DETERMINATION OF EFFECTIVENESS ABSORPTION OF THE RICE HUSK AND HAZELNUT SHELL TO PURIFICATION USED COOKING OIL

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Abstrak. Uji efektivitas daya serap arang aktif sekam padi dan cangkang kemiri terhadap penjernihan minyak goreng bekas telah dilakukan. Tujuannya untuk menentukan kemampuan daya serap dari arang aktif sekam padi dan cangkang kemiri terhadap penjernihan minyak goreng bekas. Arang cangkang kemiri dan sekam padi dibuat dengan suhu 400 °C selama 90 menit dan diaktivasi secara fisika dengan suhu 350 °C selama 1 jam. Setelah itu, arang aktif dari sekam padi dan cangkang kemiri diaplikasikan pada penjernihan minyak goreng bekas. Kadar air dan kadar abu kedua arang aktif yang dihasilkan sebesar masing-masing 3,398 % dan 6,667 % untuk arang aktif cangkang kemiri serta 3,355 % dan 8,667 % untuk arang aktif sekam padi. Setelah diaplikasikan pada penjernihan minyak goreng bekas, daya serap arang aktif cangkang kemiri dan sekam padi terhadap bilangan peroksida sebesar masing-masing 66 % dan 59 % dari total 2,73 meq dalam sampel serta asam lemak bebas sebesar masing-masing 60,6 % dan 45,4 % dari total 0,33 % dalam sampel. Dengan demikian, dapat disimpulkan bahwa penggunaan arang aktif cangkang kemiri lebih efektif bila dibandingkan dengan arang aktif sekam padi pada penjernihan minyak goreng bekas.

***Kata kunci* :** absorpsi, karbon aktif, cangkang kemiri, sekam padi

Abstract. The effectiveness of the absorption of activated rice husk and hazelnut shells on the purification of used cooking oil has been carried out. The aim is to determine the absorption capacity of the active charcoal of rice husk and hazelnut shells to purify used cooking oil. Candlenut shell charcoal and rice husk are prepared with a temperature of 400 °C for 90 minutes and activated in physics with 350 °C for 1 hour. After that, activated charcoal from rice husk and candlenut shells was applied to purifying used cooking oil. Water content and ash content of both activated charcoal were 3.398 % and 6.667 % for candlenut shell charcoal and 3.355 % and 8.667 % for activated rice husk charcoal. After being applied to the purification of used cooking oil, the absorption of candlenut shells and rice husk on peroxide numbers was 66 % and 59 % respectively from the total 2.73 meq in samples and free fatty acids of 60.6 % and 45.4 % of the total 0.33 % in the sample. Thus, it can be concluded that the use of candlenut shell charcoal is more effective when compared with activated rice husk charcoal in purifying used cooking oil.

Keywords: absorption, activated carbon, hazelnut shell, rice husk.

INTRODUCTION

Charcoal is a porous solid material that is produced through carbonization from carbon-containing materials (Mody Plate, 2011). According to Sudrajat P and Tjipto Utomo (2005), activated charcoal is activated the charcoal by immersion in the chemicals or by flowing hot steam into the material so that the material pores become more open. Because of the more active charcoal surface area, the higher absorption of the material against gas or liquid. Meanwhile, according to P. Hariprasad et al., (2016) Activated carbon is a form of carbon that has been processed to make it very porous so that it has a very wide surface area.

Basically activated carbon is characterized by physical and chemical properties. The physical properties of activated carbon, such as ash content and moisture content can affect the use of activated carbon. SNI-06-3730-1995 describes the requirement for 15% maximum activated carbon water content and 10% maximum ash content. While the specific surface area of activated carbon is classified as a chemical property. Furthermore, the porous structure of activated carbon can be characterized by various techniques such as gas adsorption (N_2, Ar, Kr, CO_2) or steam (benzene, water). To determine the ash content, the temperature must be below 600˚C to minimize evaporation of inorganic elements, and also allow ash to be in suitable conditions for further examination (Al-Qodah Z. *et al*., 2009).

The amount and size of the material to be absorbed by activated carbon depends on the pore size and surface area of the activated carbon. According to Aznar S.J. (2011) and Al-Qodah Z. *et.al*. (2009), Pores are a type of cavity or empty space that is connected to the surface of a solid and allows the release of liquid into or from the material. Basically, pores are classified into three groups according to the International Union of Pure and Applied Chemistry (IUPAC), namely Micropore (D 0.04-2 nm), Mesopores (D 2-50 nm), and Macropore (D> 50 nm) (Ansar, 2012 in Santi, 2012 and Aznar SJ, 2011). Micropore is the most important cavity because the smaller size shows a very high surface area, so it can produce a higher absorption capacity. (Aznar S.J., 2011 and Al-Qodah Z. *et al*., 2009). Mesopores has a dual function because with a diameter of 2-5 nm it can absorb / store molecules that are sized between macropore and micropore (Aznar S.J., 2011). In carbon, mesoporous can be formed by micropore enlargement (Al-Qodah Z. *et.al*., 2009). Macropores are large pores that function to facilitate the absorption of micropores and mesopores that are deeper than micropores on activated carbon. Even so, macropores can also hold large molecules, which result from the decomposition of organic matter.

Properties and quality assay of the activated charcoal produced, both from the process of activating hazelnut charcoal and from the activation process of rice husk charcoal has been carried out. For example, activation of pecan shell charcoal with heat activator and steam H_2O, $CaCl_2$, KOH, and activation of rice husk charcoal with an activator of $ZnCl_2$ solution (Lempang et al., 2012;

Darmawan et al., 2009; Zakir *et al*., 2013). According to Nur R. (2012) and Darmawan et al. (2009), carbon activation aims to enlarge the surface area of carbon by opening closed pores so that it can increase absorption.

The application of hazelnut shells and rice husks has been carried out. For example hazelnut shells as adsorbents to toluene gas (Wuntu *et al*., 2013), as raw material for briquettes (Patabang Daud, 2009), for purifying used cooking oil (Botahala L. *et al.*, 2016), and others. While the application of rice husk as an adsorbent to methylene blue dyes (Taba *et al*., 2013), as silica in red brick (Indra *et al*., 2013), as an additive to cement production (Botahala L. *et al*., 2013), and others.

Cooking oil is included in one of the food items that are needed by the society to fulfill daily needs with oil quality based on SNI-01-3741-1995 concerning cooking oil. The need for cooking oil is increasing with the increasing population in Indonesia, so the used cooking oil produced is increasing as well (Botahala L. *et al*., 2016). The use of cooking oil both for industry and households, produces used oil which still contains high enough fatty acids because it is used repeatedly (Wijayanti Kartika, 2015; Evika, 2011). Decomposition of oil component can be observed visually, namely the appearance of odor, brownish color and rancid taste caused by oil oxidation. The greater the level of free fatty acids, the lower the quality of the cooking oil (Nasir et al., 2014). Continuous use of used cooking oil harmful for human health, cause cancer, deposition of fat in blood vessels (artherosclerosis) and decrease fat digestibility, and other consequences is to reduce the intelligence of the next generation (Rukmini Ambar, 2007; Evika, 2011).

Thus, in this study a comparison of water content and ash content will be carried out, as well as absorption between the active charcoal of rice husk and hazelnut shell charcoal which is applied to the purification of used cooking oil.

MATERIAL AND METHOD

Materials and Tools

This research was conducted in January - March 2017 at the Chemistry Laboratory, Faculty of Teacher Training and Education, University of Nusa Cendana Kupang. The materials used in this study were rice husk and hazelnut shells and used cooking oil taken from Alor Regency, 16% Sodium Hydroxide (NaOH), Acetic Acid ($C_2H_4O_2$), chloroform ($CHCl_3$), saturated Potassium Iodide (KI) solution, Sodium Thiosulfate ($Na_2S_2O_3$), 1% starch solution, indicator pp, aquades and ethanol. The tools used in this study consisted of Muffle Furnace, grinder, 100 mesh sieve, Stirrer and Magnetic Stirrer, Stirring Rod, Universal Indicator Paper, Glass Cup, Erlenmeyer, Measuring Cup, Drop Pipette, Analytical Scales, Porcelain Saucer, Separate Funnel, Oven Dryers, cans and Pumpkin Measure.

Procedure

1. Making and testing hazelnut shells and rice husks

Rice husk and hazelnut shells, which are clean and dry, are heated in a furnace (Muffle Furnace) at 400 ℃ for 90 minutes until carbon is formed. After that it is cooled for 24 hours in the Muffle Furnace. then the charcoal is released and milled using pengilingan to form a powder. Charcoal is activated physically by putting it in a can and then given a small hole in the can lid after that the charcoal is heated at 350 ° C for 1 hour then the activated charcoal is ready to use.

1.1 Determination of Water Content

Weighing activated charcoal weighing 1 gram each and putting it in a dried porcelain dish. After that it was heated in an oven at 100 ° C for 3 hours, then the charcoal was cooled in a desiccator and weighed. Water content can be calculated by the equation according to Surest et al. (2008) as follows:

$$\%\ Water\ Content = \frac{a-b}{a} \times 100$$

Where:
a = cup weight + sample before heating (gram)
b = cup weight + sample after heating (gram)

1.2 Determination of Ash Content

Weighing activated charcoal weighing 1 gram each and putting it in a dried porcelain dish, after that it was heated in Muffle Furnace at 500 ° C for 3 hours, then the charcoal was cooled in a desiccator and weighed. Ash content can be calculated with the following equation:

$$\%\ Ash\ Content = \frac{c-a}{b-a} \times 100$$

Where:
a = weight of empty cup (gram)
b = cup weight + sample before heating (gram)
c = cup weight + sample after heating (gram)

1.3 Analisys of used cooking oil

This procedure is carried out by analyzing the quality of used cooking oil, as done by Padalowa N. (2015) with several modifications according to the research objectives. The tests are carried out in two stages, namely the stages of purifying used cooking oil and the testing phase.

The purification stage is intended to clean used cooking oil from other spices and impurities. While the testing phase is intended to test the effectiveness of activated charcoal absorption using the titration method.

1.4 Purification stages

1.4.1 Despicing process

A total of 250 mL of used cooking oil is added to the water with the composition of oil: water (1: 1), put into a 500 mL glass cup. Then it is heated at a temperature of 1000C until the water in the glass cupper is half. The mixture is left in a separating funnel for 1 hour, then the water fraction at the bottom is separated so that oil is free of water, after which filtering is carried out with filter paper to separate the remaining impurities.

1.4.2 Neutralization process

As much as 150 mL of cooking oil from the removal of seasonings are put in a 500 mL glass cup and heated while sterilized to 35 ° C, then 6 mL of 16% NaOH solution, then cooled for 10 minutes and filtered with filter paper and then purification process.

1.4.3 Purification process (Bleaching)

The purification process is done by using sample variables as determined based on the matrix in Table 1.

Table 1. Research matrix for the purification process (Bleaching)

No	Sample Code	Sample Name
1	S0	Used cooking oil
2	S1	Used cooking oil + activated charcoal from hazelnut shell
3	S2	Used cooking oil + activated charcoal from rice husk

Each of 10 grams of activated charcoal was mixed with 50 mL of used cooking oil neutralized at a temperature of 100 ° C in 60 minutes. Then the solution is filtered and analyzed for quality.

1.5 Testing stages

1.5.1 Determination of Peroxide Numbers

A total of 5 mL of cooking oil was put into erlenmeyer then added 30 mL of acetic acid - chloroform (3: 2), shaken until the ingredients were completely dissolved, then added 0.5 mL of saturated KI solution. Let stand for 1 minute while shaking after that 30 mL of distilled water was added. The mixture was titrated with 0.1 N Na2S2O3 until yellow, added 0.5 mL of 1% starch solution and titrated again until the blue color began to disappear. The peroxide number expressed in milliequivalents of peroxide is calculated from every 1000 grams of the sample.

$$\text{Peroxide Numbers} = \frac{\text{ml } Na_2S_2O_3 \times \text{N. } Na_2S_2O_3 \times 1000}{\text{sample (gram)}}$$

$\text{ml } Na_2S_2O_3$ = Titran volume $Na_2S_2O_3$
$\text{N. } Na_2S_2O_3$ = normality of solution $Na_2S_2O_3$ (= 0,1)

1.5.2 Determination of Free fatty acids

A total of 10 mL of cooking oil is put into a 250 mL erlenmeyer, then 25 mL ethanol is added and heated at 40 ° C, then 2 drops of pp indicator are added, titrated with 0.1 N NaOH solution until the color pink and not lost for 30 seconds. Free fatty acid (% FFA) is calculated by the formula below:

$$\%\,FFA = \frac{\text{mLNaOH} \times \text{N NaOH} \times \text{BM. palmitat acid}}{\text{sample weight} \times \ 1000} \times 100$$

%*FFA* : Free fatty acid content
mL NaOH : Volume of NaOH titrant
N NaOH : Normality of NaOH Solution (= 0.1)
BM : Molecular palmitat acid weight (256.42 g / mol)

1.5.3 Determination of water content

Erlenmeyer is heated in an oven at 105 ° C for 1 hour. Then cool for 15-20 minutes at room temperature. Then erlenmeyer is weighed, the results are recorded and repeated 3 times until the results are constant. A total of 2 mL of sample was put into erlenmeyer, then heated in an oven at 105 ° C for 2 hours. After that it is cooled and weighed erlenmeyer containing the sample. Weighing is done 3 times until a constant weight is obtained. Water content is calculated based on the equation:

$$\%\ Water\ Content = \frac{a-b}{a} \times 100$$

Where:
a = cup weight + sample before heating (gram)
b = cup weight + sample after heating (gram)

RESULTS AND DISCUSSION

1. Active charcoal quality examination

After the process of making activated charcoal with physical activation, the results of examination the water content and ash content of each sample are shown in Table 2.

Table 2. Data on the results of examination of hazelnut shell charcoal and activated charcoal from rice husk.

Sample	Water content (%)	Ash content (%)
Activated charcoal from hazelnut shell	3,398	6,667
Activated charcoal from rice husk	3,355	8,667

Table 2. shows that the water content and ash content of both activated charcoal samples meet the SNI requirements so that they can be used. Low water content and high ash content are influenced by the carbonization process with a temperature of 400 ° C and followed by a physical activation process with a temperature of 350 ° C. The physical activation process leaves impurities in charcoal which can inhibit the evaporation process, it can also increase the amount of ash in the sample.

The water content in both activated charcoal is influenced by differences in the texture (softness) of the two samples. When there is a process of evaporation of water at a temperature of 100 ° C, the rest of the water which is yield of the activated physically in the activated charcoal shell is trapped by a hard pore wall. On the contrary, the remaining water from physical activation in the activated charcoal of rice husk easily evaporates due to the softness of the pore wall. This is what causes the difference in water content in the two active charcoal, namely the water content in the activated charcoal shells higher than the water content in the activated charcoal of rice husk.

The ash content which is the mineral content of the material components contained in both activated charcoal was also influenced by differences in the texture (softness) of

the two samples. When a carbonization and activation process occurs, leaving the organic components that are not completely burned in the two samples. So that this component will turn into ash when the sample is reheated. The high ash content found in activated charcoal from rice husks can reduce the absorption of activated charcoal both in solution and gas. The mineral content contained in ash such as potassium, calcium, sodium and magnesium will spread and stick to the activated pore charcoal.

From the data from the activated charcoal activation of the two samples, it can be said that the absorption capacity of candlenut shell charcoal is better than the absorption of activated charcoal from rice husk. For proof, it is applied to clarifying used cooking oil.

2. Examination of activated charcoal shells and rice husks against used cooking oil

2.1. Peroxide Numbers

The results of examination the used peroxide number of used cooking oil before and after purification using the activated charcoal shells and activated rice husk charcoal can be seen in Table 3.

Table 3. Data on the results of examination of used cooking oil peroxide

No	Sample Code	Peroxide Numbers (meq)
1	S0	2,73
2	S1	0,93
3	S2	1,13

Table 3 shows that there is a decrease in peroxide number from the bleaching process on S1 by 66% and at S2 by 59% as seen in Figure 1. Or in other words the number of peroxide results from the bleaching process remaining at S1 is 34% and in S2 equal to 41%, as seen in Figure 2.

2.2. Free fatty acids

Data from the results of testing of free fatty acids on used cooking oil before and after purification using activated charcoal shells and activated rice husk charcoal are presented in Table 4.

Table 4. Data on the results of testing of free fatty acids in used cooking oil

No	Sample Code	Free Fatty Acid (%)
1.	S0	0,33
2.	S1	0,13
3.	S2	0,18

Table 4 shows that there was a decrease in the levels of free fatty acids resulting from the bleaching process on S1 by 60.6% and at S2 by 45.5% as seen in Figure 1. Or in other words the amount of free fatty acid results from the bleaching process left in S1 is 39.4% and in S2 is 54.5%, as seen in Figure 2.

2.3. Water content

Data from the results of testing the moisture content of used cooking oil before and after purification using activated charcoal from pecan shells and activated charcoal from rice husk are presented in Table 5.

Table 5. Data on the results of water content testing on used cooking oil

No	Sample Code	Water Content (%)
1.	S0	0,46
2.	S1	0,10
3.	S2	0,27

Table 5 shows that there was a decrease in water content from the bleaching process at S1 of 78.3% and in S2 of 41.3% as seen in Figure 1. Or in other words the amount of water content from the bleaching process remaining at S1 was 21, 7% and at S2 of 58.7% as seen in Figure 2.

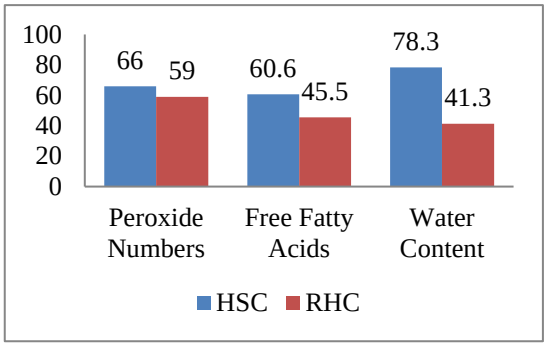

Figure 1. Decreasing concentration

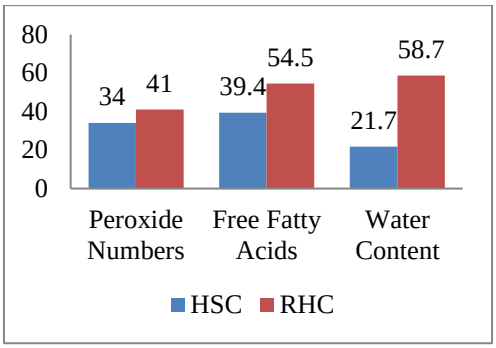

Figure 2. Concentration remaining

Figure 1 and Figure 2 describe that activated charcoal ash is very significant for the purification process. This is because candlenut activated charcoal has a large surface area and pores, so it can bind and absorb free fatty acid compounds, reduce the amount of peroxide and the amount of water from used samples of used cooking oil.

CONCLUSIONS

Candlenut activated charcoal and active rice husk charcoal meet the requirements of SNI 06-3730-1995. However, the absorption capacity of candlenut shell charcoal is better than the absorption capacity of activated charcoal of rice husk.

The concentration of peroxide numbers, free fatty acid levels and moisture content of used cooking oil absorbed by the activated charcoal from the shells is higher than the activated charcoal of rice husk.

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