The effect of active carbon adsorbents from some wastes in reducing free fatty acids and acid number to improve vco quality

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Abstract. The use of several wastes such as durian outer skin, cassava outer skin and corncobs could be used to improve VCO quality. The wastes were converted into activated carbon as an adsorbent that was activated using sodium carbonate in purifying VCO in terms of reducing free fatty acid (FFA) and acid number. VCO used was oil that has made directly in the laboratory of oleo chemistry PTKI Medan and tested to reduce level of FFA and acid numbers. A total of 5 ml VCO samples were used to determine reducing in level of FFA and acid numbers by a titrimetric method with three times repetition using 0.1 N NaOH and previously treated with activated carbon adsorbent from durian outer skin, cassava outer skin and corncobs as much as 1 gr, 2 gr, and 3 gr. Based on the results of the examination, it was found that the level of FFA and acid number of VCO had a significant decrease with the best-activated carbon adsorbent using waste from cassava outer skin where level of FFA decreased by 0.16% and acid number decreased by 0.448.

1. Introduction

Virgin Coconut Oil (VCO) is a kind of vegetable oil which become more popular nowadays because of its functions related to human health and high-value material for the health food market [1,2]. Many studies related to the benefit of VCO were done, such as people who consume VCO have fewer incidences of the digestive complaint, cancer, prostate and cardiovascular diseases [3]. Generally, the content of coconut (Cocos nucifera) fruit is 51.7% kernel, 9.8% water, and 38.5% shell [4]. Mature coconut meat contains 65% saturated fatty acids with medium-chain or called as medium-chain saturated fatty acids (MCFAs) and the chemical content of VCO such as phenolic compounds, volatile compounds and act as antioxidant activity made this oil become widely used for food and industrial purposes [5-7].

VCO could be obtained using several methods. VCO is extracted from mature coconut meat and processed through physical methods without any contamination by chemical materials [8]. In addition, VCO is not only extracted through physical method but involved chemical method using microorganisms for fermentation process with heat or without heat and centrifugation method [9-10].

Research on VCO quality showed that the highest oil yield was through the centrifugation method, but through freezing and thawing were the most preferred in sensory properties [11]. The quality of VCO influenced by many factors such as quality raw materials, processing techniques, packaging
method and storage conditions. One parameter of quality control for oil is free fatty acids (FFA) and acid number. The number of FFA might be increased because of several factors; therefore it delivered bad quality of VCO. One technique to reduce FFA and AN is using activated carbon to adsorb oils. Adsorption is a technical operation widely used in industrial applications. Carbon with excellent surface characteristics and specific functionalities should be developed to create a high affinity for the adsorption process. Activated carbon has been extensively used as material for purification contaminated or uncontaminated oil and for increasing oil quality [12].

In this research, we manufactured activated carbon from some local wastes such as durian and cassava outer skin and corncobs. This study aims to reduce FFA and AN in VCO by adsorption of modified activated carbon.

2. Experimental Methods
VCO directly produced in Laboratory of Oleochemistry Politeknik Teknologi Kimia Industri (PTKI) Medan through fermentation method using commercial tempe’s yeast. Durian outer skin, cassava outer skin and corncobs were obtained from local wastes.

2.1. Production of Virgin Coconut Oil (VCO)
Mature coconut fruit was cut and separated coconut meat and water. Then coconut meat was grated and obtained 940 gram. As much 940 mL of coconut water was mixed with coconut meat, then it was squeezed using filter woof and produced coconut milk. Coconut milk was placed in separating funnel and let it until formed three layers. The very bottom layer was discarded and poured as much 2.5 gram of yeast and fermented for 24 hours. Oil and coconut milk formed after 24 hours and collected oil (VCO) and centrifuged with 3000 x g for 5 min.

2.2. Preparation of Activated Carbon
Durian outer skin, cassava outer skin, and corncobs as local wastes were cleaned then cut into small pieces. All sample was dried by sunlight for three days and placed them in a container. It was burnt for 3 hours until formed charcoal or carbon. Furthermore, carbon was placed in desiccator and mashed up until 100 mesh. Carbon was activated with sodium carbonate 0.1 N with ratio 1:2 (m:v) for 30 min and over-heated in furnace for 30 min then cooled down in desiccator. The activated carbon was washed with aquadest to remove activator and heated in oven to remove water content.

2.3. Adsorption Technique
An experiment was performed in 250 mL Erlenmeyer flask with 50 mL VCO and mixed with 1 gram, 2 gram, and 3 gram activated carbon, respectively. It was shaked with bar stirrer for 24 hours. The supernatant was used to determine FFA and AN.

2.4. Determination of Free Fatty Acid (FFA) and Acid Number (AN)
The titration method was performed to determine FFA and AN for VCO in condition previous and after adsorption process with activated carbon. As much, 5 gram of VCO was placed in Erlenmeyer flask and mixed with 50 mL ethanol p.a. Then it was heated for 10 min and shaked vigorously to dissolve FFA. After it was cooled, then titrated with 0.1 N KOH in addition to phenolphthalein until reach permanent faint pink color. The amount of FFA and AN were calculated using this following formula

$$\text{Where} \ C \ \text{is the concentration of potassium hydroxide for standard titration (N),} \ \text{V is titration volume of potassium hydroxide (mL),} \ \text{Mw is the molecular weight of fatty acid (gram/mole),} \ \text{M is the mass of VCO (gram), and} \ \text{CF is the conversion factor. VCO contains most of lauric acid as major fatty acid composition [13]. Therefore this study used lauric acid with conversion factor 2.8.}$$
3. Results and Discussion

VCO, which directly produced through fermentation method was first analyzed the FFA and AN as one parameter to know the VCO quality. %FFA for VCO before conducted adsorption process was 0.4% and the acid number was 1.12, as shown in Table 1. The value of %FFA from this sample was higher than 0.2% for commercial VCO and not suitable for Indonesia’s National Standard for VCO (max 0.2%). It was included as non-consumable VCO because of many factors such as some contamination of other microbes or not sterile and not in good condition of raw materials. Oxidation reaction in VCO might have occurred while in storage conditions [14]. Oxidation could be delivered free fatty acids because it attacked unsaturated fatty acids in the oil and formed peroxide [15]. FFA might be formed because of hydrolysis reaction. This reaction could damage oil because of the amount of water in oil, which accelerated by heat, acidity, and impurities.

Table 1. %FFA and acid number of VCO before immersion with activated carbon.

| Sample  | %FFA | Acid Number |
|---------|------|-------------|
| VCO     | 0.4  | 1.12        |

Three different sources of carbon from local wastes named durian outer skin, cassava outer skin, and corncobs were chosen as candidate for manufacturing activated carbon as bio-adsorbents. All sample was collected from local waste and easy to find them in large amount. Utilization of local waste is one way to reduce waste in Indonesia, especially in North Sumatera, Medan, and recycling them into a new form of a good product. Based on the result of titration, the %FFA of VCO, which treated with activated carbon in various mass was shown in Figure 1.

In Figure 1, the profile of %FFA content in VCO after immersion with various mass (1-3 gram) of activated carbon for 24 hours. The activated carbon has successfully reduced %FFA in VCO with various ranges. Activated carbon made from cassava outer skin was the best one to reduce %FFA by using 3 gram and %FFA was reduced from 0.4% to 0.24%. It was obtained that activated carbon made from cassava outer skin could reduce %FFA as much 0.16%. This value of %FFA was closer to Indonesia’s Standard National with max 0.2% of FFA in VCO. Based on Figure 1, it was obtained that activated carbon made from durian outer skin and corncobs has also reduced %FFA from VCO, but the value of %FFA decrease after immersion was not higher than using activated carbon made from cassava outer skin. Activated carbon made from durian outer skin could be reduced %FFA of VCO as much 0.07% and from corncobs as much 0.1%.
The result of acid number of VCO could be determined directly with the same method, and the result was shown in Figure 2. The profile of acid number of VCO was same with the profile of %FFA. Activated carbon made from outer cassava skin was able to reduce the highest value of acid number of VCO as much 0.448. All activated carbon source was a good candidate to reduce %FFA of VCO but different ability in the adsorption process. Durian outer skin and corncobs were able to reduce %FFA of VCO as much 0.1% using mass of 1 gram, but it was different using mass of 2 gram which corncobs was better to reduce %FFA of VCO. More mass of activated carbon used, more %FFA of VCO reduced.

Activated carbon was one material that could be reduced %FFA and acid number of VCO and made better VCO quality. Local wastes were modified into carbon or charcoal and activated using chemicals; therefore it has ability to adsorb oil. This activated carbon called bio-adsorbent has a wide surface area to contact with the sample and increased adsorption capacity.

4. Conclusion
This study presents production of VCO in lab-scale using fermentation method, synthesized activated carbon made from some local wastes such as cassava outer skin, durian outer skin, and corncobs and improve VCO quality using activated carbon through determination of %FFA and acid number. The result of this study delivered that outer cassava skin was the best carbon source for synthesized activated carbon and able to reduce the highest value of %FFA and acid number of VCO. More mass of activated carbon used, more %FFA, and acid number of VCO reduced.

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