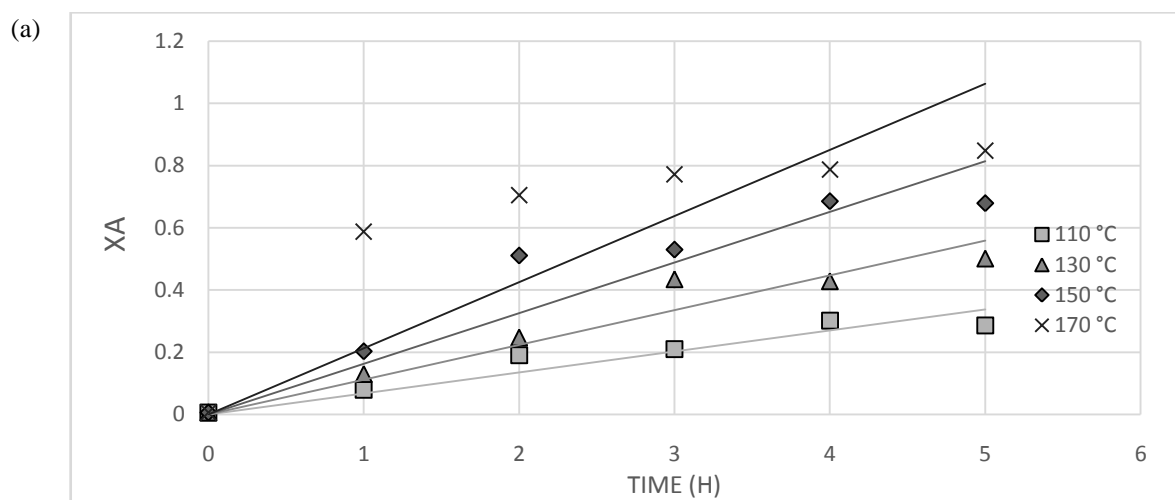


Figure 1. Conversion profile of lauric acid in every hour for 5 h of the synthesis of Glycerol monolaurate at temperature 110, 130, 150, and 170°C.



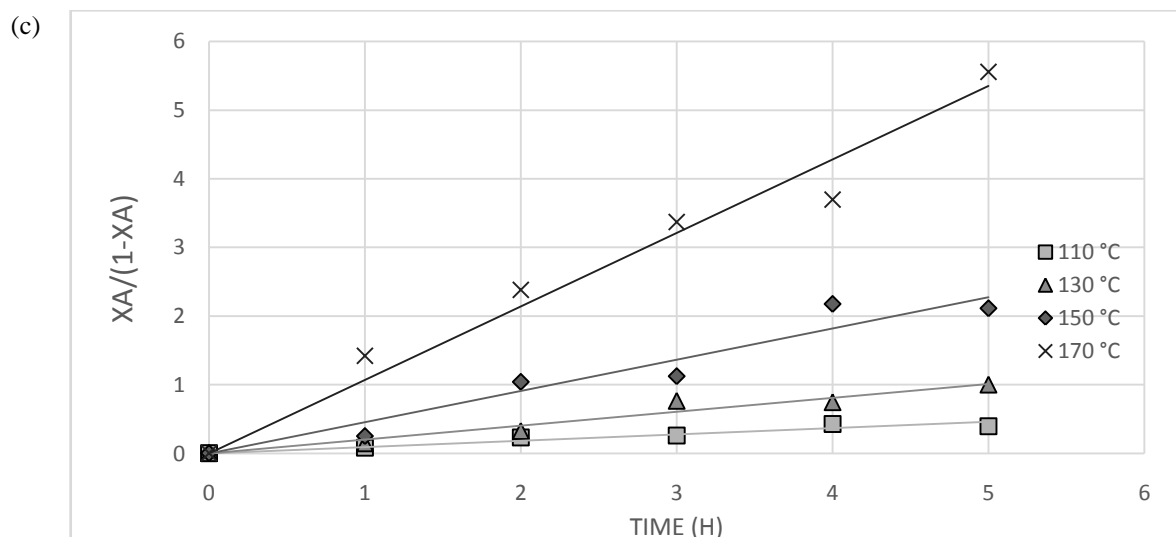


Figure 2. Linear plot of (a) pseudo-zeroth order; (b) pseudo-first order; and (c) pseudo-second order kinetic model for lauric acid conversion.

The reaction order for the consumption of lauric acid it's evaluated by modified the model expressed at the eq. (3). The reaction order proposed are pseudo-zeroth order, pseudo-first order, and pseudo-second order. The reaction rate constant for the proposed reaction order are computed as follows:

1. For pseudo-zeroth order the lauric acid conversion rate constant (k) was obtained from the slope of the plot of X_A versus reaction time, in accordance to eq. (6)
2. As for pseudo-first order the lauric acid conversion rate constant (k) was determined using the slope of the plot of $\ln(1-X_A)$ versus reaction time, in accordance to eq. (7)
3. While to calculate the lauric acid conversion rate constant (k) for pseudo-second order, it's using the slope of the plot of $X_A/(1-X_A)$ versus reaction time, in accordance to eq. (8)

$$X_A C_{A0} = k t \quad (6)$$

$$\ln(1 - X_A) = -k t \quad (7)$$

$$X_A / (1 - X_A) = C_{A0} k t \quad (8)$$

The correlation coefficients (R^2) for all pseudo kinetic models proposed can be examined at Table 1. The pseudo-second order at different reaction temperature had the highest average coefficients, it indicated that pseudo second order was a good fit for all temperature condition. The linear plot at Fig.2 also showed that for pseudo-zeroth order, at the lower temperature the data had a good fit with the linear model, however at higher temperature the data deviated sharply from the linear model. The pseudo-first order also had the same tendency that with increased temperature, the data also more deviated from the linear model, which can be examined at fig. 2(b). Therefore from the data, it's supported the selection of the pseudo-second order for the conversion of lauric acid to glycerol monolaurate with zeolite-Y catalyst as the kinetic model. The reaction rate constant of the reaction was calculated at different reaction temperature (Table 1). The value of reaction rate constant, k increase with temperature. This indicated that the conversion of lauric acid at higher temperature, increase more quickly compared to the reaction at lower temperature.

Table 1: Kinetics parameter of lauric acid catalytic conversion using zeolite-Y

Temp. (°C)	Pseudo-zeroth Order R^2	Pseudo-first Order R^2	Pseudo-second Order R^2	Pseudo-second Order $K (h^{-1})$
110	0.9732	0.9767	0.9781	0.0041
130	0.9794	0.9843	0.9832	0.0090
150	0.9624	0.9787	0.9769	0.0202
170	0.8967	0.9547	0.9907	0.0476

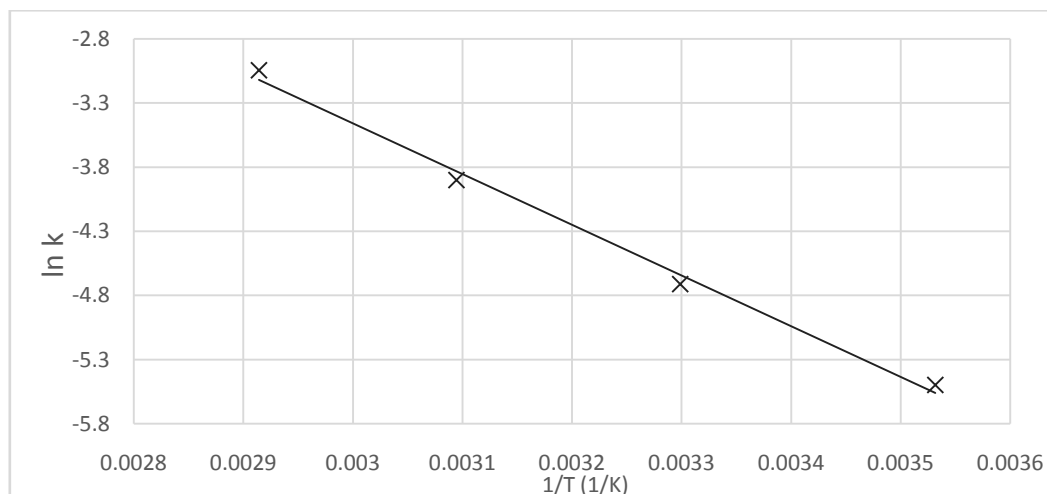


Figure 3. Arrhenius plot of ln k vs 1/T for pseudo-second order reaction.

The Arrhenius plot in Fig. 3 is used to determine the activation energy (E_a) and pre-exponential factor (A). The slope of the plot is used to calculate E_a , while the intercept of the Arrhenius plot is used to calculate A in respect to eq. (5). The constant values determined from the Arrhenius plot are listed in Table 2. The value of the activation energy is comparable enough with another work involving solid catalyst, where the activation energy for this work is 32.883 kJ/mol, while for the previous work is 42 kJ/mol [15]. With the Arrhenius parameters obtained, the reaction rate model of glycerol esterification using lauric acid with zeolite-Y catalyst expressed by the rate of conversion of lauric acid was proposed as given in eq. (9).

$$-r_a = 4474.3 \exp\left(\frac{-32.883}{RT}\right) C_A^2 \text{ mol/(L h)} \quad (9)$$

Table 2: Parameter obtained from the Arrhenius plot of lauric acid catalytic conversion using zeolite-Y

Reaction condition	Pseudo-second Order		
	R^2	E_a (kJ/mol)	A (h^{-1})
110-170°C Zeolite-Y	0.9732	32.883	4474.3

IV. DISCUSSION AND CONCLUSION

The kinetic and thermodynamic parameter for the reaction of monolaurin synthesis by esterification of glycerol with lauric acid using molar ratio (glycerol : lauric acid) 7.5:1 with zeolite-Y catalyst at temperature 110, 130, 150, 170°C and 5 hours reaction time in stirred batch reactor was successfully examined. The increase of temperature, increasing the conversion of lauric acid. For the reaction with excess glycerol, pseudo-second order reaction model is the most fitted model to represent the kinetic model. The determined rate constant that increased with the increase in temperature indicated that the reaction was more favorable with the increase in temperature. Using Arrhenius equation and from the linear plot from the experimental data the activation energy for the catalytic lauric acid conversion with glycerol using zeolite-Y was found to be 32.883 kJ/mol. Kinetic model of the rate of reaction can be expressed as $-r_a = 4474.3 \exp\left(\frac{-32.883}{RT}\right) C_A^2 \text{ mol/(L h)}$ which could be used to predict the change of the concentration of lauric acid in the reaction.

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