Use of hydrodynamic cavitation for esterification of free fatty acids in waste cooking oil

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Abstract. Esterification followed by transesterification process is widely applied for biodiesel production from oil with high free fatty acids (FFA) content to remove the FFA and increase the yield of biodiesel. The aim of this research was to study the esterification of waste cooking oil using the hydrodynamic cavitation apparatus. Waste cooking oil with initial FFA content 4.33% was esterified with methanol using sulfuric acid 1%-w/w as the catalyst. The reaction condition was kept constant for 120 minutes of total reaction time. At the best operating condition i.e. molar ratio of waste cooking oil to methanol 1:10 and reaction temperature 50 °C, the initial FFA of waste cooking oil 4.33% reduced to 0.76%. The experimental results also showed that the hydrodynamic cavitation had better performance than the conventional process using mechanical stirring.

1. Introduction

Vegetable oils undergo several chemical and physical changes during the frying process mainly due to the exposure to high temperatures and the presence of oxygen and water. One of these changes is the increase in acidity of the oil which is provoked by the release of free fatty acids (FFA). Generally, waste cooking oil as the oil produced from the frying process has a high percentage of FFA which is produced from the oxidation and hydrolysis reaction during the frying process. Waste cooking oils are regarded as an alternative to raw vegetable oils for biodiesel production due to the high cost of the vegetable oils and the threat to food security. Recent studies reported that waste cooking oil has been proved as the promising feedstock for biodiesel production because of abundant availability, low cost and have a comparative advantage compared to other feedstock [1-3].

Biodiesel is typically obtained by transesterification process, which involves the reaction of triglycerides with short-chain alcohol to produce fatty acid methyl esters (biodiesel) in the presence of a base catalyst [4]. The presence of FFA cause problems during the base-catalyzed transesterification reaction due to saponification problems. The soaps produced cause problems during the purification of biodiesel, creating an emulsion between biodiesel as the main product and the glycerol as the side product. In order to take advantage of the utilization of waste cooking oil as low-cost feedstocks for biodiesel production, therefore, a method for FFA removal is necessary. Supardan et al. [3] reported

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glycerolysis process to reduce the FFA content of waste cooking oil. Meanwhile, Wang et al. [5] carried out esterification process to reduce the FFA content of oleic acid oil. Currently, the esterification followed by transesterification process is widely applied for the biodiesel production from oil with high FFA content. The esterification process has two purposes i.e. removing the FFA and increasing the yield of biodiesel.

The performance of esterification can be affected by several factors, such as FFA content, water content, molar ratio of alcohol to raw materials, reaction temperature, amount and type of catalyst, reaction time, and the type of alcohol used [6]. Sulfuric acid (H$_2$SO$_4$) is widely used in the esterification reaction. In esterification reaction, proton H$^+$ can be substituted and binds strongly with oxygen atoms in carbon carbonyl which have a large electronegativity value. Meanwhile, 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 has higher reactivity. Many technologies have been developed to produce biodiesel efficiently. Ji et al. [7] proposed hydrodynamic cavitation to intensify transesterification reaction. Meanwhile, the intensification of the esterification reaction using acoustic and hydrodynamic cavitation was reported by Mohod et al. [8]. 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.

The aim of this study is to study the effect of process variables i.e. the molar ratio of waste cooking oil to methanol, temperature and processing time in the esterification of waste cooking oil using hydrodynamic cavitation. The acid value was determined to monitor the progress of the reaction. Furthermore, the performance of the esterification process using hydrodynamic cavitation will be compared with the conventional process using mechanical stirring.

2. Materials and method

2.1. Materials

The raw material was waste cooking oil collected around Banda Aceh, Indonesia. The chemicals used were methanol (Merck, Germany), potassium hydroxide (KOH), sodium hydroxide (NaOH), sulfuric acid 98% (H$_2$SO$_4$), phenolphthalein reagent 99% (Merck, Germany) and ethanol 96% (Merck, Germany).

2.2. Esterification of WCO

The FFA content of waste cooking oil used was 4.33%. The esterification reaction was performed in a 500 mL three-neck flask equipped with a temperature controller and a water-cooled condenser. The stirring speed was kept constant during all experimental runs at 500 rpm. The molar ratios of waste cooking oil to methanol used were 1:4, 1:6, 1:8 and 1:10. The mixture was reacted at the reaction temperature 30, 40 and 50 °C for 120 minutes. The catalyst H$_2$SO$_4$ concentration 1%-w of oil was used for all experimental runs. The catalyst was mixed into methanol and stirred until homogeneous. Furthermore, this solution was introduced into a three-neck flask that already contains waste cooking oil. After completion of the reaction, the products are transferred to the separating funnel for product separation. The top layer is analyzed to monitor the progress of the reaction. A conventional process using stirrer was also conducted for comparison.

2.3. Product analysis

FFA content of products was analyzed by the Indonesian National Standard (SNI) No. 01-3555-1998. In this method, 5 grams of product 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 phenolphthalein indicator then titrated with 0.1 N KOH. The titration ended when a reddish-brown colour change was observed.
3. Results and discussion

3.1. Effect process variables

Figure 1 shows the progress of the reaction in terms of the change in FFA content at different temperature and molar ratio of waste cooking oil to methanol. The experimental results show that the FFA content decreases with increasing reaction time. This is due to the longer reaction time will provide greater contact opportunities between the reaction mixture (waste cooking oil and methanol). Thus, the remaining FFA content will also decrease with increasing reaction time. Sendzikiene et al. [9] reported that the reaction rate changes depending on the reaction duration, especially during the first 15 min. At the end of the reaction time of 120 minutes, the final FFA content obtained was found to be dependent on the process variables. A similar trend was reported by Satriana et al. [10] for glycerolysis reaction.

![Figure 1](image1.png)

**Figure 1.** The progress of the reaction in terms of the change in FFA content for molar ratio of waste cooking oil to methanol: (a) 1:4; (b) 1:6, (c) 1:8; and (d) 1:10.

It was observed that the FFA content decreased with increasing reaction temperature. This is probably because the heating makes used cooking oil molecules more easily dispersed and distributed to methanol molecules to form reaction products. In addition, an increase in reaction temperature can also increase the movement of oil and methanol molecules so that collisions between particles will increase. The esterification reaction will take place quicker by raising the reaction temperature to near the boiling point of methanol.
Furthermore, the experimental results also showed that FFA content generally decreases from an initial value of 4.33% as the molar ratio of waste cooking oil to methanol increases. For example at reaction temperature 50°C, the FFA decreased from 1.52% to 0.76% and 1.69% to 1.02% at the reaction time between 5 minutes to 120 minutes at a molar ratio of waste cooking oil to methanol 1:10 and 1:8, respectively. Esterification is a type of a reversible reaction. The reaction is carried out in excess of reactants to produce the products at maximum quantity \[11\]. In this experiment, the use of excess methanol to the reaction mixture will shift the equilibrium to the right side, towards the side of the products. On the other hand, reducing the concentration of any product could also implemented to shift equilibrium to the right side.

3.2 Process comparison

The comparison of the process performance using hydrodynamic cavitation and conventional process using mechanical stirring at the molar ratio of waste cooking oil to methanol = 1:10 and the catalyst concentration 1% can be seen in Fig. 2. As can be seen in Fig. 2, the FFA content decreases with increasing time and temperature reaction. A similar trend was observed for both the hydrodynamic cavitation process and the conventional process using mechanical stirring. The experimental results showed that the decrease of FFA content for the hydrodynamic cavitation process is faster than the conventional process using mechanical stirring. These results proved that the cavitation produced more intensive contact between oil and methanol (through the phenomenon of formation, growth and destruction of micro bubbles in the liquid) compared to the conventional process. Hydrodynamic cavitation can increase the chemical and physical changes in media through the formation and breakdown of cavitation bubbles. The formation of micro-sized bubbles enlarges the contact surface area between oil and methanol to increase the rate of reaction. According to Ji et al. \[7\] 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 mechanical stirring.

![Figure 2. Comparison of FFA content for: (a) Hydrodynamic cavitation process; and (b) Mechanical stirring process.](image)

4. Conclusion

Esterification using cavitation hydrodynamic was successfully carried out to decrease the FFA content of waste cooking oil. It was observed that the experimental variables studied had a remarkable effect on the FFA content of waste cooking oil. Generally, FFA content decreased as the time of reaction increased. The experiment results showed that a suitable reaction condition should be used to achieve an optimum level of FFA conversion. The best operating condition was obtained at a molar ratio of waste cooking oil to methanol 1:10 with reaction temperature 50 °C in which initial FFA of waste
cooking oil 4.33% reduced to 0.76%. It can be concluded that the reaction using hydrodynamic cavitation had a better performance than those using mechanical stirring.

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