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Free Fatty Acid Reduction in a Waste Cooking Oil as a Raw Material for Biodiesel with Activated Coal Ash Adsorbent

Endang Susilowati¹, Abu Hasan¹, and Aida Syarif¹

¹Applied Master of Renewable Energy Engineering, State Polytechnic Sriwijaya, St. Srijaya Negara, Palembang, 30139, Indonesian

Email: Endangsusilowati786@gmail.com

Abstract. The development of globalization era which was followed by industry and the economy and also the increasing number of people caused an increase in amount of energy consumption and issues of environmental problems. Therefore, further research is needed on energy conservation in order to reduce non-renewable energy consumption. One of the alternative energy source that can be used as fuel and environmentally friendly is biodiesel. Biodiesel through two stages, the first one is esterification process aims to convert fatty acids from triglycerides in the form of esters. And the second one is transesterification process. It is the conversion of triglycerides or vegetable oils into alkyl esters. In this study coal ash waste and cooking oil as raw material are used for making biodiesel. Coal ash is used as an adsorbent to bind free fatty acids (FFA) toward cooking oil because coal ash has a high silica content. This research was conducted in several stages, namely activation of coal ash, characteristics of coal ash, free fatty acid test (FFA), waste cooking oil adsorption process. Coal ash is activated physically with time and temperature as the variables. From the activation process, the best coal ash iodine value was obtained at 60 minutes warm up time and 140 °C temperature was 682,173 mg / g. The adsorption process is carried out with a period of 1 gram of adsorbent, 2 grams, and 3 grams. Coal ash can reduce the levels of free fatty acids in used cooking oil by 87.44% in the adsorption process with a time variable of 60 minutes and a temperature of 150°C.

1. Introduction

Waste cooking oil is waste oil that can be derived from other types of cooking oil, the remaining usage of house hold used, cooking oil cannot be used continuously because it can disrupt human health, therefore waste cooking oil is used as an alternative energy source, biodiesel due to its availability the most and the exhaust gas test results show the superiority of FAME compared to diesel fuel, especially the decrease of particulate / dust by 65%, biodiesel from waste cooking oil also fulfills the SNI requirements for biodiesel [1].

However, in the content of waste cooking oil, there are also free fatty acids (FFA) in used cooking oil as a result of repeated heating. Free fatty acids are fatty acids that have escaped from the glycerol molecule. Oils containing more than 1% free fatty acids will form a difficult emulsion of soap during the separation of biodiesel. Therefore, the waste oil which used must be purified first, in order to fulfill the biodiesel standard it is a necessary to pretreatment before managing the used cooking oil as biodiesel [2].

In a previous study conducted by R.B Istiningrum et al. On the Utilization of Rice Husk Ash for Purification of Raw Materials and Biodiesel Products from waste Cooking Oil. In this study rice husk



ash is used as an adsorbent in making biodiesel process from waste cooking oil. Coal ash is applied in refining waste cooking oil as well as biodiesel products. This research was conducted in several stages, they are the characteristics of ASP, purification of biodiesel with ASP 1.3.5% and characteristics of biodiesel. But the quality produced does not fulfill SNI requirements [3].

There fore in this study the lowering of FFA in waste cooking oil as raw material for biodiesel using coal ash adsorbent. In purifying waste cooking oil with the physical method, the adsorption process on used cooking oil was carried out to bind and reduce free fatty acids using coal ash adsorbent. According to SNI 03-6414-2002 defines the meaning of fly ash coal is waste from coal combustion in a steam power plant furnace which is smooth, round and pozolanic. Fly ash is a material that has a fine grain size, grayish color and obtained from the combustion of coal. In essence fly ash contains of several chemical elements including silica (SiO_2), alumina (Al_2O_3), ferrous oxide (Fe_2O_3) and calcium oxide (CaO), also contains of other additional elements such as magnesium oxide (MgO), titanium oxide (TiO_2), alkaline (Na_2O and K_2O), sulfur trioxide (SO_3), phosphorus oxide (P_2O_5) and carbon. Fly ash does not have the ability to bind like cement, but in the presence of water and its fine size, silica oxide contained in coal ash will react chemically with calcium hydroxide formed from the hydration process of cement and will produce substances that have binding ability. [4] because of that coal ash is able to bind free fatty acids and reduce the levels of free fatty acids optimally, it can fulfill the SNI biodiesel standard. Coal ash is a residual combustion waste that can be utilized to reduce environmental pollution.

2. Methods and experimentl set-up

The purpose methode of Free Fatty Acid reduction oil as a raw material for Biodiesel with activated coal ash adsorbent, in this paper is presented in figure 1.

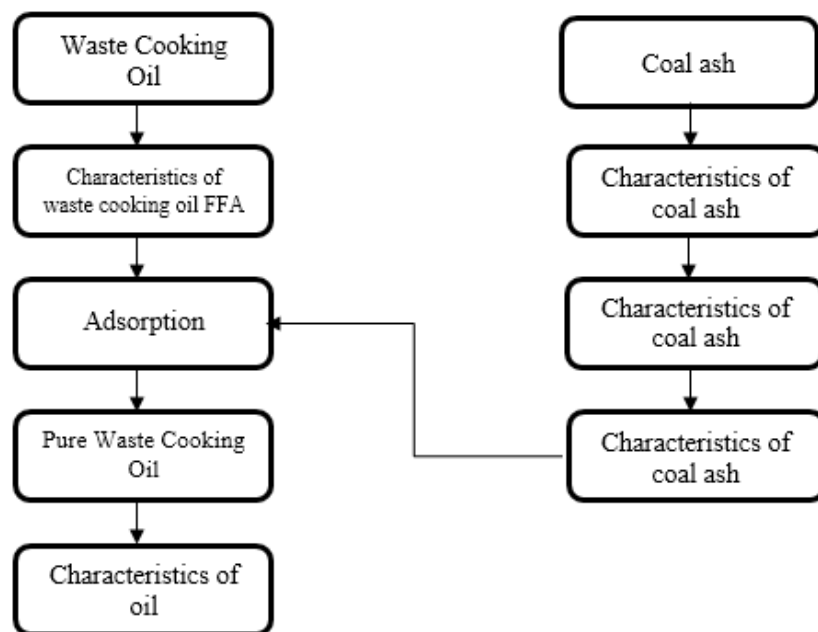


Figure 1. Block diagram of the activation & adsorption process.

In this study the raw material used is waste cooking oil, first waste cooking oil is characterized by checking the levels of free fatty acids (FFA) contained in waste cooking oil by taking waste cooking oil samples before the adsorption process, which is taking 5 grams of waste cooking oil then adding methanol 98% as much as 50 ml and add 3 drops of phetroleum indicator then titrate with NaOH solution until the solution turns pink. Then the FFA number is determined by the following formula [5]:

$$\% FFA = \frac{256 \frac{gr}{mol} \times V \times N}{m \times 1000} \quad (1)$$

where: v = volume NaOH, N= concentration of NaOH, m= sample mass

Both coal ash is characterized by knowing the water content contained in coal ash, after that Making of an iodine solution then adding 1 gram of activated coal ash sample then stirring for 10 minutes after it is filtered using filter paper, then the filtrate is taken and added 3 drops of starch indicator then titrated with a solution of thiosulfate with a concentration of 0.1N. Iodine numbers are obtained by calculation using the formula below [6] :

$$Number\ of\ IOD = \frac{(B-S) \times N \times 12,69}{G} \quad (2)$$

where: B = Number of Na₂SO₃ of 0.1N on blank titration, S = Number of Na₂SO₃ of 0.1N on sample titration, N = Normality of Na₂SO₃ of 0.1N solution after standardization, G = Sample weight, 12.69 = Iodine atomic weight / 10.

After that coal ash is activated physically by heating, first weighing the weight of the empty cup then adding 50 grams of coal ash sample and then heating it using furnaces by heating temperature variables of 130 °C, 140 °C, and 150 °C by a heating time of 60 and 90 minutes, after that put into the desiccator and then weighed the final weight of coal ash.

The oil sample was taken as much as 25 ml and then activated coal ash samples were added with sample weight of 1 gram, 2 grams and 3 grams then stirred for 60 minutes, after that the samples were filtered using 42 mm whatman filter paper, then the filtrate was taken and the volume was measured. The final step is to re-measure the value of FFA in waste cooking oil adsorbed using activated coal ash by taking 5 grams of waste cooking oil sample then adding 98% of methanol as much as 50 ml and adding 3 drops of phenolphthalein indicator then titrating with NaOH solution until the solution changes color to pink. Then calculate the final FFA value.

3. Results and discussions

3.1. From the analysis of coal ash in the activation process

From the research that has been done, the characteristics of coal ash are as follows:

Table 1. Data on characteristics analysis of coal ash from activation.

No	Time (minute)	Temperature °C	Analysis	
			Iodine Number (ppm)	Water Content (%)
1	60	130	611,213	0,285
	90		615,888	0,969
2	60	140	682,173	0,235
	90		634,649	0,267
3	60	150	565,611	0,263
	90		640,289	0,284

From the data analysis of coal ash during the activation process physically and calculations can be seen from table 1. The best iodine number is obtained when activation by the time of 60 minutes and a temperature of 140 °C which is equal to 682,173 mg / gr.

3.2. Analysis of the effect of time and activation temperature in decreasing FFA

This study shows that the time and temperature of activation is very influential on decreasing the FFA value in each waste cooking oil sample. It is shown from the results of observations in the figure below the research results by 60 minutes activation time and temperature variations of 130°C, 140°C and 150°C. And the highest reduction of free fatty acids was obtained in the variation of the adsorbent by 2 grams and at a temperature of 150°C as much as 87.44% while the lowest decrease in free fatty acid level was at adsorbent variation of 1 gram and at a temperature of 130°C as much as 14.28%. From this figure it can be analyzed that the activation temperature affects the enlargement of the coal ash surface area and this results in increasing the number of free fatty acid molecules attached to the surface of the coal ash.

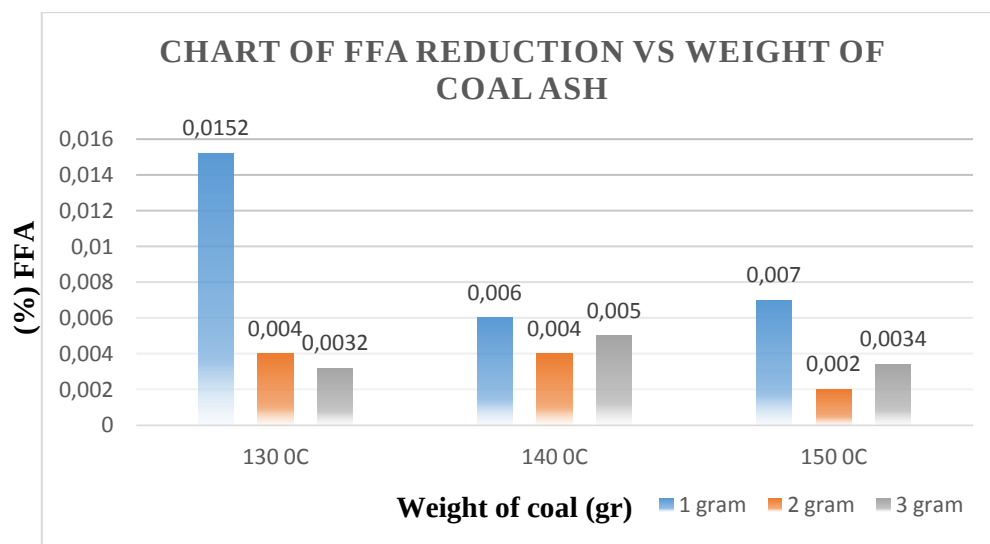


Figure 2. At 60 minutes of activation time.

Whereas the sample activated by 90 minutes and with temperature variations of 130°C, 140°C and 150°C. It can be seen below that the highest decrease in free fatty acids was in the variation of 2 grams of the adsorbent with a temperature of 150°C as much as 85.15% and the lowest when using 1 gram of coal ash samples as adsorbents with a temperature of 150°C which was 28.57%.

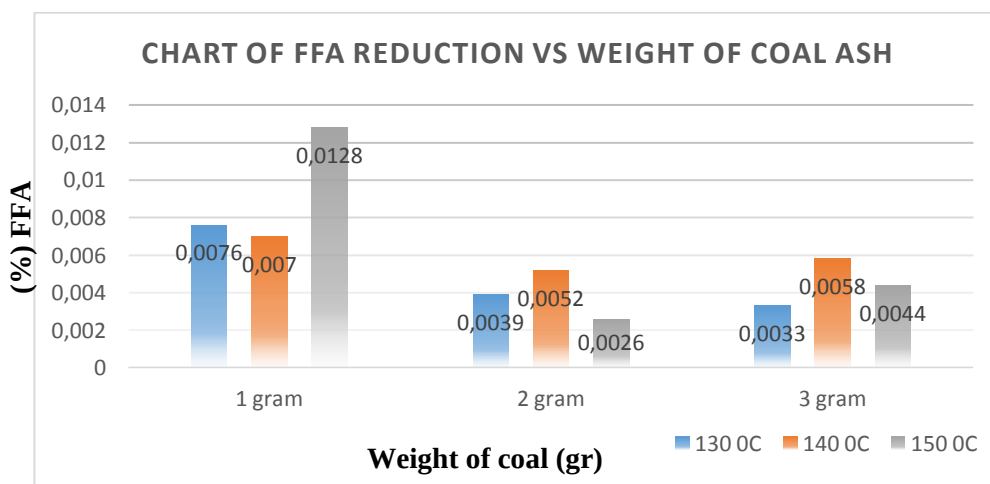


Figure 3. At 90 minutes of activation time.

From the figures attached above, it can be seen that the process of decreasing the optimal free fatty acid content, which is activated by 60 minutes and 150°C with a weight of 2 grams of adsorbent can reduce free fatty acids in waste cooking oil by 87.44% and by the variation of coal ash which was activated by the time of 90 minutes and a temperature of 150 °C by weight of 2 grams adsorbent could reduce the levels of free fatty acids in waste cooking oil by 85.15%. It shows that coal ash is suitable to be used as an adsorbent to reduce free fatty acids in waste cooking oil and the results obtained after the adsorption process have fulfilled SNI -7182.2.2015 maximum waste cooking oil of 3%, so waste cooking oil can be used as raw material making biodiesel.

3.3. FFA analysis data on waste cooking oil

After the FFA value is known from each waste cooking oil sample, in this study it can be analyzed that the coal ash adsorbent can reduce the levels of free fatty acids (FFA) in waste cooking oil by physical adsorption of free fatty acids in waste cooking oil and coal ash acts as a non-polar molecule so free fatty acid particles approach the surface of the adsorption of coal ash through a hydrogen bond [11].

From this study, the lowest value of free fatty acid (FFA) in waste cooking oil samples adsorbed with coal as much as 1 gram was 6.04% with the treatment of coal ash activation time for 60 minutes and at a temperature of 150 °C. and the lowest value of free fatty acid (FFA) when using 2 grams of coal ash adsorbent obtained FFA value of 2.25% with a treatment time of activation for 60 minutes and a temperature of 150 °C. while the lowest level of free fatty acids (FFA) with adsorption of coal ash as much as 3 grams of 3.43% with the treatment time of activation for 60 minutes and with a temperature of 130 °C.

4. Conclusions

The process of purifying waste cooking oil as a raw material for making biodiesel against the content of free fatty acids can be carried out physically through the adsorption method. The adsorbent was carried out using 170 mesh coal ash which was physically activated. Coal ash process is carried out by heating at temperatures of 130 °C, 140 °C and 150 °C with variations in time of 60 and 90 minutes. The optimum rate of reduction of free fatty acids is that which occurs in conditions with the adsorbent which is activated at a temperature of 150°C and 60 minutes with a weight of 2 grams of adsorbent. Coal ash can absorb free fatty acids in waste cooking oil as much as 0.1567%.

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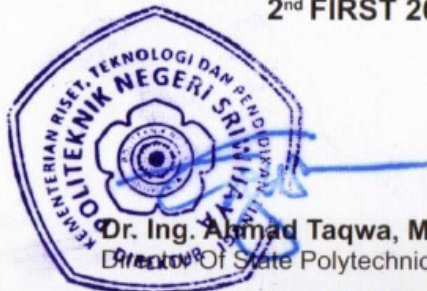
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