Study of glycerolysis of lactic acid

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Abstract. Increasing production of a biodiesel industry, will also increase the by-product of the industry, glycerol. Further processes were investigated to get an added value of the byproduct. Glycerol esters of lactic acid and in particulars glycerol monolactate is one of the more value of derivative material from glycerol, which is known as safe, nontoxic and biodegradable emulsifier in food, cosmetics, and pharmaceutical industries. This research aims to study the effect of temperature and reactant ratio to the rate of catalyst free glycerolysis reaction of lactic acid. Experiments were conducted in a three-necked flask equipped with a thermometer, a stirrer and a reflux condenser. The reactions were conducted for 4 hours at 100°C – 140°C while the mole ratios of glycerol to lactic acid were varied 1:1 to 5:1. The conversion of lactic acid to ester increased by increasing the reaction temperature. The results also showed that more glycerol ratio to lactic acid, the higher conversion of the acid was obtained. As of the variables studied, maximum conversion was 86.28% at mole ratio of reactants was 5:1, 140°C within 4 hours. Irreversible homogeneous second order reaction model was suitable with the experimental data.

Keywords: Lactic acid, glycerol, esterification

1. Introduction
The development of biodiesel industry led to an increase in glycerol production. So that, many researches were done to study the process to make monoglyceride, a derivative of the by-product (glycerol) which widely used as emulsifier and has higher economic value [1]. Glycerolysis of various oils and fats or esterification of glycerol with various acids are the methods for preparing monoglycerides. Commercially, glycerolysis of oils and fats involve either high reaction temperature with or without catalysts. Various types of homogenous and heterogenous catalysts are reported [2].

Esterification reactions of glycerol with acids are used an acid catalyst to accelerate the reaction. High esterification reaction temperatures are used to shift the equilibrium forward towards glycerol esters. Due to their abilities to form stable emulsions, monoglycerides more important than diglycerides or triglycerides. Thus, many efforts were directed towards increasing the yields of monoglycerides, such as applying molar ratio glycerol/acid higher than equimolar [2]. While high pressure in carrying out glycerolysis is to aid in the attainment of homogeneity and thus yields or conversions improved. The use of solvents enables a much higher conversion. This is due to the immiscibility of glycerol in fat like phases was overcome by carrying out the reaction in a solvent medium. While solvents offer high yields at relatively low temperature, but disadvantages in their handling, toxicity, noxious odors, etc. and the need to remove them completely from products explains the very limited efforts directed towards the synthesis in solvents [3].

All the commercial methods for the synthesis of monoglycerides can be classified in two categories. The first, nonsolvent method requires high temperatures and generally results in a mixture of mono, di and triglycerides with low selectivity towards monoglycerides formation. Those prepared with heterogenous catalyst such as molecular sieves or in the presence of alkaline or acidic catalyst which requires neutralization step. Those have questionable applicability if the product is intended for food use. The second method involving solvents which offer better selectivity have also major disadvantage in that the solvents employed are not food grade. Since monoglycerides are important emulsifiers used in food, pharmaceutical, and cosmetic industries, hence there is need for an alternative catalyst free process, but at the same time under homogenous environment, which gives high yields of monoglyceride [4]. In the preparation of a monoglyceride by reacting a fatty acid and...
glycerol, Thengumpillil et al. [4] improved the process by using a food grade polar solvent that is acceptable to the food industry and that also functions as a suitable solvent for glycerol and avoiding the use of catalysts. The food grade polar solvent used is selected from methyl lactate and lactic acid. In this research, lactic acid is used as a reactant which has the characteristic of being soluble in glycerol, so no additional solvent is needed to increase its solubility in the mixture.

2. Materials and experimental method

2.1 Materials
Technical grade of glycerol as well as lactic acid were used as raw materials. The density of glycerol and lactic acid were 1.25 g mL⁻¹ and 1.19 g mL⁻¹ respectively. Volumetric method was used to analyze the acid content in the mixture.

2.2 Experimental method
Seventy five grams of glycerol in an Erlenmeyer flask was properly weighed, then heated up to 100°C and maintained temperature constant. At the same time certain amount of lactic acid (mole ratio lactic acid: glycerol = 1:3) was poured into a 250 mL three-neck flask and heated up to 100°C. Then hot glycerol was poured into the flask and mixed with hot lactic acid. The reaction is carried out at constant temperature 100°C for 240 minutes. Samples were taken every 30 minutes for acid content analysis by volumetric method prior to calculate the acid conversion. Experiments were continued by carrying out at different reaction temperatures and different reactant ratio to have kinetics model.

3. Results and discussions

3.1 Effect of reaction temperature
Reaction temperature is an important parameter in esterification. Theoretically, reaction temperature can influence the reaction rate as well as the equilibrium conversion. But as shown in Fig. 3, at an initial glycerol: lactic acid molar ratio of 3:1, temperature range from 100 to 140°C, the equilibrium conversion of lactic acid has not yet reached.

![Figure 1](image_url)

*Figure 1. Conversion of lactic acid at various reaction temperatures*

Three irreversible homogeneous reaction models were tested: first order with respect to lactic acid concentration, first order with respect to lactic acid and glycerol concentrations respectively, and second order with respect to lactic acid concentration. Comparing the three models, the best model was the second order reaction:

\[
(-r_A) = kC_A^2
\]

(1)
This assumption based on its highest average coefficient of determinations, $R^2 = 0.9246$ of the linear regression of:

$$\frac{x_a}{1-x_a} = kC_{ao} t + c \quad (2)$$

The evaluated rate constant $k$ for various reaction temperatures are presented in Table 2 and the graph related the $\ln k$ versus $T^{-1}$ is presented in Figure 2.

### Table 2. Second order irreversible reaction at various reaction temperature

| Reaction temperature, K | Rate constant $k$, mL mole$^{-1}$h$^{-1}$ |
|-------------------------|---------------------------------------------|
| 373                     | 158.2999                                   |
| 383                     | 185.8382                                   |
| 393                     | 218.1551                                   |
| 403                     | 239.5583                                   |
| 413                     | 436.0306                                   |

**Figure 2.** Relation of $\ln k$ versus $T^{-1}$

The effect of reaction temperature on the rate constant is presented by equation

$$k = 1649204.71 e^{-3482.562 T^{-1}} \quad (3)$$

### 3.2 Effect of reactants molar ratio

Figure 3 shows the effect of reactant molar ratio on the esterification at 120°C. As shown, at the same molar ratio of glycerol to lactic acid, allows lactic acid reacts more, so that the conversion of lactic acid increases. The maximum conversion of lactic acid at temperature of 120°C within 4 hours reaction was 52.48% when using reactant ratio of 1:1. The higher the ratio of glycerol to lactic acid, the higher the conversion is.

**Figure 3.** Conversion of lactic acid at various reactant ratios

The increasing content of glycerol, simultaneously improved the conversion as well as the reaction rate. By assuming the reaction rate to be second order with respect to acid concentration, equation (1) can be modified as

$$\frac{dx_a}{dt} = kC_{ao}(1-X_A)^2 \quad (4)$$
Then the rate constant $k$ can be evaluated using integral method and the results are presented in table 2. Based on experimental data that higher reactants ratio cause higher conversion, then the effect of molar reactant ratio on reaction rate might be expressed through factor frequency of Arrhenius equation:

$$ k = A \exp \left\{ -\frac{E}{RT} \right\} $$  \hspace{1cm} (5)

Due to the higher reactant ratio causes higher frequency of collision between reactant molecules, so the relation of reactant molar ratio with the factor of frequency is assumed by the expression

$$ A = aM^b $$ \hspace{1cm} (6)

The rate constant equation (5) at certain reaction temperature becomes

$$ k = aM^b\exp \left\{ -\frac{E}{RT} \right\} = a\exp \left\{ -\frac{E}{RT} \right\} M^b $$ \hspace{1cm} (7)

By equation (7), the relation of reactant ratio $M$ to rate constant can be expressed by equation (8) and figure 4

$$ k = cM^b = 32.7925M^{1.5264} $$ \hspace{1cm} (8)

Table 2. Rate constant at 120°C for various reactant ratio

| M (molar ratio glycerol to fatty acid) | Rate constant $k$, mL•mol$^{-1}$•h$^{-1}$ |
|--------------------------------------|------------------------------------------|
| 1:1                                  | 33.43                                    |
| 2:1                                  | 85.27                                    |
| 3:1                                  | 201.41                                   |
| 4:1                                  | 262.65                                   |
| 5:1                                  | 375.10                                   |

Figure 4. Relation of ln $k$ versus ln $M$

Conclusions
The work carried out concerned catalyst free glycerolysis process of lactic acid in the influence of various parameters, such as temperature and reactant molar ratio. The conversion of lactic acid to monolactic ester increased by increasing the reaction temperature. The results also showed that more glycerol ratio to lactate acid, the higher conversion of the acid was obtained. Within the variables were studied, maximum conversion was 86.28% at mole ratio of reactants was 5:1, 140°C within 4 hours. The reaction was considered to be homogeneous second-order with respect to the concentration of lactic acid.

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