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Kinetic Study on Esterification of Oleic Acid with Ultrasound Assisted

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Abstract

As the limitation of nonrenewable energy resourcesand for covering energy demand in future, it is important to search and apply the renewable energy resources which is effective, efficient and sustainable. The literatures of kinetic reaction of biodiesel from oleic acid arerare and most literatures used conventional method. The objective of this research isto examine kinetic reaction of oleic acid esterification which is assisted by ultrasonic wave. Variables that used in this research are catalyst concentration and reaction temperature. Oleic acid and methanol are reacted inside three neck flask and assisted by ultrasonic wave. Gas Chromatography is used to identify contain of FAMEin biodiesel. The highestconversion for the temperature variable is 86.67% at 70 ^{o}C, and the highest conversion for the catalyst variable is 87% at 1.4% wt. Model of kinetic reaction is reversible second order reaction with R^2 0.986 for temperature variable and 0.975 for catalyst variable.

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*Keywords:*energy; biodiesel; oleic acid; ultrasonic wave; reaction kinetic

1. Introduction

Non-renewable energy such as fossil fuel is used to fulfil energy demand. With the limitation of non-renewable energy resources, to fulfil energy demand in future, it is important to search and apply renewableenergy which is efficient, effective, sustainable and environmental-friendly. One of that solution is biodiesel. Biodiesel is one of the potential alternative fuel to replace diesel oil because it contains mono-alkyl esters of long chain fatty acids that is derived from vegetable oil or animal fat [1]. Biodiesel can be produced by triglycerides with based catalyst or also

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can be produced by free fatty acid by using acid catalyst [2].

Biodiesel production processes that have been researched were homogenous catalyst trans-esterification and esterification [3], heterogeneous base-catalyst [4], enzymatic trans-esterification [5], non-catalyst supercritical trans-esterification[6], microwave-assisted trans-esterification [7], and ultrasound-assisted [8]. Base-catalyst trans-esterification has deficiencies in catalyst separation so that need large energy demand. Saponification reaction also occur in base-catalyst process if there is no pretreatment of the raw material. Acid-catalyst trans-esterification has low reaction rate. Enzymatic trans-esterification has high cost. Non-catalyst supercritical trans-esterification has difficult condition and high cost. Yield and reaction time of microwave-assisted trans-esterification are lower than ultrasound assisted production. Ultrasound-assisted production is an efficient method and haveshort reaction time than conventional method. With this method, high conversion (92%) is obtained in 70 second whereas for 91% conversion needs 1 hour reaction time on conventional method [9].

Generally, biodiesel production needs reactor as a place to convert materials to the biodiesel and for biodiesel production which is assisted by ultrasound. To make and design reactor, it is important to know the kinetic model of reaction, and after that volume of the reactor can be calculated. Research about reaction kinetic of esterification oleic acid and methanol has been done by Cardoso [10]. He used SnCl and H_2SO_4 as a catalyst in a batch reactor for 2 hours reaction time, and the yield was 90 %. Reaction model that he got was first order reaction. Aulia [11]studied about trans-esterification of cooking oil with KOH as catalyst, obtained reaction model which fit with second order reversible reaction, and the yield was 89%. The objectives of this research are to know the type of the reaction is it reversible or irreversible, is first order or second order, and also made the equation of kinetic reaction model from acid-catalyst esterification reaction of oleic acid and methanol assisted by ultrasound.

2. Materials and Methods

First,three-neck flaskarranged withcondenser andput inan ultrasoniccleaner. The research used oleic acid as raw material for biodiesel production and reacted with methanol. Before oleic acid and methanol were reacted, 1.2% wt. H_2SO_4 was added to oleic acid, and both of raw materials were heated according to variable temperature on separated place. After oleic acid and methanol reach the temperature variable, both of them put into three neck flask for esterification process and then assisted by ultrasound. Reaction time began after materials were pouredintothree-neck flaskandevery 9 minutes 10mlsamples were takenforanalysis ofresidualfattyacid and stopped after 45 minutes. The temperature which gave highest conversion from experiment of temperature variable was used as fix temperature for catalyst loading variable.

GasChromatography was used to analyze FAME content in biodiesel. Theresidualfattyacid that would be usedforcalculatingk value was calculated by titrimetric analysis. Sample was taken 10 ml and thenaddedneutralethanol and after that, the mixtures were cooledat room temperaturein order tostopthe reaction. Add3drops ofindicatorPPandthe solutionswere titratedbyKOHforFFA contentanalysis.Normality of oleic acid calculated by:

$$V_{Oleic} \times N_{Oleic} = V_{KOH} \times N_{KOH} \tag{1}$$

Normality of residual oleic acid calculated by this equation:

$$V_{Sample} \times N_{Sample} = V_{KOH} \times N_{KOH} \tag{2}$$

Methyl ester conversion calculated by:

$$X = \frac{N_{Oleic} - N_{Sample}}{N_{Oleic}} \tag{3}$$

FAME was calculated from oleic acid because FAME was formed from oleic acid and methanol. With assumption