Performance of Indion ion exchange resin as solid catalyst for the esterification of oleic acid with glycerol

by Arif Hidayat

Performance of Indion Ion Exchange Resin as Solid Catalyst for The Esterification of Oleic Acid with Glycerol

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Abstract. *Glycerol Monooleate (GMO) is an emollient and emulsifier that is widely used in cosmetics and food products. GMOs are produced by esterification of oleic acid with glycerol. In this study, Indion Ion Exchange Resins were used to develop low-cost and efficient catalysts for esterification of oleic acid with glycerol. The performance of catalyst was studied under various operating conditions (reaction temperature, the molar ratio of oleic acid to glycerol, and catalyst loading). Effect of the catalyst mass ratio on acid (1-5%), the molar ratio of oleic acid/glycerol (1: 1-1: 8), and the reaction temperature (120-170oC) on acid conversion were studied to obtain the optimal reaction conditions. The optimal condition was obtained on 5%wt of catalyst loading, the molar ratio of oleic acid/glycerol 1:3 at 170oC for 180 minutes. Under the optimal conditions, the prepared catalyst provides an acid conversion of 78%.*

INTRODUCTION

According to the blueprint of national energy management 2005-2025 explained that starting in 2011 the Indonesian government will establish biodiesel plant capacity of 30,000 to 100,000 tons/year. This means that the production glycerol will reach 15,000 tons/year. The utilization of glycerol as an abundant by-product should be considered to avoid undesirable effects. Glycerol from biodiesel plants can be utilized to produce high-value derivative products. Research on the utilization of glycerol needs to be done to provide alternative solutions for handling biodiesel by-products. One of feasible possibility is converted glycerol into an emulsifier i.e. Glycerol Monooleate (GMO). In addition, the issue of non-halal emulsifiers that developed recently is quite worrying among the people of Indonesia who are predominantly Muslim. This is because GMO emulsifiers are still being imported which is the raw material for its manufacture using oleic acid derived from animal fat. The commonly used animal fat is lard. Therefore, it is necessary to substitute the source of oleic acid which can be ascertained its halal. GMOs are used as emollient and emulsifier materials in cosmetics and food products.

Parhusip et al. (2012) performed an experiment by reacting oleic acid with glycerol using NaOH as the catalyst. The study was conducted by varying the number of catalysts and reaction times [1]. The results showed that the best concentration of glycerol monooleate was 98% obtained in the addition of 0.1 gram of catalyst and reaction time of 70 minutes with a ratio of glycerol with oleic acid 1: 3. Wee et al. (2013) conducted an experiment over several catalysts [2]. The ratio of oleic acid and glycerol used is 1: 1 at a temperature of 120 ^{o}C. It was found that reaction between glycerol and oleic acid without catalyst with a reaction time of 8 hours gave an oleic acid conversion of 45% with selectivity to GMO of 63%. Reaction over 5% HPW / Cu3 (BTC) 2 catalyst for 3 hours obtained oleic acid conversion of 31% with selectivity to GMO was 75% while using 2% Y-zeolite catalyst resulted in 32% oleic acid conversion with 77% selectivity to GMO.

Another study was conducted by Setiadi et al. (2016) by reacting oleic acid and glycerol using natural zeolite catalysts [3]. The research was carried out by varying the reaction temperature from 180 – 220 ^{o}C, the ratio of glycerol

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with oleic acid from 1: 1 to 1: 8, and stirring variations were carried out from 400 – 1500 rpm. The results of the experiments showed that the best results were obtained by reacting glycerol and oleic acid with a ratio of 1: 3 at a temperature of 220°C with a stirring speed of 800 rpm. Using that condition, it achieved oleic acid conversion of 87.2% with selectivity to GMOs of 55.47%.

Another way to produce GMO is by reacting methyl oleate with glycerol using MgO catalysts. A study conducted by Ferretti et al. (2009) shows that by reacting methyl oleate with glycerol with a ratio of more than 2 at the temperature between 220 – 300°C, yield GMO in a range of 73 - 77% [4]. These results are higher than using homogeneous catalysts, which only obtained GMO yields of 40 - 60%.

This study utilizes glycerol, a by-product of biodiesel, and oleic acid from vegetable oils to produce GMO as emulsifiers. Vegetable oil is used as a source of oleic acid in order that the emulsifiers produced are halal products that can be consumed by the Muslim community. In addition, the development of biodiesel by-products can also increase the economic value by producing high-value glycerol derivative products. For the benefit of the reaction, heterogeneous catalyst from ion exchange resin was applied. The use of catalysts from ion exchange resin due to its low cost and highly efficient catalysts.

In this research, the esterification of oleic acid with glycerol over Indion ion exchange resin as the catalyst was studied. The performance of catalyst was studied under various operating conditions (reaction temperature, the molar ratio of oleic acid to glycerol, and catalyst loading).

MATERIAL AND METHODS

Materials

Materials that were used in the experiments are: oleic acid (Bratachem, Yogyakarta), glycerol 95% (Bratachem, Yogyakarta), sulfuric acid 98% (Merck) was 98%, ethanol p.a. (Merck), KOH. Indion ion exhange resin at particle size range of 0.5 – 0.65 mm in the proton form was used as the cation-exchange resin catalyst.

Methods

Preparation of Material

The indion ion exchange resin was stirred in sulfuric acid solution at room temperature for 1 hour. The Indion ion exchange resin sample was washed with distilled water and then filtered until the sulfate ion was no longer detected in washing water. Furthermore, The Indion ion exchange catalyst was dried at 80°C for 3 hours to remove water.

Procedures of GMO Synthesis

Oleic acid and catalyst (Indion Ion exchange resins) were poured into the multi-neck round bottom flask which was then placed in the oil bath at 150°C. Stirring was carried out to complete the acid adsorption on the surface of the catalyst. Glycerol which heated to 150°C in another flask was then added to the solution (glycerol and catalyst) and stirring was continued for 3 hours until the yellow solution is obtained.

The reaction temperature, the molar ratio of oleic acid/glycerol, and the catalyst loading were used to determine the performance of the catalyst. Effect of the catalyst mass ratio on acid (1 - 5%), the molar ratio of oleic acid/glycerol (1: 1 - 1: 8), and reaction temperature (120 - 170°C) on the conversion of oleic acid were studied to obtain optimal reaction conditions [1,2].

Samples were analyzed by titration procedures to evaluate free acid residues. Weighted samples were dissolved in neutralized ethanol and few drops of phenolphthalein were added to the solution as an indicator. Then the sample was heated for 15 minutes to dissolve the free acid and titrated with a 0.05 mol/L NaOH solution until the color changes to pink. Acid values were determined using Equation (1).

$$AV = \frac{40 \times M \times V}{W} \quad (1)$$

where AV is the acid value of the sample (mg NaOH/g), V is amount of sodium hydroxide used for titration of the sample (mL), M is molarity of NaOH used for titration (mol/L), W is the weight of the sample (g), and 40 is the molecular weight of NaOH. Equation (2) were used to calculate the conversion of free acid.

$$X = \left(1 - \frac{AV_2}{AV_1}\right) \times 100 \quad (2)$$

Where X is the conversion of acid, AV_1 is the initial acid value of the sample and AV_2 is the acid value of sample after reaction [5].

RESULTS AND DISCUSSION

Effect of temperature on acid conversion

The production of GMO is influenced by various factors depending on the reaction conditions used. Experiments were carried out to investigate the effect of several reaction parameters i.e. reaction temperature, catalyst loading, and reactant molar ratio, on acid conversion. The effect of temperature was studied by varying the reaction temperature from 120 to 170°C by applying the molar ratio of oleic acid to 1: 3 glycerol and the amount of catalyst of 3%wt of acid. Figure 1 shows the effect of temperature on acid conversion. It displays that acid conversion increased from 44% to 78% when the temperature increased from 120 to 170°C. Increased acid conversion occurs because of the increase in the rate of reaction with the increasing temperature. An increase in temperature also affects acid conversion because of some increase in the limit of mass transfer between reactants and catalysts. When the reaction temperature increases, the kinetic energy of all reactant molecules will increase which will accelerate the mass transfer rate between the oleic acid-glycerol-catalyst phase [5].

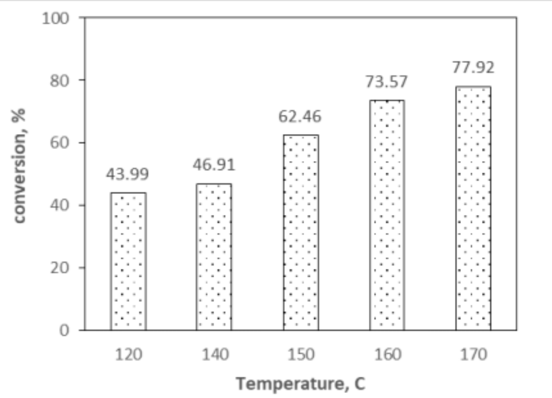

FIGURE 1. Effect of temperature on acid conversion

There is a possibility of an increase in conversion at temperatures higher than 170°C. But the experiments were carried out at a maximum temperature of 170°C considering the durability of the catalyst used in this study. Indion ion exchange resin best performance is at temperature up to 160°C. Above 160°C, the performance of indion ion exchange resin will decrease (burnt) and the reusability of the heterogeneous catalyst cannot be achieved.

Effect of catalyst loading on acid conversion

To investigate the effect of catalyst loading, several variations in the amount of catalyst were carried out by setting a temperature of 150°C and molar ratio of oleic acid/glycerol 1:3. Figure 2 shows the effect of the catalyst loading on acid conversion. The highest conversion of 65.68% was obtained by loading a catalyst of 5%wt of acid. The acid conversion will increase with increasing of the catalyst loading.

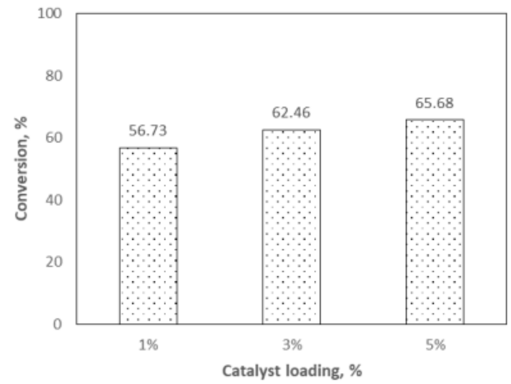

FIGURE 2. Effect of catalyst loading on acid conversion

Effect of oleic acid to glycerol molar ratio on acid conversion

One of the important factors affecting acid conversion is the ratio of reactant. Theoretically, GMO production requires one mole of oleic acid per mole glycerol. The use of excess glycerol is designed in order to increase the rate of esterification reactions catalyzed by heterogeneous catalysts and to limit the production of glycerol dioleate and glycerol trioleate. In this study, the molar ratio of oleic acid to glycerol varied from 1: 1 to 1: 8. Figure 3 describes the effect of the molar ratio of oleic acid to glycerol in acid conversion at 170°C within 3 hours of reaction and catalyst loading 3%wt of acid. It can be seen from Figure 3, when the reactant ratio increased from 1: 1 to 1: 8, acid conversion increased from 45% to 63%.

The maximum conversion was obtained at the reactant ratio of 1: 8. However, the addition of glycerol after the molar ratio of 1: 3 gives no significant improvement in acid conversion. Esterification is a reversible reaction. Excessive use of glycerol can shift the equilibrium reaction to the reaction product. But on the other hand, this will reduce the concentration of oleic acid so that the reaction rate decreases. Therefore, the optimal molar ratio of oleic acid to glycerol is 1: 3.

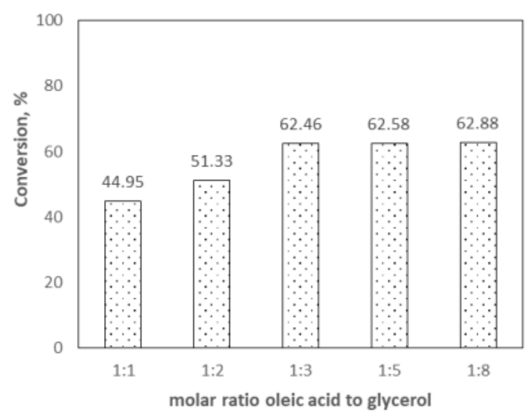

FIGURE 3. Effect of oleic acid to glycerol molar ratio on acid conversion

CONCLUSIONS

The Indion ion exchange catalyst was studied for esterification of oleic acid with glycerol. Effect of catalyst loading (1-5%), the molar ratio of oleic acid to glycerol (1: 1–1: 8), and reaction temperature (120–170°C) on acid conversion studied for optimizing the reaction conditions of GMO production. The results showed that the optimum condition was oleic acid for glycerol 3: 1 molar ratio, catalyst amount 5% by weight of oleic acid, and the reaction temperature of 170oC.

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