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Oil Esterification Using High-Free Fatty Acid Acid Using Hydrodynamic Cavitation Process

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Abstract: *In thisstudy,the fattyacid methy lester was synthesized through the esterification stage. Esterification is the reaction between used cooking oil and methanol(CH_3OH) using sulfuric acid (h_2SO_4) as a catalyst to produce fatty acid methyl esters (FAME) and water. cooking oil waste used must have free fatty acid levels above > 2% so that the esterification process can be carried out. This research is focused on reducing the optimal levels of fatty acid methyl esters between the hydrodynamic cavitation process and the stirring process. a decrease in methyl ester fatty acids of 0.72% was obtained under reaction conditions (temperature 50^oC, 120 minutes, waste cooking oil /methanol ratio 1:10, catalyst amount 1% -w/w with process hydrodynamic cavitation). esterified methyl ester fatty acids can continue at the stage of the transesteri fication process for the manufacture of biodiesel.*

Keywords:*, free fatty acids , waste cooking oil , esterification, hydrodynamic cavitation*

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I. Introduction

Generally, the processes of biodiesel producing from vegetable oils are going through the stages of esterification and transesterification of oil so that it becomes biodiesel. Indonesia has many types of oil-producing plants that can be used as raw material for biodiesel, but some vegetable oils have poor quality with high free fatty acids (FFA) level. One type of oil is waste cooking oil [1].

Waste Cooking oil contains a lot of FFA which is produced from the oxidation and hydrolysis reaction during the frying process. The presence of free fatty acids in waste cooking oil can cause side reactions namely lathering reactions, which if in the process of making biodiesel directly using the esterification reaction. The greater the level of free fatty acids in oil, the worse the quality of oil will be. An esterification process with an acid catalyst is needed if vegetable oil contains FFA above 5%. If the FFA oil content is above of 5%, the esterification process is carried out so that it becomes a fatty acid methyl ester [2].

The esterification results can be affected by several factors, including: water content, free fatty acids, molar ratio of alcohol to raw materials, reaction temperature, amount and type of catalyst, reaction time, and the type of alcohol used [3]. The catalyst used in the esterification reaction is sulfuric acid (H_2SO_4) because it is a strong acid where proton H^+ can be substituted and binds strongly with oxygen atoms in carbon carbonyl which have a large electronegativity value. The selection of methanol in the esterification process is based on its reactivity. This is because methanol is an alcohol compound with the shortest carbon chain. In which, the shorter carbon chain the alcohol used the higher the reactivity [4].

A number of technologies have been developed to produce biodiesel through an esterification reaction efficiently. The technology is using hydrodynamic cavitation techniques and ultrasonic waves[6]. Hydrodynamic cavitation is a phenomenon of the formation, growth and breakdown of micro bubbles in liquids that occur due to pressure variations in the flowing liquid resulting in changes to the geometry of the flowing system during the esterification process [7]. Hydrodynamic cavitation has several advantages, which is the most inexpensive and efficient method of using energy for cavitation formation, the equipment used in the formation of hydrodynamic cavitation is also simple [8].

The purpose of this study is to study the effect of the methanol mole ratio to cooking oil waste, temperature and processing time to decrease free fatty acid levels, study the kinetics of the esterification process reaction using hydrodynamic cavitation and compare the performance of the hydrodynamic cavitation esterification process with the stirring process.

II. Methodology

2.1. Equipments and Chemicals

The raw material was waste cooking oil (WCO) from Banda Aceh. The chemical compound used were methanol 96%(Merck Indonesia), Potassium hydroxide (KOH), Sodium hydroxide (NaOH), sulfuric acid 98%

(H_2SO_4) Phenolphthaleinreagent 99% (Merck Indonesia), ethanol 96% (Merck Indonesia). Meanwhile, the equipments used were hot plate (Yamato MH-800), cavitation pump (Ossel 70 psi), Three neck flask 500 mL (Duran), reflux condensor glassed, magnetic stirrer, thermometer 150^oC, beaker glass 500 mL (pyrex), erlenmeyer 250 mL (pyrex), stopwatches, burette 50 ml (pyrex).

2.2. Fatty acid methyl esters (FAME) synthesis

In this study, the esterification stage was carried out on free fatty acids (FFA) of waste cooking oil. The first esterification between waste cooking oil (WCO) and methanol became fatty acid methyl ester (FAME).

2.2.1. The First esterification (syntesis of FAME).

The first esterification is the reaction between waste cooking oil (WCO) and methanol to produce fatty acid methyl esters (FAME) as presented at equation (1).

$$\underset{\text{Fatty acids (triglycerides)}}{CH_2COOR\text{-}CH_2COOR'\text{-}CH_2COOR} + \underset{\text{methanol}}{CH_3OH} \overset{H_2SO_4}{\underset{\text{Catalyst}}{\leftrightarrow}} \underset{\text{FAME}}{R\text{-}COO\text{-}CH_3} + \underset{\text{Water}}{H_2O} \qquad (1)$$

In this study, free fatty acids (FFA) of WCO were 4.33% esterified but if the FFA of WCO was>2%, it had to be esterified before transesterification [13]. The FAME synthesis was reacted in a 500 mL three neck flask with a relux condenser. WCO added methanol with a molar ratio (1:4, 1:6, 1:8 and 1:10) and the amount of catalyst H_2SO_4 1% -b/b. The mixture was reacted at the reaction temperature (30^oC, 40^oC and 50^oC) for 120 minutes by cavitation and stirring. The results of the reaction are transferred to the revision funnel and set aside within 18 hours making two layers. The top layer is FAME and the bottom layer is air. FAME and water resolved. FAME recover with hot water (50^oC) to remove air, methanol and catalyst residues. FAME is purified at 110^oC to remove any residual water and methanol. Finally, the FAME was conducted to analyze the levels of free fatty acids

2.3. Analysis of fatty acid methyl esters (FAME)

Fatty acid methyl esters are implemented with Fourier transform infrared spectroscopy (FTIR) Shimadzu Prestige 6400. This analysis is carried out to determine the functional groups of fatty acid methyl esters based on wavelength. So the variety formed in the fatty acid methyl ester product can be determined by comparison with the functional group in the relevant reference. Basically, FTIR analysis is carried out to prove that it has been completed to produce fatty acid methyl esters (FAME)

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2.4. Determination of the physico-chemical properties of FAME

The physico-chemical properties of the fatty acid methyl esters analyzed in this study are the levels of free fatty acids and acid numbers. free fatty acid levels were analyzed by the SNI 01-3555-1998 standard method. Where 5 grams of FAME is put into the 250 ml erlenmeyer. Then 50 ml of 96% alcohol is added and then heated for 10 minutes. The solution is then added with 2 drops of phenolphtalein indicator then titrated with 0.1 N KOH brick red color until it looks pink.

III. Results and discussion

3.1. Effect of FFA level to time, temperature and mole ratio

The esterification reaction was carried out on waste cooking oil (WCO) in Aceh with a value of 4.33% free fatty acids and then added a 1% b/b H_2SO_4 catalyst and methanol with a molar ratio (1:4, 1:6, 1: 8 and 1:10). The experiment was carried out under the same temperature and stirring conditions as the reaction temperature (5 minutes -120 minutes). Furthermore, the mixture is separated into two phases, namely fatty acid methyl esters and water.

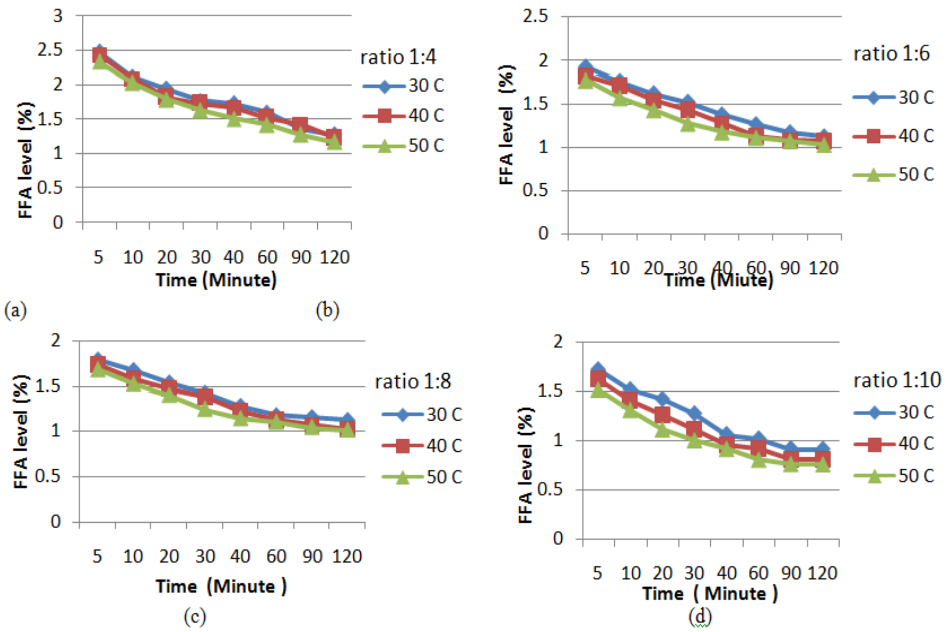

Figure 1. The effect of reaction time (a) (b) (c) (d) to the free fatty acid levels in the ratio of 1:4 mole, 1:6 mole, 1:8 mole and 1:10 mole at reaction temperature 30^{o}C, 40^{o}C and 50°C

Figure 1 shows that the levels of free fatty acids (FFA) decreases with increasing reaction time (5, 10, 20, 30, 40, 60, 90 and 120 minutes). This is caused by the length of time of the esterification reaction, thus giving the molecule compound a chance to react are getting bigger (between waste cooking oil and methanol added H_2SO_4 catalyst), so the remaining FFA is decreasing in fatty acid methyl esters [9].

The FFA level decreases with increasing reaction temperature used (30, 40 and 50°C). This is The existence of heating causes the used waste oil molecules to be dispersed and distributed to the methanol molecule form a methyl ester bond. In addition, the increase can also increase the movement of oil-methanol molecules so that the collisions between the particles will increase [10].

FFA levels decrease as increasing mole ratio used (1:4, 1:6, 1:8, and 1:10 mole). Like the FFA levels of cooking oil waste after the hydrodynamic cavitation process at a ratio of 1:10 at 50°C, the FFA decreased from 1.52% to 0.76% at the reaction time between 5 minutes to 120 minutes. This is caused by the solvent of methanol shifting to the right of the product (fatty acid methyl ester). with the reduction of methanol in the liquid phase can reduce the reaction between free fatty acids from waste cooking oil with methanol, so that there is an increase in ALB levels in raw materials and with the addition of the amount of methanol used will accelerate the reaction thereby reducing ALB levels. The reaction temperature affects the decrease in free fatty acid levels in methyl esters. The esterification reaction will take place quickly by raising the reaction temperature to near the boiling point of methanol [11].

3.2 Comparison of FFA levels in the Hydrodynamic cavitation process with the stirring process

FFA levels of the hydrodynamic cavitation process with the stirring process are affected by several factors between the reaction time, reaction temperature and mole ratio so that we can see the comparison between the two processes.

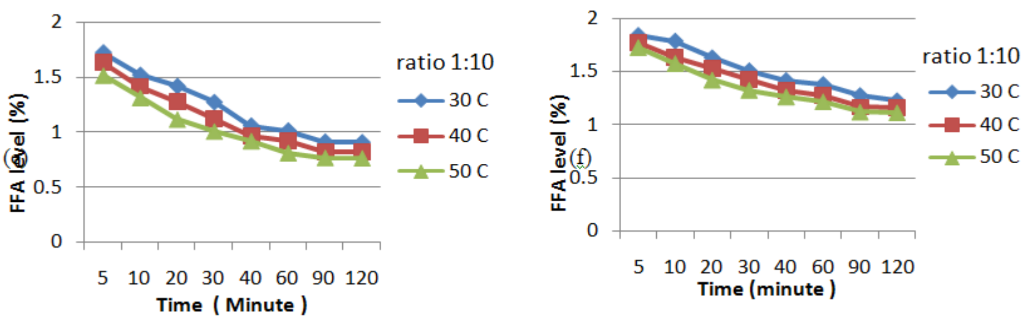

Figure 2. Comparison of FFA levels (e) Hydrodynamic cavitation process (f) Stirring process with a ratio of 1:10 mole at a reaction temperature of 30^{o}C, 40^{o}C, and 50°C

From figure 2 we can conclude that the decrease of FFA levels of the hydrodynamic cavitation process is faster than the decrease of the FFA levels of the stirring process. This is caused by increased contact between oil and methanol using cavitation (the phenomenon of formation, growth and destruction of micro bubbles in the liquid). The formation of micro-sized bubbles enlarge the contact surface area between oil and methanol so as to increase the rate of reaction. According to Ji et al. (2006) the use of hydrodynamic cavitation has been shown to accelerate the reaction, reduce the amount of catalyst used and reduce the mole ratio of oil to methanol used and lower energy consumption compared to the process using a mechanical stirrer. This is due to the effects caused by hydrodynamic cavitation can increase the chemical and physical changes in a media through the formation and breakdown of cavitation bubbles[12].

IV. Conclusion

Esterification cooking oil waste (WCO) in Banda Aceh using methanol (CH_3OH) as a solvent successfully obtained fatty acid methyl ester (FAME). Free fatty acid in cooking oil waste sample is 4.33% and after doing the esterification is obtained free fatty acid levels that is 0,76%. The highest yield of cooking oil waste esterification was obtained at a cooking oil / methanol ratio of 1:10 mol with reaction temperature (5 minutes to 120 minutes). The use of the hydrodynamic cavitation process method gives a significant effect on the quality and quantity for the reduction of free fatty acid methyl ester levels in waste cooking oil samples.

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