

Effect Of The Contact Time Of Candlenut Shell Charcoal And H_3PO_4 Activator As On The Purification Process Of Used Cooking Oil

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Abstrak. Penelitian tentang pengaruh waktu kontak arang kulit kemiri dengan aktivator H_3PO_4 pada proses pemurnian minyak goreng bekas telah dilakukan. Tujuan penelitian ini untuk menentukan kemampuan cangkang kemiri yang diaktivasi dengan H_3PO_4 terhadap penjernihan minyak goreng bekas. Variasi jumlah cangkang kemiri yang digunakan adalah 1 gram, 2 gram, dan 3 gram serta variasi waktu kontak yakni 10 menit, 30 menit, dan 60 menit. Hasil penelitian menunjukkan bahwa aktivasi arang cangkang kemiri menggunakan H_3PO_4 memenuhi syarat SNI 16-3730-1995, sedangkan hasil penjernihan minyak goreng bekas dengan jumlah arang aktif sebanyak 2 gram pada waktu 60 menit menghasilkan penurunan bilangan peroksida sebesar 64,58% dan asam lemak bebas sebesar 54,84%.

Kata kunci: arang aktif, minyak goreng bekas, asam lemak, aktivasi kimia, H_3PO_4 .

Abstract. Research on the effect of the contact time of candlenut shell charcoal and H_3PO_4 activator on the purification process of used cooking oil has been conducted. The purpose of this study was to determine the ability of candlenut shells activated with H_3PO_4 against purifying used cooking oil. The variation of the number of candlenut shells used is 1 gram, 2 grams, and 3 grams, and the variation of contact time is 10 minutes, 30 minutes, and 60 minutes. The results showed that the activation of hazelnut shell using H_3PO_4 fulfills SNI 16-3730-1995, while the results of used cooking oil purification with 2 grams of activated charcoal in 60 minutes resulted in the decrease of peroxide number of 64.58% and free fatty acids of 54, 84%.

Keywords: activated charcoal, cooking oil, fatty acids, chemical activation, H_3PO_4 .

INTRODUCTION

Cooking oil is one of the basic human needs as a food processing material that serves to improve the appearance and physical texture of food, provide a savory taste and add nutritional value (Ketaren, 2005 in Aisyah et al., 2010).

Oil is a triglyceride compound produced by condensation of 1 glycerol molecule with 3 molecules of fatty acids. According to Kusnander (2010), the bond formed is between the carboxyl group on fatty acids and the hydroxyl group on glycerin. Each formation of covalent bonds

will release one water molecule so that the reaction is called the condensation polymerization reaction. Because glycerol has three hydroxyl groups, glycerol can bind to a maximum of three fatty acid chains and can release a maximum of three water molecules to form triglycerides. The triglyceride formation reaction can be seen in Figure 1.

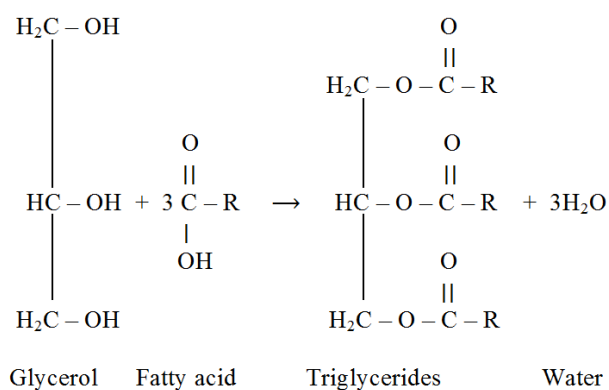


Figure 1. Formation of simple triglyceride

The nature of oil resistance is very dependent on its constituent components, especially the content of fatty acids and non-fat in the form of impurities (Raharjo, 2011). Fatty acids are generally increasingly reactive to oxygen by increasing only the number of double bonds in the molecular chain (Suroso, 2013). The speed of oxidation of fat left in the air will increase with the increase in temperature and decrease with the decrease in temperature (Taufiq M., 2007).

Peroxides are groups of compounds that have a single oxygen-oxygen (O – O) bond. Peroxide ion is O_2^{2-} anion, which also has a single oxygen-oxygen bond. These ions are very basic, and often present as impurities in ionic compounds. Pure peroxides containing only cations and peroxide anions are usually formed by burning alkali metals or alkaline earth metals in the air or oxygen (Anonymous, 2019). Cooking oil quality standards, according to Anonymous (2013) as listed in Table 1.

Table 1. Quality standards for cooking oil

No	Criteria	Requirements
1	Smell	Normal
2	Colors	Normal
3	Number acid	Max. 0,6 mg KOH/g
4	Pelican oil	Negative
5	Water content	Maximum 0,15%
6	Free fatty acid	Maximum 2 %
7	Peroxide number	Maximum 1 10 meq/kg

Most fryers do not use new oil but use used cooking oil for further frying because it is considered more economical and economical. Oil damaged by oxidation and polymerization will produce compounds that are carcinogenic, as well as damage to some vitamins and essential fatty acids contained in oil (Istighfaro, 2010) which cause poisoning in the body and cause various diseases, such as diarrhea, deposition of fat in blood vessels, cancer, and reduce the value of fat digestion and can reduce the intelligence of the next generation (Widayat et al., 2006). For this reason, proper handling needs to be done so that the waste cooking oil waste can be beneficial and does not cause harm in terms of human health and the environment.

Research on the purification of cooking oil by using activated carbon as an adsorbent has been widely carried out, for example by Wahjuni et al. (2008) using activated carbon of rice husk ash with KOH as activator reduced peroxide rate by 84.4% from traditional coconut oil, Istighfaro (2010) and Aisyah et al. (2010) using *Moringa oleifera* activated carbon with NaCl as activator reduced the peroxide number by 48% and 31.4% of used cooking oil, respectively. Botahala et al., (2016) have conducted research on the purification of used cooking oil using candlenut shells with HCl as an activator. Botahala et al. (2019) have also conducted research on the purification of used cooking oil using candlenut shells and rice husk, with the result that the absorption of candlenut shells is better when compared to the absorption of rice husk.

Various studies on the use of activated carbon in various applications have been carried out, including the use of activated carbon from agricultural waste, namely rice husks as adsorbents (Zakir et al., 2011 and 2013) and candlenut shells as raw material for making charcoal (Bukasa et al., 2012 and Lempang et al., 2012). Research on active candlenut shell charcoal with H_3PO_4 activator has been conducted by Darmawan et al. (2009) with the results

of the analysis fulfills SNI 06-3703-1995. Application of activated carbon adsorption of candlenut shells against Fe metals in dug well water has been carried out by Botahala et al. (2018).

Charcoal is a porous solid material produced through the carbonization process of materials containing carbon (Lembang, 2014). Activated charcoal is charcoal that is activated by immersion in chemicals or by flowing hot steam into the material so that the pores of the material opened because of the more activated charcoal, the higher the absorbability of the material to a gas or liquid. The quality of activated carbon/charcoal based on the requirements of SNI-06-3730-1995 (Botahala, 2019) is as shown in Table 2.

Table 2. Quality Requirements for Activated Carbon

Requirements type	Parameters (%)
Water content	Max. 15
Ash content	Max. 10
volatile substances content	Max. 25
bonded carbon content	Max. 65

Activators are substances or chemical compounds that act as activating reagents, and these substances will activate carbon atoms so that the absorption is better (Dahlan et al., 2013). Activated carbon is obtained by combustion (carbonization) and activation (Botahala, 2019). Chemical activation is the process of breaking the carbon chains of organic compounds with the use of chemicals, while physical activation is the process of breaking the carbon chains of organic compounds through heating (Botahala et al., 2018). Chemical activation using activating ingredients such as phosphoric acid (H_3PO_4). Chemical activation is carried out by soaking charcoal in a solution of chemical compounds before heating (Manocha, 2003 in Lembang et al., 2012 and Dahlan et al., 2013).

MATERIAL AND METHODS

Materials

The materials used in this study were candlenut shells from Lembur Barat Village, Alor Regency, used cooking oil was taken from Alor Regency, Teluk Mutiara District, Mutiara, Aquadest, H_3PO_4 solution, 97% chloroform, a solution of Potassium Iodide (KI) 15%, Sodium Thiosulphate ($Na_2S_2O_3$) 0.1 N, acetic acid (CH_3COOH) 95%, Sodium Hydroxide (NaOH) 16%, 95% ethanol, and p.p. (phenolphthaline) indicator.

Methods

1. Manufacture of active candlenut shell charcoal

Candlenut shells that have been cleaned are then heated to a furnace at $500^\circ C$ for 90 minutes. Furthermore, the candlenut shell charcoal, which is produced from the burning of the Furnace, is cooled for 24 hours and mashed to powder form. Candlenut shell charcoal powder at sieved and activated with a 10% H_3PO_4 solution by soaking it for 1 day. The activated charcoal is then washed with distilled water until the pH of the laundry is neutral ($pH = 7$). The activated charcoal is then put into a porcelain cup and heated in the furnace at $400^\circ C$ for 2 hours. Furthermore, the water content and an ash content of the activated charcoal was tested based on research conducted by Botahala et al. (2016) with some adjustments for research purposes.

2. Determination of the water content

Activated charcoal weighed as much as 1 gram and be put into a dried porcelain cup, then be put in the oven at $100^\circ C$ for 2 hours. Then the sample is chilled in a desiccator and weighed. Moisture content can be calculated by the following equation:

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

Note:

a = weight of the cup + sample before heating (grams)

b = weight of the cup + sample after heating (grams)

3. Determination of the ash content

Activated charcoal weighed as much as 1 gram and put into a porcelain cup. After that, it is heated in the Furnace at 500 ° C for 3 hours, then chill in desiccant and weighed. Calculated ash content by the following equation:

$$\text{Ash content} = \frac{b}{a} \times 100\%$$

The results of the activated charcoal are then used in the process of used cooking oil purification.

4. Purifying Cooking Oil

The process of purifying used cooking oil is based on research conducted by Aisyah Siti et al. (2010) with some adjustments for research purposes.

5. The process of desciping/ removing herbs.

As much as 250 mL of used cooking oil was added to water with a ratio of oil and water is 1: 1. The mixture was added into a 500 mL glass beaker. Next, the container and sample are heated in an oven at 100 ° C until the water in the glass beaker remaining half from the initial volume. The mixture is put into a separating funnel and allowed to stand for 1 hour. The water fraction at the bottom is separated to obtain water-free oil. After that, filtering is done with filter paper to separate the remaining dirt. The filtering results was used in the neutralization process.

6. The process of neutralization.

As much as 150 mL of cooking oil resulting from seasoning removes put in an Erlenmeyer, heated in the temperature of 35 °C, then added 6 mL of 16% NaOH solution. The mixture was stirred for 10 minutes at 40 ° C, then cooled for 10 minutes and filtered. The neutralization results are then added of activated charcoal with a specific time variation for the purification of used cooking oil.

7. Purification process.

As much as 1 gram, 2 grams, 3 grams of activated carbon of candlenut shells, respectively, were interacted with 50 mL, which has been neutralized cooking oil, with a time variation of 10, 30, and 60 minutes. These purification results are used to determine the peroxide number and free fatty acids.

8. Analysis of the quality of the cooking oil

The process of purifying used cooking oil is based on research conducted by Aisyah Siti *et al.* (2010) with some adjustments.

9. Determination of the peroxide number.

Purification result cooking oil at each stage and neutralization results weighed 2,275 grams, put into a 250 mL Erlenmeyer, and then added 30 mL of 95% acetic acid solution and chloroform 97% (3: 2), shaken until homogeneous. Furthermore, the mixture was added 0.5% KI solution. Stirred for 1 minute, after is that added 30 ml of distilled water. The mixture is titrated with 0.1 N Na₂S₂O₃ until the yellow color is almost gone, then added 0.5 mL of 1% starch solution and titrated again until the blue color begins to disappear. Peroxide numbers can be calculated which expressed stated in milliequivalents in every 1000 gram sample with the equation:

$$\text{Peroxide number (meq/kg)} = \frac{\text{ml Na}_2\text{S}_2\text{O}_3 \times \text{N}_{\text{thio}} \times 1000}{\text{sample (g)}}$$

Note :

ml Na₂S₂O₃ = Titrant volume Na₂S₂O₃
N_{thio} = Normality solution of Na₂S₂O₃

10. Determination of free fatty acids (FFA).

Purification result cooking oil at each stage, and neutralization results were weighed 1.82 grams, put into a 250 mL Erlenmeyer, then 33 mL 95% ethanol was added and heated at 40 °C. After that, the

mixture was added 2 mL pp indicator, carried out titration with 0.05 M NaOH solution to the appear pink and not disappear for 30 seconds. Then Calculated free fatty acids (% FFA).

$$\% \text{ FFA} = \frac{\text{ml NaOH} \times \text{M NaOH} \times \text{BM Palmitic Acid}}{\text{sample weight} \times 1000} \times 100$$

Note:

- % FFA : Free Fatty Acid content
 mL NaOH : Volume of NaOH titrant
 M NaOH : Molarity of NaOH solution (mol/L)
 BM : Molecular weight of palmitic fatty acid (256 g/mol).

RESULTS AND DISCUSSION

After the process of making activated charcoal with chemical activation using H₃PO₄, obtainable the results of testing the

water content and ash content were 1.715% and 3.667%, respectively. This value has fulfilled the requirements stipulated in SNI so that this activated charcoal can be used in the process of used cooking oil purification.

The used cooking oil used in the purification process has a peroxide number of 1,054.95 meq/kg and a free fatty acid content of 1.55%. The peroxide number in this sample exceeds the SNI standard, which is a maximum of 10 meq/kg, while free fatty acid levels are still within normal limits because based on SNI standards a maximum of 2%. Furthermore, the results of testing activated charcoal for used cooking oil showed in Table 3.

Table 3. Data on the results of testing peroxide numbers and free fatty acids

Active Charcoal Mass (gr)	Contact Time (minutes)	Peroxide Number (meq/kg)	FFA Content (%)
1	10	654,94	0,56
	30	654,95	0,84
	60	698,90	0,56
2	10	435,65	0,70
	30	439,56	0,70
	60	373,63	0,70
3	10	404,40	0,70
	30	492,31	1,13
	60	703,30	0,56

From Table 3 it can be seen that the greatest decrease in peroxide number occurred in the addition of 2 grams of candlenut shell activated charcoal into the sample with a contact time of 60 minutes, from 1,054.95 meq/kg to 373.63 meq/kg or decreased by 64.58%. This result is different from the SNI standard, which sets a maximum of 10 meq/kg but has at least reduced the peroxide rate by 64.58% or more than 50%. Whereas the used cooking oil free fatty acids obtained in this study reached 1.55%. This does not affect oil damage based on SNI 3741-2013 (Anonymous, 2013), which sets a maximum of free fatty acid levels in cooking oil of 2%.

CONCLUSION

Activation of hazelnut shell charcoal using H₃PO₄ meets SNI 16-3730-1995, while the purification results of used cooking oil using 2 grams of activated charcoal in 60 minutes results in a decrease in the amount of peroxide 64.58%.

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