

The Effectiveness of Biosorbent from Chicken's Egg Shell and Durian Peel towards the Quality of Biodiesel Product from Waste Cooking Oil

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Abstract- Indonesia is the largest exporter of palm oil with 85 - 90% of the world's total palm oil production. The consumption of palm oil in Indonesia is increasing every year, thus the waste are also increase. Waste cooking oil contains carcinogenic substances which causes various diseases. Biodiesel is an environmentally friendly substitute fuel for diesel made from vegetable oil as raw material. Used cooking oil can be used as raw material for biodiesel production, but it needs to be purified before further processing. Chicken egg shell contains 90% of CaCO_3 can be used as a biosorbent of used cooking oil. Durian skin contains 50% - 60% of cellulose also has the potential as a biosorbent. This research was conducted to investigated the effectiveness of the combination of chicken egg shell biosorbent with durian skin for the purification process of used cooking oil as a raw material of biodiesel. Biosorbent was produced by carbonization process in a furnace at a temperature of 550°C for durian skin and 900°C for chicken egg shells. The results show that the acid number of used cooking oil has met the parameters of the SNI 3741: 2013, namely 0.43 mgKOH / gr and FFA levels of 0.0024% with a yield of 62.76%. The purified cooking oil was then continued with the transesterification process to produced biodiesel. The biodiesel obtained had the cetane numbers B100 of 33.8 and B30 of 45.2.

Keywords - waste cooking oil, biosorbent, chicken egg shells, durian peel, biodiesel

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1. Introduction

Biodiesel is an environmentally friendly substituent of diesel fuel. It was produced from vegetable oil with transesterification and esterification process. Palm oil, candlenut oil, nyamplung oil, jatropha oil, coconut oil and peanuts oil have the potential as raw material of biodiesel. Biodiesel has a higher oxygen content than conventional fossil fuel due to its complete combustion which has a positive impact on the environment and reduces the greenhouse effect. Used cooking oil is household waste in the form of used palm oil which has carcinogenic properties. The used cooking oil waste needs a treatment so that it does not cause harm in the future. Activated carbon is carbon resulting from a process that has been activated into open pores to facilitate the adsorption. Activated carbon is obtained from a carbon-containing material,

namely coal. In addition, to save and to reduce the use of activated carbon coal, it can also made from waste [1]. This study aims to determine the effectiveness of biosorbents from chicken eggshells combined with durian skin and to investigate the optimum conditions of biodiesel production according to SNI 04-7182-2006 [2].

1.1. Fatty Acids and Free Fatty Acids

Fatty acid is a monocarboxylic acid with a long chain. Fatty acids are long-chain organic acids that have 4-24 carbon atoms, have a single carboxyl group and long nonpolar hydrocarbon ends causing almost all lipids to be insoluble in water and appear oily or fatty. Free fatty acids are fatty acids that exist as free acids that are not bound as triglycerides. Free fatty acids produced by hydrolysis and oxidation are usually combined with neutral fats. Free fatty

acids are obtained from the hydrolysis process, namely from the breakdown of fats or triglycerides by water molecules which produce glycerol and free fatty acids [3].

1.2. Waste Cooking Oils

Waste cooking oils cooking oil that is used several times by consumers. This used cooking oil contains a lot of free fatty acids [4]. The results of the frying usually contain 5 - 40% oil [5]. In its use, cooking oil that is heated repeatedly at high temperatures (200 - 250°C) can cause damage to the oil so that it is not suitable for use [6]. The initial damage from cooking oil is the formation of aclorein in cooking oil [7]. This aclorein causes itching sensation in the throat when consuming foods that are fried using cooking oil repeatedly. Aclorein is formed from the hydration of glycerol to form unsaturated aldehydes..

1.3. Biosorbent

Adsorbents, namely substances naturally have high pores and surface area to absorb the desired substance towards the surface of the adsorbent with intermolecular forces. Adsorption is a process that occurs when a substance on the surface is in contact with a solution and there is an accumulation between solution molecules on the surface of the solid. The factors that influence the adsorption process are surface area, contact time, stirring, pore size distribution, and particle size. Indonesian people generally consume a lot of chicken eggs as a complement to nutrition in the body, but unconsciously the chicken eggs we consume produce waste in the form of egg shells and have not been fully utilized. The eggshell has 10,000 - 20,000 pores so it is estimated that it can absorb a solute which can be used as an adsorbent. The mineral composition of egg shells is crystal CaCO₃ (90.9%), Magnesium (0.40%) [8]. Durian is a plant that grows in tropical areas, one of which is in Indonesia, with the Latin name *Durio zibethinus L.* Durian has abundant potential [9]. Durian's biomaterials contain functional groups, namely amino, sulfate, polysaccharide, carbosil, lignin, and sulfihydrile which have good adsorption ability [10]. Durian peel has a carbon content of 60%. which is found in durian skin is used as a biosorbent for purification of used cooking oil.

1.4. Biodiesel

Biodiesel is a diesel fuel made from biological materials, especially vegetable fats and animal fats [11]. Vegetable oils that can be used as raw material for biodiesel can come from donkey nuts, coconut, palm oil, rice, corn, jatropha, papaya and many more through a simple transesterification process. The transesterification reaction using an alkaline catalyst is a process commonly used for biodiesel production. This reaction is faster to form methyl esters than the esterification reaction using an acid catalyst [12-13]. This biodiesel production process produces a by-product in the form of glycerol and can be used as an ingredient in cosmetics, soaps, and many more [14].

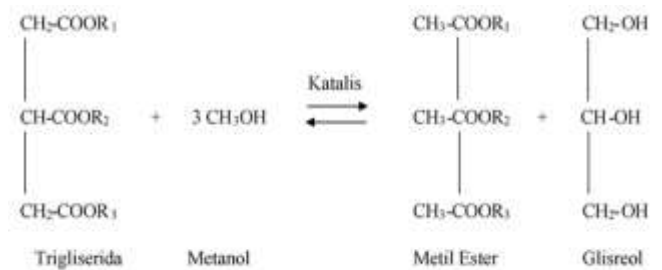


Figure 1. Reaction Scheme Transesterification

Table 1. Biosolar Characteristic of PT. Pertamina

No.	Characteristic	Unit	Standard value	Analysis Method
1.	Cetane number	-	48	D 613-95
2.	Density at 15°C	kg/m ³	815 - 860	D 1298/ D 4052-96
3.	Flash point	°C	60	D 93-99c

The biodiesel production process is very slow and requires high temperatures and pressures without using a catalyst [15]. FFA (Free Fatty Acid) free fatty acids are one of the most important parameters in making biodiesel, if the oil raw material has an FFA number <0.5% then use a transesterification process with an alkaline catalyst while the FFA number > 5% uses the Ice process - Trans (Esterification - Transesterification) [16]. The catalyst is divided into several parts homogeneous catalyst, heterogeneous catalyst and enzyme catalyst. The catalysts that are often used are alkalis, acids, or enzymes. The alkalis that are often used are sodium methoxide (NaOCH₃), sodium hydroxide (NaOH), potassium hydroxide (KOH).

2. Methods

2.1 Materials

The main ingredient of this research is waste cooking oil from household waste and food traders as well as chicken egg shells and durian skin. Other research materials are: technical H₃PO₄, methanol 98%, technical NaOH, and aquadest.

2.2 Apparatus

This research uses a hot plate magnetic stirrer. Meanwhile, other tools used include: furnace, oven, Whatman paper no.1 and no.40, two-neck flask, pycnometer, digital scale, pH indicator, and back cooler.

2.3 Experimental Procedures

The research was conducted starting with the purification of used cooking oil using a biosorbent combination of chicken egg shells and durian skin (A1- and A2), operating temperatures of 60°C and 80°C and the duration of the adsorption process of 60 and 120 minutes. Then the purification results are filtered using Whatman paper no.1 and no.2, the acid number test is carried out to determine the next process of esterification or transesterification. The transesterification process was carried out under operating conditions for a long time of 120 minutes and a temperature of 60°C. The volume of raw material for purified starch oil is 100 mL. Then the

biodiesel product quality test is carried out, namely the cetane number, density, and flash point.

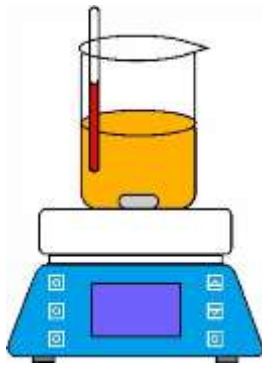


Figure 2. Research equipment

3. Results and Discussions

3.1 Purification of Waste Cooking Oil

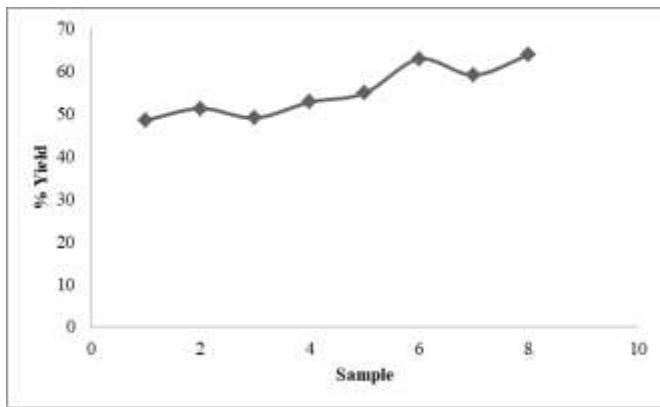


Figure 3. % Yield Purification Waste Cooking Oil

Yield produced from the refining process of waste cooking oil using chicken egg shell and durian skin biosorbent. The biosorbent ratio variable (Rb) obtained more oil volume and higher yield levels at the upper (+) A2 (60% chicken egg shell composition: 40% durian skin) in this study to determine the most influential process variables by means of quicker method to calculate the main effect and the interaction with the yield produced and look for the quality of used cooking oil that has been adsorbed to be used as raw material for the production of used cooking oil. The following is the calculation of the effect on yield.

Table 2. Main Effect and Interaction

Effect	Result
R _b	4,78
T	1,83
t	9,79
R _b T	-0,59
R _b t	1,55
Tt	0,80
R _b Tt	-1,03

From the results shown in Table 2, of the three changing variables, namely the ratio of biosorbent, temperature, and duration of adsorption, it is known that the most influential variable is t (duration of the adsorption process) with an effect value of 9.79.

3.2 Characteristics of Purification Results of Waste Cooking Oil

The process of refining used cooking oil is carried out, the used cooking oil is tested for analysis of its free fatty acid levels first. From the preliminary test results, it was found that used cooking oil had an acid number of 8.45 mgKOH / g which was very far from the SNI threshold for cooking oil, namely 0.6 mgKOH / g so that the raw material could not be used directly for biodiesel production. Therefore, the adsorption process must be carried out to bind free fatty acids to used cooking oil.

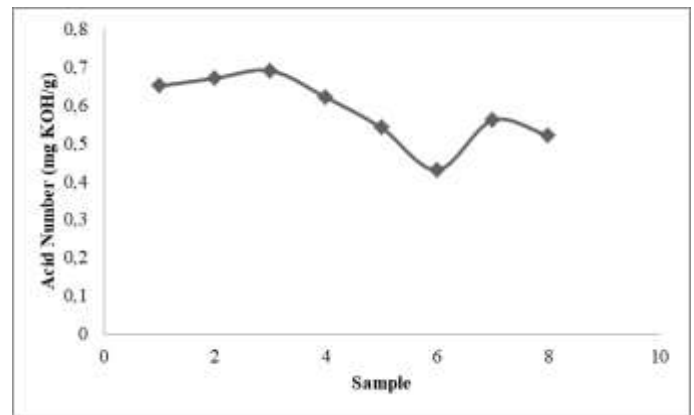


Figure 4. Acid Numbers in used cooking oil after purification

The graph above shows that in experiment 6 (Biosorban A2, T = 60°C, t = 120 minutes) got the lowest acid number. This is based on the longer time the used cooking oil is adsorbed and the amount of total mass of the added biosorbent causes the free fatty acids found in used cooking oil to be completely bound to the surface of the biosorbent that has been added. Before purification, used cooking oil had an acid value of 8.45 mgKOH / gr, while in the 6th experiment, the acid value content decreased to 0.43 mgKOH / gr. When compared with research in the form of purification of used cooking oil using only activated carbon from durian peels [17], the results obtained are in the form of derivatives of the value of free fatty acids contained in used cooking oil. It is based on the longer time it takes. adsorption and the amount of adsorbent mass added, the free fatty acid value will decrease. In addition, the same number can decrease due to the length of contact between used cooking oil and the adsorbent surface, as well as the amount of adsorbent mass added, the more free fatty acids will be absorbed by the adsorbent surface due to the large surface area.

3.3. Characterization of Biosorbent FTIR Spectrophotometer

FTIR spectrophotometry observes the interaction of molecules and electromagnetic radiation is able to show the functional groups contained in a material at a certain wavelength. The appearance of waves in the transmittance spectrum indicates the presence of particles that interact with infrared radiation at these wavelengths. The waves or depressions indicate functional groups in the material being analyzed. The structure of the biosorbent is observed in the transmittance spectrum waves shown in Figure 5 and Figure 6.

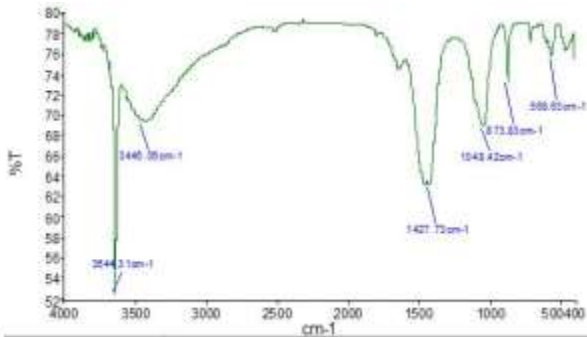


Figure 5. Graph of Biosorbent FTIR Spectrophotometer Test Results before adsorption

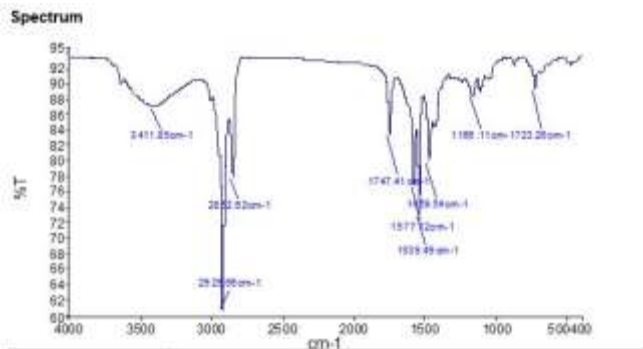


Figure 6. Graph of Biosorbent FTIR Spectrophotometer Test Results after adsorption

Biosorbent before adsorption, it is known that the N-H amine bond with a sharp concave at wave number 3644.31 cm^{-1} ($\lambda = 2744.003 \text{ nm}$) has a transmittance value of 1331.09% (absorbance = -1.12), the O-H bond is acidic. carboxylate wave number 3446.06 cm^{-1} ($\lambda = 2901,864 \text{ nm}$) with a transmittance of 3146.24% (absorbance = -1.49) and a -C-NO₂ Nitro Aromatic bond with a wave number of 1427.73 cm^{-1} ($\lambda = 7004.125 \text{ nm}$) the transmittance value is 3699.26% (absorbance = -1.56). Based on the explanation above, the N - H amine bond has a greater absorbance value than other bonds.

In the biosorbent after adsorption, it is known that the O - H bond of carboxylic acid with a wave number of 3411.85 cm^{-1} ($\lambda = 2930.961 \text{ nm}$) has a transmittance value of 2760.95% (absorbance = -1.44). The C - H alkane bond shows a wave number of 2925.66 cm^{-1} ($\lambda = 3418.032 \text{ nm}$)

has a transmittance value of 1282.63% (absorbance = -1.10) besides that the frequency is not too far followed by the C-H aldehyde bond at the wave number 2852.62 cm^{-1} ($\lambda = 3505.549 \text{ nm}$) with a transmittance value of 342.38% (absorbance = -0.53). After that, at the wave number 1747.41 cm^{-1} ($\lambda = 5722.755 \text{ nm}$), it is known that the C = O bond carbonyl group with a transmittance of 981.59% (absorbance = -0.99). The C = C aromatic ring bond is shown at wave number 1577.12 cm^{-1} ($\lambda = 6340.671 \text{ nm}$) with a transmittance value of 573.12% (absorbance = -0.75) indicating that the C = O bond there is an increase in carbon content besides that also the adsorption process that has occurred, besides that the presence of a C = C bond strengthens the presence of fatty acids bound to the biosorbent after the adsorption process. Based on the explanation above, the bond that has a greater absorbance value is the C - H aldehyde bond.

3.4. Characteristics of Biodiesel

The results of the purification study of waste cooking oil, the best results were obtained in experiment 6 with the analysis test results of the acid number 0.43 mgKOH / gr and % FFA 0.0020%. These results when compared with palm oil have almost the same acid number, namely 0.40 mgKOH / gr. So that the biodiesel production process uses the transesterification method because the specification of purified used cooking oil raw material has an FFA number <0.5% with an alkaline catalyst (Freedman et al., 1986).



Figure 7. Biodiesel B100 and B30

The operating conditions in the transesterification process were ($T = 60 \text{ }^\circ\text{C}$, $t = 120 \text{ minutes}$) 1% NaOH catalyst to the mass of used cooking oil and a 6: 1 methanol mole ratio using a Hot Plate Magnetic Stirrer. The following is a comparison table of biodiesel from used cooking oil purification with Pertamina biodiesel parameters and SNI 7182: 2015.

Table 3. Comparison of Biodiesel Parameters Research Results with Biosolar Pertamina and SNI Biodiesel

Characteristic	Results		Biosolar Pertamina	SNI 7182:2015
	B100	B30		
Cetane Number	33,8	45,2	48	51
Density (kg/m ³)	875	855	815 - 860	850 - 890
Flash point (°C)	85	75	60	100

The results of research with the standard parameters of Biosolar PT. Pertamina and SNI 7182: 2015 [18]. The density of B100 and B30 is in accordance with SNI 7182: 2015 and Biosolar Pertamina. The flash point of biodiesel from the research results shows that it meets Pertamina's Biosolar standard, but SNI 7182: 2015 does not meet the standard where SNI Biodiesel for flash point 100 OC the higher the cetane number, the lower the flash point will be. The cetane figure obtained by B100 is not in accordance with Pertamina's biodiesel standard and SNI 7182: 2015, which is 33.8. B30 has a cetane number of 45.2 which is almost close to the biodiesel standard of PT. Pertamina. Biodiesel from research B30 has a cetane number of 45.2, where the fuel has a tendency to ignite in a mixture of 45.2 parts of normal cetane ($C_{16}H_{34}$) which has no delay in ignition and 54.8 parts of methyl naphthalene ($C_{10}H_7CH_3$) which has a large turnaround delay. Cetane numbers are influenced by the composition of the fatty acids contained in the oil. The less saturated the oil, the lower the cetane number.

4. Conclusion

The production of biodiesel from used cooking oil as raw material which is pre-treated first by means of adsorption with a biosorbant combination of chicken egg shell and durian skin can be applied to reduce acid levels so that the quality of used cooking oil is the same as palm oil and the biodiesel production process is only transesterification takes place but the quality of the biodiesel produced does not comply with Pertamina's biodiesel standards and SNI 7182: 2015 Biodiesel ..

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