Purification of Used Cooking Oil Using Activated Carbon Adsorbent from Durian Peel

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Abstract. Repeatedly use of cooking oil can cause increasing free fatty acids and peroxide value contained. Therefore, continuous exposure to used cooking oil has known resulting hazardous impacts on the environment and also to human health. Hence, it is necessary to purify used cooking oil before it is discharged to the environment. Durian peel contains high cellulose ranging from 50% - 60%, which is eligible to be used as carbon adsorbent’s raw material for used cooking oil purification. This study produced a kind of carbon adsorbent from durian peel through a carbonization process that lasted for 2 hours at 500°C combustion temperature with a chemical activation using H2SO4 1 N. This study was carried out with the adsorbent weight of 6 grams and various contact times of 30, 60, 90, 120, and 150 minutes. The most favorable results obtained after contact time was 0.0637% of free fatty acid, 0.41 meq O2/kg of peroxide value, and 0.9022 gr/ml of density, respectively, at 150 minutes contact time.

Keywords: Durian Peel, Activated Carbon Adsorbent, Cooking Oil Purification

1. Introduction

In Indonesia, durian (Durio zibethinus murr) is a kind of seasonal fruit that is very well known as “the king of fruits” has a very distinctive aroma, thorny peel, abundant availability and is highly demanded by the public during its season. With its enormous amount, the environmental problem arises, that is the accumulation of durian peels. Proportionally, durian peel contains lignocellulose consisting of cellulose of 50%, 60%, lignin of 5%, and starch of 5% [1]. Lignocellulose found in any raw materials can be used to make activated carbon. The utilization of activated carbon as an effective and affordable adsorbent has been investigated for many years. The previous study shows that activated carbon as a ceramic adsorbent is highly useful to remove heavy metals pollutant contained in acid mine drainage [2]. Besides, ceramic composite adsorbent of zeolite-activated carbon can be an alternative to treat wastewater containing heavy metals derived from the pulp and paper industry [3].

On the other hand, waste cooking oil handling is still considered insufficient. The use of cooking oil more than surely will darken its color and releases a kind of odor. Besides, the number of peroxides and free fatty acids also become higher. The changes in the chemical properties of cooking oil are due to hydrolysis, polymerization, and oxidation, these are caused by heating cooking oil at a high
temperature accompanied by air contact [4]. These conditions are resulting in hazardous impacts on human health. Therefore, it is necessary to purify used cooking oil before it is discharged to the environment.

There are various efforts to purify used cooking oil, one of those is by using adsorption process. There are several studies regarding the adsorption process of used cooking oil using H$_2$SO$_4$ activators with various raw materials. A previous study used ketapang activated carbon as an adsorbent for used cooking oil purification using H$_2$SO$_4$ activator with the most favorable results on free fatty acids of 0.78% [5]. A previous study also examined the quality of used cooking oil after using carbon adsorbent from bagasse with H$_2$SO$_4$ as the activator. It obtained the most favorable peroxide value of 6.4295 meq/kg [6]. Also, another study utilized corn stalks for used cooking oil treatment using two different activators of HNO$_3$ and H$_2$SO$_4$, the best results obtained were 0.0548% for FFA value and 14.78 meq/kg for peroxide value [7]. There are many kinds of activated carbon from various raw materials have been used for adsorption process of used cooking oil purification, but unfortunately, there are some other results that do not meet Indonesian standard quality (SNI 7709: 2012) [8]. This research is aimed to investigate the quality of used cooking oil using activated carbon adsorbent from durian peel. The result is expected to produce an environmentally friendly used cooking oil using a more economical process.

The proximate analysis of durian peel shows that its water content is 14.5%, ash is 0.4%, flying substances is 64.4%, fixed carbon is 20.7%, and heating value is 13.8 mj/kg [9]. The carbon content in durian peel meets the requirement to be used as the raw material for activated carbon. The repeated use of cooking oil for frying process accompanied by heating with high temperatures can cause damages to its chemical contents due to changes in the chemical composition regarding the oxidation of components in the cooking oil. One of the characteristics of the oxidation reactions is the color of the cooking oil turns darker as cooking oil is used more often. Also, FFA value is to measure the oxidation and hydrolysis reactions in the cooking oil, whereas the amount of water contained in the cooking oil is because of its hydrolysis process. Repeatedly used cooking oil can also cause foam formation, increased viscosity, and density due to unwanted components from the results of hydrolysis, oxidation, and polymerization reactions in the cooking oil [10].

2. Material and Method

2.1. Making Activated Carbon

A batch of durian peel is washed using deionized water to remove its impurities, then cut into small pieces and dried for three days with the help of sunlight. Then the durian peel is carbonized in the furnace for 2 hours with a combustion temperature of 500 ºC. The carbon resulted from durian peel is then smoothed with a grinder to refine its size. Afterward, durian peel carbon is activated using a 1 N H$_2$SO$_4$ solution. The activation process lasts for 24 hours. Activated carbon is washed with deionized water until pH 7 and then filtered. The activated carbon is dried to remove its water content at 110 ºC for 2 hours. Lastly, the activated carbon is mashed and sifted using a sieve measuring 0.328 mm.

2.2. Purification Process

500 grams of used cooking oil is weighed and then mixed with deionized water with the composition of (1:1). The mixture of oil and water is heated to reduce its volume to half of the initial. Next, the oil layer is taken and deposited for 1 hour using a separating funnel. After that, the oil layer is filtered to separate the remaining impurities. Used cooking oil of 450 gr is heated at 35 ºC for odor removal process, 18 ml of 16% NaOH was added to used cooking oil and stirred for 10 minutes with a heating temperature of 40 ºC. The mixture is left for 10 minutes until it cools down, the mixture of oil and NaOH will produce soap, and it has to be removed from the oil. 200 mL of used cooking oil is mixed and stirred with 6 gr of activated carbon at room temperature, the contact times between used cooking oil and activated carbon are varied of 30, 60, 90, 120, and 150 minutes. Finally, purified cooking oil is filtered with filter paper for analysis.
3. Results and Discussion

Table 1. Free fatty acids at various contact time

| Used Cooking Oil (gr) | Adsorbent Weight (gr) | Contact Time (min) | Free Fatty Acids (%) |
|-----------------------|-----------------------|--------------------|----------------------|
|                       |                       | 30                 | 0.1513               |
|                       |                       | 60                 | 0.1311               |
| 450                   | 6                     | 90                 | 0.1085               |
|                       |                       | 120                | 0.0839               |
|                       |                       | 150                | 0.0637               |

Figure 1. Effect of Contact time on Free Fatty Acids Percentage

3.1. Free Fatty Acids

Free fatty acids are produced in any of the steps of the process by hydrolytic reactions. Free fatty acids contained in palm oil are normally < 1%, the higher the level of free fatty acids can reduce the quality of oil, the value of free fatty acids > 1% causes oil becomes rancid, and it can be tasted on the surface of the tongue [11]. Besides, the free fatty acid is known as the cause of metabolically unhealthy obesity, and type diabetes to human and likely contributes to end-stage kidney disease irrespective of the underlying kidney disease [12].

Based on figure 1 and table 1, the values of free fatty acids tend to get lower along with longer contact time. The longer the contact time, the smaller the value of free fatty acids, this is because the long contact time causes more intense contact between the surface of the adsorbent and the used cooking oil. In addition, the more mass of adsorbent is used, the more surface of the adsorbent is produced so that the adsorbent can adsorb more free fatty acids. It was stated that the better the adsorption process is because, the more surface area where the adsorption process takes place and the longer contact time causes the freer fatty acids bound by the adsorbent’s surface, and the reactions took place were both oil hydrolysis and unsaturated fatty acid oxidation.

The carbon is activated using H$_2$SO$_4$ 1 N, where the carbon is immersed in H$_2$SO$_4$ solution to increase its pores length and width, which are covered by materials or organic metal oxide components. Thus, these carbon pores play a role in adsorbing impurities so that it can reduce the free fatty acids contained in used cooking oil. Based on the analysis results, the free fatty acids contaminant is significantly reduced after the adsorption process. This occurs due to the more prolonged the use of the adsorbent, the higher the level of adsorption. The adsorbent adsorbed
impurities into the carbon pores during the adsorption process, and the activation process is resulting in increases the rate of adsorption.

Table 2. Peroxide value at various contact time

| Used Cooking Oil (gr) | Adsorbent Weight (gr) | Contact Time (min) | Peroxide value (meq O₂/kg) |
|----------------------|-----------------------|--------------------|---------------------------|
| 30                   | 2.28                  | 30                 | 2.28                      |
| 60                   |                       | 60                 | 2.16                      |
| 450                  | 6                     | 90                 | 1.80                      |
| 120                  |                       | 120                | 1.72                      |
| 150                  |                       | 150                | 0.41                      |

Figure 2. Effect of Contact time on Peroxide value

3.2. Peroxide value

A chloroform-acetic acid mixture is used to dissolve the used cooking oil, and this mixture is subjected to an excess of iodide via a saturated solution of potassium iodide. The peroxides present oxidize the iodide to iodine, and the iodine is then titrated to a colorimetric endpoint using sodium thiosulfate with starch as an indicator. The amount of iodine produced is directly proportional to the peroxide value. In general fresh oils, the peroxide value is >10 mEq/Kg while peroxide values in the 30-40 mEq/Kg range are generally associated with a rancid taste. Therefore, peroxide value in oil is also used to determine the damage degree to oil. Table 2 and figure 2 above show that the graph represents peroxide value gradually decreases with longer contact time. The decrease in peroxide value due to the termination of the double bonds in oil. Besides that, peroxide contains oxygen as a polar compound so that it is more comfortable to bound to the adsorbent [13]. Thus, the lower the peroxide value, the smaller the damage to the oil.

The carbon used in this study is activated with H₂SO₄ 1 N so that it has a large surface area and pores to be able to bind and adsorb more peroxide compounds in the oil. Also, the adsorption process does not use heating, so that the decrease in peroxide value is not inhibited [14] if the adsorption process is accompanied by heating, it actually can cause the reformation the peroxide compounds. Increasing peroxide values occurs because of the oxidation process of unsaturated fatty acids in oil with the aid of oxygen.
From the analysis of peroxide value, it can be seen that the adsorption process uses activated carbon from durian peel resulting in peroxide values that meet Indonesian Standard (SNI 7709: 2012) [8] which is <10 meq O₂/kg with 30 minutes contact time. Thus, the carbon-based adsorption process is considered effective for the adsorption process.

Table 3. Free fatty acids at various contact time

| Used Cooking Oil (gr) | Adsorbent Weight (gr) | Contact Time (min) | Density (gr/ml) |
|-----------------------|-----------------------|--------------------|-----------------|
| 30                    | 0.9085                | 30                 | 0.9085          |
| 60                    | 0.9073                | 60                 | 0.9073          |
| 450                   | 6                     | 90                 | 0.9070          |
| 90                    | 0.9062                | 90                 | 0.9062          |
| 120                   | 0.9022                | 120                | 0.9022          |
| 150                   |                       | 150                |                 |

Figure 3. Effect of Contact time on Density

3.3. Density

Based on figure 3, it can be seen that the density of used cooking oil decreases quite sharply. The decrease is because the adsorbent has adsorbed significant amount of the impurities contained in used cooking oil, therefore the molecular bonds in the oil become reduced causing the removal of odors and dark coloring in the oil [15], determination of density is influenced by the water content and the level of impurities attached to oil. From the density analysis of used cooking oil after being adsorbed using activated carbon shows that used cooking oil for all samples does not meet the Indonesian Standard (SNI 7709: 2012) [8] which is 0.900 gr/ml at the mass of adsorbent 6 gram with 150 minutes contact time.

4. Conclusions

The results of the analysis of the value of free fatty acids, peroxide values, and the best density using the adsorbent without activating, respectively, are at the contact time of 150 minutes and the mass of 6 grams of adsorbent is 0.0637%, 0.41 meq O₂/kg, and 0.9022 gr/ml. The results of the analysis of the value of free fatty acids, peroxide values, and the best density of the oil using the activated adsorbent are at the contact time of 150 minutes, and the mass of 6 grams of adsorbent is 0.0637%, 3.04 meq O₂/kg, and 0.9052 gr/ml.
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