The synthesis of javanese bamboo charcoal for purifiying cooking oil

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Abstract. Synthesis of bamboo charcoal from Javanese bamboo has been carried out at a temperature of 400°C with a yield of 30.86%. The synthesis of javanes bamboo charcoal by heating process with activated using NaCl. Activated bamboo charcoal was characterized using reference to SNI 06-3730-1995 regarding technical activated charcoal including water content, volatile content, total ash content, carbon content, iodine absorption and absorption of methylene blue. Activated bamboo charcoal also characterized its functional groups using FTIR and morphology using SEM. The activated bamboo charcoal which has the characteristics of a water content of 4.36% (w/w), an ash content of 1.28%(w/w), a vapor content of 5.28%(w/w), a carbon content of 80.08% (w/w), an iodine absorption capacity of 1146.35 mg/g and the absorption capacity of Methylene blue 421.46 mg/g which according to SNI 06-3730-95 standards concerning activated charcoal. From the FTIR result activated bamboo charcoal shows an absorption at (1500-1600) cm$^-1$, indicating the presence of a C=O bond, the hydroxyl group which is bound O-H (3400-3500) cm$^-1$ and CO (1300-1400) cm$^-1$ which is capable of absorb color and free fatty acids. The morphological characteristics of activated bamboo charcoal are more porous than non-activated bamboo charcoal, thereby increasing its surface area and adsorption ability. The ability of activated bamboo charcoal in processing used cooking oil is able to reduce turbidity, color and odor, water content, acid number and peroxide number of cooking oil after the adsorption process. The result showed that the water content is 0.08% (w/w), peroxide number 5.45 mek O$_2$/Kg, FFA 0.24 mg KOH/g which fulfills SNI 3741: 2013 Standard.

Keywords: synthesis, javanes bamboo, charcoal

1. Introduction
Repeated use of cooking oil at relatively high temperatures (160 -180)$^\circ$C will cause damage. Various kinds of reactions can occur during the frying process such as oxidation reactions, hydrolysis, polymerization, and reactions with metals that can cause oil to become damage[1–3]. Oil damage during the frying process will affect the quality and nutritional value of fried food ingredients. The damage to cooking oil is mainly caused by the oxidation process, namely the formation of peroxides and aldehydes[4]. The decomposition of cooking oil due to the frying process is influenced, among others the composition of frying, the type of oil used for frying and the condition of cooking oil damage cannot be prevented, but can be slowed down by taking into account several influencing
factors. First, oxygen. The more oxygen the faster it is oxidized; Second, double bonds. The more unsaturated fatty acids, the easier it is to oxidize; Third, temperature. The high frying and storage temperature will speed up the reaction; Fourth, light metal ions and copper and iron which are catalysts for the oxidation process, and Fifth, antioxidants. The higher the added antioxidants, the more resistant to oxidation.

An alternative method that has often been used to process used cooking oil is through purification using several adsorbents using adsorbents so that the quality of cooking oil is maintained[5]. Research has been carried out using bentonite and activated carbon showing that refined cooking oil has been able to reduce acid and peroxide numbers, but is still below the value of the Indonesian National Standard for cooking oil. Purification of used cooking oil is based on the degradation reaction of the separation of products in the form of water, peroxides, free fatty acids, aldehydes and ketones from the oil [6]. Several other studies using activated carbon from bagasse show that this type of activated carbon is still effective enough to purify used cooking oil because it does not sufficiently reduce the levels of free fatty acids. Activated charcoal as a metal producer which is influenced by pH and the ability of carbon concentration to overcome environmental problems. Several previous researchers has been doing purification research used cooking oil to use adsorbent from natural ingredients with make use of by-products or agricultural waste, such as bagasse [7], activated charcoal from coconut husk [8], activated carbon from Moringa seeds [9], dregs of palm starch and bentonite [10] and activated charcoal from bark skin [11]. Each type adsorbent has deep selectivity absorbs certain components which is in used cooking oil.

Currently, worldwide consumption of activated carbon reaches 300,000 tonnes/year. From this figure, around 10.12% is activated carbon made from coconut shells. This provides an opportunity to make activated charcoal from ingredients other than coconut shells, for example bamboo which is very easy to find in Indonesia. Activated carbon is used by all types of industries, including medicine, food, beverage, water treatment, and many more. Research using coconut shells was successful in reducing water content and approaching the quality threshold of 0.1 mg/L. It was achieved during the 60.25 minute treatment period (0.411 mg/L) [12].

This study aims to determine the ability of activated bamboo charcoal and charcoal to purify used cooking oil produced by the fried industry around Ngaliyan, Central Java in terms of the water content, acid number and peroxide number so that it can be concluded whether the used cooking oil in the area can still be used. used, in accordance with the quality threshold set by SNI. The use of activated bamboo charcoal is expected to reduce the cost of treating used cooking oil by reducing the acid and peroxide numbers efficiently.

2. Methods

2.1 Activated bamboo charcoal synthesis and Characterization
Bamboo charcoal was synthesized from javanese bamboo by heating process. The javanese bamboo were cut into tiny size wrapped in aluminum foil and heated in a furnace for 2 hours with various temperatures as 400°C. The activation process of bamboo charcoal is carried out by soaking bamboo charcoal in 9% NaCl, leaving it for 24 hours then filtering, washing and neutralizing. Activated bamboo charcoal was characterized using reference to SNI 06-3730-1995 regarding technical activated charcoal including water content, volatile content, total ash content, carbon content, iodine absorption and absorption of methylene blue. Activated bamboo charcoal also characterized its functional groups using FTIR (Fourier-Transform Infared Spectroscopy) and morphology using SEM (Scanning Electron Microscopy).

2.3 Purification Process
Cooking oil sample used 150 mL was inserted into a beaker glass then added bamboo charcoal powder into the oil by mass of 2 grams. Next do the stirring for 2 hours. Oil mixture and bamboo charcoal separated by filtration and the filtrate is taken for analysis of water content, acid number and
number peroxidants. In the same way, the process of purifying used cooking oil is carried out using activated bamboo charcoal. Mix oil and activated charcoal separated by means filtration and the filtrate was taken for analysis. The filtered oil is determined by the free fatty acid content by the acid-base titration method, the water content in oil using the oven method at a temperature of 150°C for 4 hours, and the number of peroxides using the titration method.

3. Results and Discussion

3.1 Activated bamboo charcoal synthesis and Characterization

Synthesis of bamboo charcoal carried out in three stages, dehydration, carbonization and activation by heating process using heating at 400°C for 2 hours giving 30.46% yield. Visually, activated bamboo charcoal and charcoal have a black color. The activation carried out in this research is chemical activation with the aim of enlarging the pores by breaking hydrocarbon bonds or oxidizing surface molecules so that the charcoal changes in physical and chemical properties, namely the larger surface area will affect its adsorption ability. The main purpose of the activation process is to increase or expand the pore volume and increase the pore diameter that has been formed during the carbonization process and to create new pores. The interaction between the activating agent and the structure of the carbonized carbon atoms is the mechanism of the activation process. During activation, carbon is burned in an oxidation state which will increase the number or volume of pores and the surface area of the product by eliminating or removing volatiles from pyrolysis products. The process of activating bamboo charcoal in this study uses a chemical method. The results of activation are strongly influenced by the type and amount of activator used. The constituent elements of the activator will enter the carbon and open pores or surfaces that were initially closed by other chemical compounds which cause the pore size to increase in size. By using NaCl for activator it will give different results both in surface area and pore size.

Characterization of bamboo charcoal aims to determine that the bamboo charcoal produced is in accordance with the criteria for activated carbon, referring to SNI 06-3730-1995 regarding technical activated charcoal. Characterization carried out in this study included yield, water content, ash content, volatile substance content, carbon content, iodine absorption and methylene blue absorption as shown in Table 1.

Table 1. Physical characteristics of activated bamboo charcoal and bamboo charcoal

| Characteristics          | bamboo charcoal | activated bamboo charcoal |
|--------------------------|-----------------|--------------------------|
| water content (%)        | 4.49            | 4.12                     |
| ash content (%)          | 4.82            | 1.04                     |
| volatile substance content (%) | 8.64    | 5.02                     |
| carbon content (%)       | 81.82           | 89.80                    |
| iodine absorption (mg/g) | 646.12          | 1246.32                  |
| methylene blue absorption (mg/g) | 342.12  | 496.12                  |

Overall, the water content of activated bamboo charcoal and bamboo charcoal has a small water content, this indicates that the charcoal process is optimum so that all of the bound water content has been released during the charring process. The water content of activated carbon greatly determines the properties or absorption of activated carbon, if the water content is large it will reduce its adsorption ability. The process of determining the level of ash in bamboo charcoal aims to determine the metal oxide content in bamboo charcoal. Ash content can be interpreted as mineral residue left during carbonization, because the basic material for its manufacture does not only contain carbon compounds, but also some minerals contained therein because they are natural ingredients. Part of this mineral content will be lost during the carbonization and activation process, but it does not rule out the
possibility that it will still be left in bamboo charcoal. This remaining mineral content will react with oxygen to produce ash.

The level of this volatile substance is the substance that is lost by heating 950°C, the level of this volatile substance is the decomposition of the activated carbon constituent as a result of the carbonization process. The presence of this volatile substance can be minimized by increasing the temperature of carbonization or pyrolysis, because if the temperature is less and the pyrolysis process does not run optimally, it will cause the decomposition or decomposition of non-carbon compounds to be not optimal and consequently the levels of volatile substances will increase. So, the amount of volatile substance content is largely determined by the temperature and time of carbonization. The carbon content in bamboo charcoal can be called bound carbon or pure activated carbon or the carbon fraction bound in bamboo charcoal in addition to the fraction of water, ash and volatile substances.

The determination of iodine absorption in this study aims to determine the ability of bamboo charcoal to absorb odors/aromas. The value of iodine absorption is strongly influenced by the activator used. The higher the activator concentration added, the iodine absorption will increase, this is because the increasing concentration of the activator will increase the surface area of bamboo charcoal which will make it easier for the compounds to be absorbed to enter the pores and will increase their absorption. The greater the absorption of iodine, the better the ability of bamboo charcoal in the absorption process. The determination of the absorption of methylene blue for characterization of bamboo charcoal is to determine the surface area. Surface area is a very important parameter in the adsorption process and is one of the determinants of the quality of an activated carbon in the adsorption process. This absorption of methylene blue can be used as a rough benchmark for determining the surface area of bamboo charcoal. The absorption of methylene blue is proportional to the surface area, the greater the absorption of methylene blue, the greater the surface area of bamboo charcoal.

According to Table 1 the physical characteristics of bamboo charcoal and activated bamboo charcoal have accordance to SNI 06-3730-95 standards, namely a maximum of 15% for water content, a maximum of 10% for ash content, a maximum of 25% for volatile substance content, a minimum of 65% for carbon content, a minimum of 750 mg/g for iodine adsorption and a minimum of 120 mg/g for power absorb methylene blue. From the results of FTIR analysis showed an increase in absorption intensity at wave numbers (3500-2700) cm⁻¹. The wave number is the absorption area for the OH group, where the activated carbon has the highest intensity after the activation process. The increase in absorption intensity at wave numbers (3000-2700) cm⁻¹ is an indication of the formation of aromatic compounds. Vibration at the (1500-1600) cm⁻¹ on activated carbon indicates the presence of a C=O bond. The functional group on the activated carbon is a hydroxyl group which is bound O-H (3400 - 3500) cm⁻¹ and C-O (1300 -1400) cm⁻¹ as shown at Table 2. This shows that bamboo charcoal and activated bamboo charcoal have the same functional group as standard activated carbon.

Table 2. FTIR data for activated bamboo charcoal and bamboo charcoal

| Functional Group | bamboo charcoal | activated bamboo charcoal |
|-----------------|----------------|--------------------------|
|                 | Wave number (cm⁻¹) | intensity | Wave number (cm⁻¹) | intensity |
| O-H             | 3426.94         | 38.632       | 3428.12         | 49.451    |
| C=O             | 1584.4          | 50.616       | 1592.74         | 62.19     |
| C-O             | 1380.45         | 53.392       | 1165.44         | 64.008    |

Characterization using SEM to determine the morphological changes of bamboo charcoal before and after activation. SEM results show that the pores in bamboo charcoal are still closed, but with the activation it appears that the pores are opening more. With the increasing number of open pores on the surface of bamboo charcoal, it will increase the surface area so that the absorption capacity will increase. SEM Results with a magnification of 5000 times shows that activated bamboo charcoal have morphology which more porous than bamboo charcoal (Figure 1). Morphology observed by SEM in
the form of shape, size and arrangement of particles. Difference in surface morphology of bamboo charcoal before and after activation. Activated bamboo charcoal shows a more regular pore distribution with more than before activation. This is due to activation causing more pores formed and the ability to absorb increases.

Figure 1. SEM image of (a) bamboo charcoal (b) activated bamboo charcoal

3.2 Purification Process
Determination the main damage to the cooking oil is water content, because in the presence of water, cooking oil easier to hydrolyze, otherwise by heating and in contact with air, the oxidation and hydrolysis of cooking oil will occur faster, hydrolysis itself is accelerated by water[13]. The results showed that bamboo charcoal and activated bamboo charcoal can reduce the acid number and fatty acid content of the used fatty acids cooking oil. The free fatty acid content is calculated based on molecular weight as a percentage palmitic acid. Peroxide is a compound resulting from oxidation due to contact with air and accelerated by temperature and lighting, where the calculation of the peroxide number is carried out to determine the level of pungent odor in used cooking oil. Analysis of the peroxide number in used cooking oil, using the iodometric method. This research proves that activated bamboo and bamboo charcoal are able to reduce water content, acid numbers and peroxide number as shown in Table 3.

Table 3. The result of activated bamboo charcoal to reduce acid levels in used cooking oil.

| Characteristics     | bamboo charcoal | activated bamboo charcoal |
|---------------------|-----------------|---------------------------|
| FFA (mg KOH/g)      | 0,94            | 0,32                      |
| Peroxide number (mek O₂/Kg) | 20,45      | 7,61                      |
| Water conten (w/w)  | 0,12            | 0,08                      |

Table 3 shows that activated bamboo charcoal can reduce acid levels in used cooking oil. The adsorption process by bamboo charcoal involves three stages; the compound is absorbed outside carbon walls, enter through the pores, and are reabsorbed by the inner wall carbon, which can lower the acid number. The peroxide adsorption by bamboo charcoal is possible because of the potential difference between the adsorbent surface and the solution. Peroxide numbers are usually associated with rancidity in used cooking oil, with adsorption using activated bamboo charcoal being able to reduce the peroxide number which organoleptically can also be observed by reducing/eliminating the rancidity of used cooking oil. The result was accordance to the SNI 3741: 2013 standard [14].
4. Conclusion
The activation process on bamboo charcoal can open the pores so that the morphology of activated bamboo charcoal becomes more porous which increases the surface area and increases the adsorption ability. Based on IR results indicate that bamboo charcoal and activated bamboo charcoal have the same functional group as standard activated carbon. The characteristics of bamboo charcoal and activated bamboo charcoal include water content, ash content, volatile substance content, carbon content, iodine absorption and methylene blue absorption according to SNI 06-3730-95, namely the standard on technical activated charcoal. The ability of activated bamboo charcoal in processing used cooking oil is seen from water content, acid number and peroxide number of cooking oil after the adsorption process, according to the SNI 3741: 2013 standard with a water content of 0.08% (w/w), peroxide number 5.45 mek O₂/Kg and FFA 0.24 mg KOH/g.

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