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The Effectiveness of Activated Carbon as an Adsorbent in Reducing Acid and Peroxide Levels in the Refining of Rice Bran Oil *(Oryza sativa L.)*

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ABSTRACT
Rice bran is one of the by-products of the rice milling process that has the potential to be utilized because it contains 10-13% bran oil. Rice bran oil can be used as raw material for pharmaceuticals, cosmetics, and food oils. The purpose of this study was to determine the effect of activated carbon concentration and blanching process time on the quality of rice bran oil and it is hoped that bran oil will meet quality standards by looking at 3 parameters, namely acid number, peroxide number, and color inspection. The purification process is carried out in 4 stages, namely the extraction, distillation, degumming, and bleaching processes. The dependent variable in this study was the concentration of activated charcoal carbon and the bleaching time where the concentrations used 5%, 6%, 7% of the weight of the oil and the bleaching time was 15 minutes, 25 minutes, 35 minutes. The independent variables are the value of the acid number and the peroxide number which will be compared before and after purification. The best research results on acid number using 7% activated charcoal carbon concentration and a bleaching time of 35 minutes the value is 0,36 mg NaOH/g with a percentage decrease of 61%. The best results on the peroxide number using activated charcoal carbon concentration of 7% and bleaching time of 25 minutes the value is 6,7 mek O_2/Kg with a percentage decrease of 77%. The results of the analysis, activated charcoal can be used as an adsorbent in the bran oil purification process because it provides a significant value before and after purification.

***Keywords**: Rice bran oil; activated carbon; purification.*

INTRODUCTION
In Indonesia, there is not much use of rice bran to make rice bran oil. Rice bran oil is a type of oil that has high nutrition because it contains fatty acids, antioxidant components and biologically active components.

Nowadays, rice bran is usually only used as a component of animal feed for several types of poultry. One method for utilizing rice bran is by processing the rice bran into oil. Oil production from rice bran can increase economic value in rural rice agro-industry systems (Hadipernata, 2007). Processing rice bran into oil is only done by people who are sensitive and critical of what is around them.

Rice bran contains oil, protein, carbohydrates and dietary fiber, and is also rich in various types of phenolic compounds (Feridoun S. A., Omid, P., and Yoshidaa, 2010). Rice bran also contains around 20-30% oil (Most et al., 2005). According to Fajriyati and Pabbenteng (2016), rice bran oil has extraordinary properties compared to other vegetable oils. Rice bran oil contains 36-38% oleic acid, 35-38% linoeic acid, and 1.8-2.4% α-linoleic acid, which are unsaturated fats, as well as 21-25% palmitic acid and 2.7-8.0% stearate. % which are saturated fatty acids (Gopala, 2006). Rice bran oil contains phytochemical compounds that have natural antioxidant activity, especially α, β, γ, δ tocopherol and tocotrienol, as well as the oryzanol fraction (Xu, Z., Hua, N., and Godber, 2001).

The color substances in rice bran oil are yellow, brownish yellow and reddish because the rice bran oil contains high levels of acid and peroxide numbers. This is because the triglyceride components in rice bran oil are broken down by lipase into acid and peroxide numbers. Apart from containing high levels of

acid and peroxide numbers, rice bran oil also easily becomes rancid, thus affecting the quality of the rice bran oil produced. The cause of rancidity is the activity of the lipase enzyme which hydrolyzes rice bran oil into glycerol and fatty acids. Hydrolysis causes a soapy taste, increased acidity, changes in functional characteristics, and susceptibility of fatty acids to oxidation. Therefore, rice bran oil cannot be called pure rice bran oil. So even though rice bran oil is known to have important health benefits, this oil is still very minimally used as pure rice bran oil. So it is necessary to make certain efforts to increase the use value of the rice bran oil by purifying the rice bran oil so that good quality rice bran oil can be obtained.

An alternative to processing rice bran oil is through a purification process using a number of adsorbents. The rice bran oil refining process was carried out using activated carbon for purification which showed that the acid and peroxide numbers also decreased. The quality of rice bran oil is determined from the acid and peroxide levels. Therefore, it is necessary to reduce the acid and peroxide levels in rice bran oil by using activated carbon as an adsorbent.

From the description above it can be concluded that this research aims to determine other benefits of rice bran apart from being used as feed for livestock and some poultry. In this research, activated carbon was used to purify the extracted rice bran oil.

METHOD

1. **Sample Preparation**

   1150 grams of rice bran was filtered using a 90 mesh sieve and then wrapped in aluminum foil. After that, the sample was oven-treated for 15 minutes at 110 °C, then cooled to room temperature. Dried samples were stored at 4 °C for further analysis (Moko, et al., 2014).

2. **Extraction**

   Rice bran extraction was carried out by soxhletation using n-hexane solvent. The rice bran sample was weighed at 50 grams, then wrapped using filter paper shaped like a cylinder, the size of which corresponded to the size of the soxhlet used. Next, the sample is put into a soxhlet which has been assembled with a condenser and boiling flask. Put 200 mL of n-hexane solvent into a three-neck flask, then extract for ± 1.5 hours. So the extraction results are obtained in the form of a mixture of rice bran oil and solvent.

3. V**acuum Rotary Evaporator**

   The vacuum rotary evaporator is a continuation of the extraction process. The results of the extraction process were then evaporated using a rotary evaporator at a temperature of 50 ℃ for 1 hour. The purpose of this evaporation process is to evaporate the solvent used in the extraction process to produce a more concentrated rice bran extract.

4. **Degumming**

   In the degumming process, the rice bran oil is heated at a temperature of 80 °C using phosphoric acid with a concentration of 85% with a volume of 9% of the weight of the oil at 300 rpm for 40 minutes. Then the rice bran oil was centrifuged for 30 minutes. After the rice bran oil is centrifuged, the rice bran oil is filtered or filtered.

5. **Activated Carbon**

   This carbon activation process functions to increase the carbon adsorption capacity itself. First of all, 30 grams of carbon is soaked in 60 mL of 6 M HCl solution which functions as an activator solution. Then the mixture was stirred for 3 hours using a magnetic stirrer. After that, a carbon paste sample was obtained. The mixture of activated carbon and 6 M HCL was filtered and washed with distilled water until the filtrate was neutral. The activated carbon residue is oven at 100 ℃ for 2 hours (Wardhani et al., 2016).

6. **Bleaching**

   The degumming rice bran oil is heated to a temperature of 70 °C using a hot plate. Then 5 ml of sample was weighed. Then the oil samples were varied using activated carbon concentration (5%, 6%, 7%) and bleaching process time (25 minutes, 35 minutes, 45 minutes). Then the rice bran oil was centrifuged for 30 minutes and the rice bran oil was obtained as a result of purification using activated charcoal.

7. **Rice Bran Oil Quality Test**

7.1. Determination of Acid Number (Acid-Alkalimetric Method)

A sample of rice bran oil was weighed as much as 1 gram into a 250 ml Erlenmeyer flask. Then, 25 ml neutral alcohol was added to the sample and dissolved. After that, 3 drops of phenolphthalein indicator were added. Then, it was titrated with a standard 0.1 N NaOH solution until the end point, where the first pink color change occurred and did not disappear for 30 seconds.

7.2. Determination of Peroxide Number (Iodometric Method)

The rice bran oil sample was weighed at 1.5 grams using a 250 ml Erlenmeyer flask. Then 15 ml of a mixture of glacial acetic acid and chloroform was added in a ratio of 3:2. After that, the sample was shaken until the sample dissolved. Then 0.3 ml of saturated KI solution was added and left for 2 minutes in the dark while shaking. After that, 15 ml of distilled water was added to the sample. Add 0.5 mL of 1% starch solution. Then the sample was titrated with 0.1 N Na2S2O3 until the purplish blue color disappeared.

7.3. Colour Check

Determining the color of rice bran oil is to determine the color changes in each treatment carried out by physical and subjective observation.

8. **Data Analysis**

The data obtained in this research were rice bran oil samples that had been given purification treatment using activated carbon adsorbent. After that, the quality of the rice bran oil was tested using the acid number (acid-alkalimetric titration), peroxide number (iodometric titration), and subjective colour examination. The results were seen by comparing the quality test between the rice bran oil before refining and the rice bran oil resulting from purification using activated carbon.

After that, the data obtained in this study was analyzed using two-way Analysis of Variance (ANOVA). And if there are differences between treatments, then the Dunchan's Multiple Distance Test is continued to find out in detail which data is significantly different.

RESULT AND DISCUSSION

Result

1. Acid Number Testing

In this research, an acid number test will be carried out on rice bran oil. This acid number test aims to measure the amount of free fatty acids contained in the oil. The larger the acid number means the higher the free fatty acid content, while the free fatty acids contained in the sample can come from the hydrolysis process or due to poor processing.

Table 1. Acid number value of rice bran oil after purification

Bleaching Time (minutes)	Acid Number		
	Activated Carbon Concentration (%)		
	5	6	7
15	$0,44 \pm 0,01^{cc}$	$0,42 \pm 0,01^{bc}$	$0,39 \pm 0,01^{ac}$
25	$0,43 \pm 0,01^{cb}$	$0,41 \pm 0,01^{bb}$	$0,38 \pm 0,00^{ab}$
35	$0,40 \pm 0,01^{ca}$	$0,39 \pm 0,01^{ba}$	$\mathbf{0,36 \pm 0,00^{aa}}$
Value of acid number before purification: 0,92 ± 0,02			

Different subset notations (a, b, and c) on each row show significant differences ($p < 0.05$)

Based on the results of the F test on variations in activated charcoal carbon concentration relative to the acid number, the calculated F value with a probability (sig.) of 0.000 is smaller than the alpha value (α=0.05), so H0 is rejected. Thus, it can be stated that there is an influence of activated charcoal carbon concentration on the acid number. Then the results of the bleaching time variation test on the acid number showed that the calculated F value with a probability (sig.) of 0.000 was smaller than the alpha value (α=0.05), so H0 was rejected. Thus, it can be stated that

there is an influence of bleaching time on the acid number. In the test results of variations in the combination of activated charcoal carbon concentration and bleaching time, it was found that the calculated F value with a probability (sig.) of 0.045 was smaller than the alpha value (α=0.05), so H0 was rejected. Thus, it can be stated that there is an influence of activated charcoal carbon concentration and bleaching time on the acid number. In Dunchan's further tests it was discovered that at activated charcoal carbon concentrations of 5%, 6% and 7% there were significant differences. Then in Dunchan's further test at bleaching times of 15 minutes, 25 minutes, 35 minutes there was a real difference. From these data it can be seen that the acid number at an activated carbon concentration of 7% and a bleaching time of 35 minutes shows the best results.

Based on Table 1, it is shown that the acid number value decreases as the mass of activated carbon increases. All results of determining the value of acid number in purified rice bran oil with the addition of variations in the mass of activated carbon and bleaching time meet the requirements of SNI 3774:2013 with a maximum value of acid number, namely 0.6 mg NaOH/g sample. The most optimum results were variations in the addition of 7% activated charcoal and a bleaching time of 35 minutes with an acid value of 0.36 ± 0.00 mg NaOH/g.

2. Peroxide Number Testing

The peroxide number is an index of the amount of fat or oil that has undergone oxidation. The purpose of carrying out a peroxide value test is to determine the degree of damage to oil or fat. Unsaturated fatty acids can increase oxygen in their double bonds to form peroxides. Peroxide is formed due to heating which causes damage to oil or fat. The peroxide number is very important to identify the level of excess oil oxidation of used cooking oil (Suroso, 2013). Oils containing unsaturated fatty acids can be oxidized by oxygen to produce peroxide compounds.

Table 2. Value of peroxide number in rice bran oil after purification

Waktu Pemucatan (menit)	Bilangan Peroksida Konsentrasi Karbon Arang Aktif (%)		
	5	6	7
15	$13,3 \pm 0,00^{ab}$	$11,1 \pm 3,85^{aab}$	$8,9 \pm 3,85^{aa}$
25	$11,1 \pm 3,85^{ab}$	$8,9 \pm 3,85^{aab}$	**$6,7 \pm 0,00^{aa}$**
35	$13,3 \pm 0,00^{ab}$	$11,1 \pm 3,85^{aab}$	$8,9 \pm 3,85^{aa}$
Nilai bilangan peroksida sebelum dimurnikan : 29 ± 3,64			

Different subset notations (a and b) on each row indicate significant differences ($p < 0.05$)

Based on the results of the F test on variations in activated charcoal carbon concentration against peroxide value, the calculated F value with a probability (sig.) of 0.026 is smaller than the alpha value (α=0.05), so H0 is rejected. Thus, it can be stated that there is an influence of activated charcoal carbon concentration on the peroxide value. Then the results of the bleaching time variation test on the peroxide value showed that the calculated F value had a probability (sig.) of 0.250 which was greater than the alpha value (α=0.05), so that H0 was accepted. Thus, it can be stated that there is no influence of bleaching time on the peroxide value. In the test results of variations in the combination of activated charcoal carbon concentration and bleaching time, it was found that the calculated F value with a probability (sig.) of 1,000 was greater than the alpha value (α=0.05), so that H0 was accepted. Thus, it can be stated that there is no influence of activated charcoal carbon concentration and bleaching time on the acid number. In Dunchan's further tests it was discovered that the 5% activated charcoal carbon concentration was not significantly different from the 6% concentration, but was significantly different from the 7% concentration. Meanwhile, the 7% concentration is not significantly different from the 6% concentration, but it is significantly different from the 5% concentration. Then in Dunchan's further test at bleaching times of 15 minutes, 25 minutes, 35 minutes there was no real difference. From these data it can be seen that the acid number at an activated charcoal carbon concentration of 7% and a bleaching time of 25 minutes shows the best results.

Based on Table 2, it is shown that the peroxide value value decreases as the mass of activated carbon is added. However, not at the bleaching time, at the bleaching time at 15 minutes

it decreased continuously until the bleaching time was 25 minutes but at 35 minutes it increased again, this shows that the optimum contact time was 25 minutes. The optimum reaction time is the effective and efficient time for reducing the peroxide value in rice bran oil. This is because the adsorbent is already saturated at that time so absorption is not optimal. All determinations of peroxide value in rice bran oil which has been added with activated carbon adsorbent with a combination of bleaching time, some meet the requirements of SNI 3774:2013 and some do not meet the maximum value of peroxide number, namely 10 mek O2/Kg. The most optimum results were in the variation of adding activated carbon of 7% of the weight of the oil with a combination of a bleaching time of 25 minutes, namely obtaining a peroxide value of 6.7 ± 0.00 mek O2/Kg.

3. Colour Check

This colour inspection test aims to compare the colour of rice bran oil before purification and after purification using activated carbon. Rice bran oil contains pigments such as chlorophyll, lutein, xanthopyll, carotenoids, and a degraded protein called brown pigment. These pigments can cause a dark colour that does not match the colour of the oil (Jono Suhartono, 2011). With the oil refining process, these pigments can be removed so that clearer rice bran oil will be produced. Colour comparison results of rice bran oil before purification and purified rice bran oil which refers to the SNI 3741:2013 standard.

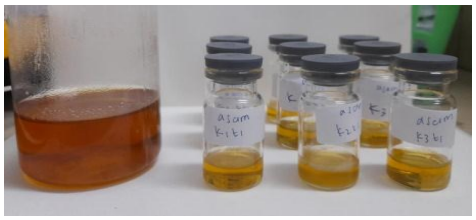

Figure 1. Comparison of rice bran oil colour

The research results showed that the addition of activated carbon was successful in purifying the oil by adsorption of impurities in the rice bran oil. This turbidity and dark brown color is caused by the oxidation and hydrolysis process which can reduce the quality of rice bran oil.

Discussion

1. Acid Number Testing

The results of calculating the acid value of rice bran oil in this study ranged from 0.36 ± 0.00 – 0.44 ± 0.01 mg NaOH/g, all results obtained met the free fatty acid standard (SNI. 3741: 2013) with a maximum of 0 .6 mg NaOH/g. The percentage decrease in the acid number value that occurs with the treatment of increasing the activated charcoal carbon concentration and the longer the bleaching time shows that the greater the activated charcoal carbon concentration and the longer the bleaching time used, the higher the decrease in the acid number value of the rice bran oil. This is because increasing the mass of activated carbon causes the resulting adsorbent surface to become wider so that more free fatty acids can be absorbed by the activated charcoal adsorbent. The longer the bleaching time also causes the activated carbon to have a very large number of micro pores and can cause capillary symptoms which cause absorption of the acid number value of the rice bran oil.

According to Ketaren (2005), acid numbers are formed due to hydrolysis reactions, water and water vapor will hydrolyze triglycerides at high temperatures to produce monoglycerides, diglycerides, glycerol and free fatty acids. The result of the hydrolysis reaction is a rancid odor in the oil, an increase in the acid number not only occurs during processing but also during storage (Kusnandar, 2010). The oxidation reaction begins with the formation of peroxides and hydroperoxides. Furthermore, the fatty acids will decompose accompanied by the conversion of hydroperoxides into aldehydes and ketones as well as free fatty acids (Ketaren, 2005). The oxidation process takes place by abstracting hydrogen ions from free fatty acids contained in the oil. These bonds will be replaced by oxygen and form radical alkyl compounds, which then react further to form radical peroxide compounds. This purification process for rice bran oil removes

impurities in the oil such as acid value, phosphatides, water, gum, and so on, resulting in a decrease in the acid value of the refined rice bran oil.

2. Peroxide Number Testing

The results of calculating the peroxide value of rice bran oil in this study were in the range of 6.7 ± 0.00 – 13.3 ± 0.00 mek O2/Kg, all the results obtained either met or did not meet the free fatty acid standard (SNI. 3774 : 2013) maximum 10 mek O2/Kg. The percentage decrease in the acid number value that occurs with the treatment of adding activated charcoal carbon concentration shows that the greater the activated charcoal carbon concentration used, the higher the decrease in the peroxide value value of the rice bran oil. However, not at the bleaching time, at the bleaching time of 15 minutes it experienced a continuous decrease until at the bleaching time of 25 minutes but it increased again. This is because the adsorbent is already saturated at that time so absorption is not optimal.

Oxidation reactions occur when there is contact with oxygen (Ketaren, 1986). The oxidation process takes place by abstracting hydrogen ions from free fatty acids contained in the oil. These bonds will be replaced with oxygen and form alkyl halide compounds which then react further to form radical peroxide compounds. This can be shown by the appearance of peroxide numbers in the oil.

CONCLUSION

In the acid number, the results of the combination test of variations in activated charcoal carbon concentration and bleaching time showed that the calculated F value with a probability (sig.) of 0.045 was smaller than the alpha value (α=0.05) so that it could be stated that there was an influence of activated charcoal carbon concentration and time. bleaching of the acid number. Meanwhile, for the peroxide number, the results of the combination test of the combination of activated charcoal carbon concentration and bleaching time showed that the calculated F value with a probability (sig.) of 1,000 was greater than the alpha value (α=0.05) so that it could be stated that there was no influence on the activated charcoal carbon concentration. and bleaching time at acid number.

The addition of activated carbon and bleaching time treatment in the acid number and peroxide value tests provided significant values. The addition of 7% activated charcoal and a bleaching time of 35 minutes in the acid number test gave the best results with a value of 0.36 ± 0.00 mg NaOH/g. Meanwhile, the addition of 7% activated charcoal and a bleaching time of 25 minutes in the peroxide value test gave the best results with a value of 6.67 ± 0.00 mek O2/Kg.

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