



Purification of Used Cooking Oil by Alkali Neutralization and Bleaching of Bayah Natural Zeolite

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Abstract

Cooking oil that is used repeatedly at high temperatures will reduce the quality of cooking oil. This will trigger the hydrolysis and oxidation processes that will change the characteristics of the oil, such as an increase in free fatty acid levels and peroxide numbers. Purification of used cooking oil can be carried out physically and chemically. The physical purification of oil is carried out by using adsorbents, while chemically purification process is carried out with an alkaline solution. Physically, natural materials such as zeolite can be used, where zeolite is a natural rock or mineral which chemically has a large surface area to be used in the adsorption process. Chemically with alkaline solution you can use sodium hydroxide (NaOH). In this study, used cooking oil is purified by three stages of the process, namely despicing, neutralization and bleaching to comply with the SNI quality standards. The purpose of this study was to determine the optimum operating conditions for the purification of used cooking oil in accordance with the quality standards for cooking oil. based on the results obtained by adding a NaOH concentration of 19% in the neutralization process and a zeolite concentration of 90% can reduce the acid number value of 2.4 mg NaOH/gr, the peroxide number is 7 mekO₂/kg, the color degradation of used cooking oil is 51.83%.

INTRODUCTION

Used cooking oil is an oil that has been used more of two or three fryers and is categorized as waste because it can damage the environment and can cause a number of diseases. Can be concluded that people who cook and eat fried foods with used cooking oil is more at risk of developing high blood pressure and a risk of causing it less cancer compared to those who frequently change their cooking oil for cooking (Alamsyah, 2017).

Used cooking oil is cooking oil which contains carcinogenic compounds. Where the sustainable use of used cooking oil can damage human health, cause cancer, deposit fat in blood vessels, and consequently reduce intelligence (Alamsyah, 2017). As a result of these processes some triglycerides will break down into other

compounds, one of which is free fatty acids (Suirta, 2009).

The declining in the quality of used cooking oil (used cooking oil) can be seen from the color of the oil darker and less clear, unpleasant oily aroma, consistency the oil is thicker, as well as the free fatty acid (FFA) content and the peroxide number high. The amount of FFA in oil does not depend on the level of linoleic acid and tocopherol (Aladedunye & Przybylski, 2013). There are several parameters that indicate the cooking oil is in good condition, namely the acid number and the peroxide number. as stated in SNI 3741 of 2013 concerning the quality requirements for cooking oil, it is stated that the maximum limit for the acid number in cooking oil is 0.6 mg KOH / g while the peroxide number is 10 mek O₂ / kg (SNI 3741, 2013).

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Purification of used cooking oil aims to degrade its components undesirable and restores the characteristic properties of cooking oil. Purification used cooking oil can be done in two ways, namely physically with using adsorbents and chemicals using alkaline solutions. Purification physically used cooking oil that has been done, among others, with magnesol xl (Suseno, 2012), activated charcoal (Irmawati, 2018), bagasse (Fuadi, 2010). Meanwhile, the chemical refining method of used cooking oil is carried out mixing oil with lye solution. Purification of used cooking oil with lye which has been done, among others, with NaOH (Huang and Sathivel 2010). The neutralization method is a method that can applied in bulk to improve the quality of used cooking oil with reduce the impurities contained in the oil with NaOH (Huang & Sathivel, 2010). The bleaching process also occurs during neutralization process, so that refining by this method produces oil with characteristics that are better than physical purification (Wayan, 2017).

Zeolites have a distinctive structure, that is, almost all of them are canals and pores that cause zeolites to have a large surface area. Therefore, zeolites can be used for adsorption processes, ion exchangers, and as catalysts zeolite has the potential in refining used cooking (Isni, 2016). As for the purpose of This study was to determine the effectiveness of zeolite in the process of refining used oil by doing a visual analysis of the color of used cooking oil after adsorption using zeolites. This study aims to determine treatment of NaOH concentration in the neutralization process and mass percent of natural bayah zeolite in the bleaching process in the process of refining used cooking oil so that it can follow the quality standards of cooking oil.

MATERIALS AND METHODS

Materials

Used oil in this study is obtained from household waste. The raw material used is natural zeolite from Bayah, Lebak Regency, Indonesia. The alkaline solution used is NaOH obtained from a chemical store. The distilled water used was obtained from the energy processing and production laboratory of the Faculty of Engineering, Sultan Ageng Tirtayasa University.

Methods

Despicing Process

The despicing process is carried out by contacting the used cooking oil with steam in the vigrek column, putting brown oil in a separating funnel at the top of the vigrek column and steam flowing from the bottom from the boiler. The despicing process takes place at a mass flow rate of oil of 0.139 kg / s. The oil resulting from the despicing process will then be separated from the water using a separating column.

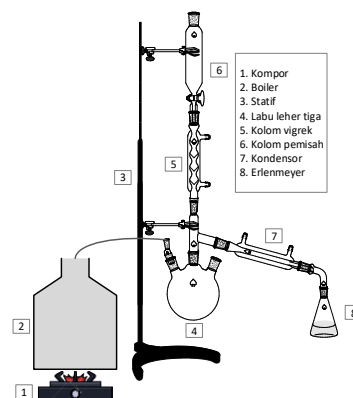


Figure 1. Series of Despicing Process Equipment.

Neutralization Process

The neutralization process was carried out using oil samples from the despicing process, the oil was weighed as much as 100 grams and put into the Erlenmeyer flask, then added 5 mL of NaOH solution with levels (13%, 15%, 17% and 19%) at a temperature of 40°C, and with stirring speed of 500 rpm, this process is carried out for 10 minutes, then the filtering process is carried out using filter paper.

Bleaching Process

The bleaching process was carried out using oil samples from the neutralization process, 100 grams of oil was mined and then mixed with an adsorbent in the form of natural zeolite by 30%, 50%, 70% and 90% (w / w) according to variations. The experiment was carried out for 60 minutes with stirring speed of 500 rpm at each variation, then separated the bleached oil with the adsorbent.

Analysis Methods

Acid Number Analysis

The oil sample was weighed as much as 10

Table 1. Results of the analysis of the neutralization process.

No	NaOH Concentration Treatment	Acid Number (mgNaOH/gr)	Peroxide Number (mekO ₂ /kg)	Color Number at the wavelength 410nm (abs)
1.	Before treatment	15.30	10.95	3.000
2.	13%	6.00	8.96	2.809
3.	15%	5.27	8.42	2.792
4.	17%	4.51	7.86	2.776
5.	19%	4.33	7.48	2.759

grams - 50 grams and then put into Erlenmeyer, after that 50 ml of 95% ethanol solution was added and 3-5 drops of phenolphthalein (pp) indicator, after which acid-base titration was carried out on the sample using a standard solution in the form of 0.1N NaOH until a pink color forms (the pink lasts for 30 seconds). The titration process takes place until the end point of the titration is visible, then the data analysis results are processed.

Peroxide Number Analysis

The oil sample was weighed as much as 5 grams and 30 mL of a mixture of 20 mL glacial acetic acid, 25 mL 95% ethanol and 55 mL chloroform was then added. After that, 1 gram of potassium iodide was added and it was stored in a dark place for 30 minutes. Then 50 mL of CO₂-free distilled water was added. Then titrated with a standard solution of 0.02N sodium thiosulfate with starch solution as an indicator. A blank determination and calculate the number of peroxides in the example were then conducted.

Spectrophotometry Analysis

Spectrophotometry analysis was carried out at a wavelength of 410nm, the oil sample was stored in a cuvette, then the absorbance of the oil sample was tested at a wavelength of 410nm, then the absorbance value was recorded on the UV-Vis genesis 10 spectrophotometry tool.

RESULTS AND DISCUSSION

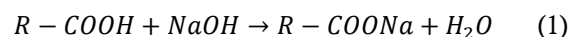
This research was conducted to improve the quality of used cooking oil using this method despicing, neutralization, bleaching and studying the effect of NaOH concentration on the neutralization process and the mass percent of natural zeolite in the bleaching process used cooking oil purification. Cooking oil quality can be determined by several parameters one of which is the acid number, peroxide number, color and water content.

Neutralization Process

The results of the analysis of used cooking oil at the beginning and after the neutralization treatment showed a significant decrease. the results of the analysis consisting of acid number, peroxide number and color number is shown in Table 1.

Effect of NaOH Concentration to Acid Numbers

The acid number expresses the amount of free fatty acids in the oil, and is usually associated with the hydrolysis of oil associated with oil quality. Requirements for the quality of the acid number in cooking oil according to SNI 3741: 2013, The maximum allowed value of the acid number is 0.6 mg KOH/g. Reaction on The equation that occurs in determining the acid number is the acid reaction with bases that produce salt (Aswita, 2015).



The results of the acid number analysis show the differences that occur in each treatment. The lowest acid number was obtained at 19% NaOH concentration treatment with the acid number value is 4.33 mg NaOH/g and the highest is the treatment 13% NaOH concentration with an acid number value of 6.00 mg NaOH/g. Neutralization reaction in Eq. (1) is the reaction between free fatty acids and NaOH salt and water form. The value of the acid number is closely related to the amount of NaOH which is used to neutralize per gram of oil. The acid number value of the oil will be directly proportional to the level of free fatty acids in the oil. The freer fatty acid which reacts with NaOH then the free fatty acid content and number the acid in the oil will decrease according to Table 2. So that with 19% NaOH treatment the acid number was degraded by 71.68 %.

Primary and secondary oxidation parameters are closely related to color, smell, taste and other impurities in fish oil (Suseno et al., 2012). Free fatty acids in oil is a parameter in

determining the quality of oil. Oil that has a high percentage of free fatty acids will have a bad taste and aroma (Sathivel et al., 2003).

Table 2. Effectiveness Concentration NaOH to Acid Number.

No	NaOH Concentration Treatment	Effectiveness (%)
1.	13%	60.77
2.	15%	65.55
3.	17%	70.51
4.	19%	71.68

Free fatty acids in oil will be easily oxidized so derivative products, namely aldehydes and ketones, will easily form and make oil becomes more easily rancid (Wayan, 2017).

Effect of NaOH Concentration to Peroxide Number

The peroxide number is the number of milliequivalents of active oxygen present in 1000 grams of oil or fat. Peroxide number quality requirements in cooking oil according to SNI 3741: 2013 a maximum of 10 mekO₂/Kg of oil (Aswita, 2015).

Peroxide value analysis results at the beginning and after neutralization treatment shows a significant reduction value. Analysis of the value of the peroxide number can be seen in Table 3. Peroxide value of used cooking oil at the lowest in the treatment the concentration of NaOH was 13% with a value of 8.96 mek O₂/kg and the most the highest concentration of NaOH treatment was 19% with a value of 7.48 mek O₂/kg, thus the effectiveness of NaOH to reduce the peroxide number in used cooking oil is equal to 31.65% in the highest NaOH concentration treatment, namely 19%. Efficiency of number values the peroxide obtained was 28.22%. The greater the NaOH concentration used, the greater the decrease in the value of the peroxide number in used cooking oil. Saponification or neutralization reactions according to Eq. (1) above are presumed is a factor that causes the decrease in the value of the peroxide number.

The hydroperoxide compounds present in the oil bind to the soap formed in the reaction (Alamsyah, 2017). The formation of peroxide compounds is a sign of the primary oxidation process in fish oil. Compound hydroperoxides formed in oil are caused by various factors, among

others freshness factors and treatment temperature (Aidos et al. 2003).

Table 3. Effectiveness Concentration NaOH to Acid Number.

No	NaOH Concentration Treatment	Effectiveness (%)
1.	13%	18.18
2.	15%	23.11
3.	17%	28.17
4.	19%	31.65

Effect of NaOH Concentration to Color Degradation

The absorption of UV-Vis light results in an electronic transition, namely the promotion of the electron- electrons from ground state orbitals which are low energy to excited state orbitals higher energy. The greater the absorbance of a solution, the solution is the cloudier, and the worse the quality of the solution (Frima, 2015). Table 4 shows the effect of NaOH concentration on the absorbance of oil. Value result the absorbance obtained by reading the instrument Spectrophotometry is used cooking oil that has been neutralized at a concentration of 19% has the smallest absorbance value compared to the NaOH concentration another on the neutralization process. And the greatest effectiveness is also found in treatment 19% NaOH concentration. The color degradation efficiency obtained was 8.03%.

Table 4. Effectiveness Concentration NaOH to Color Degradation.

No	NaOH Concentration Treatment	Efektivitas (%)
1.	13%	6.37
2.	15%	6.93
3.	17%	7.47
4.	19%	8.03

As the NaOH concentration increases, the absorbance value will increase shrinking or the color degradation of used cooking oil will be greater. Concentration The high NaOH used causes free fatty acids to bind to Na⁺ ions and become soap. The saponification reaction that occurs also binds the pigment components so that the color of the neutralized oil is brighter than the crude oil. Character visually between treatments showed no significant color difference (Wayan, 2017).

So it can be said that in this study the best NaOH concentration was used obtained in 19% NaOH treatment with the results of the analysis of

Table 5. Results of the analysis of the bleaching process.

No	Zeolite Concentration Treatment	Acid Number (mgNaOH/gr)	Peroxide Number (mekO ₂ /kg)	Color Number at the wavelength 410nm 410nm
1.	30%	2.96	7.37	1.978
2.	50%	2.63	7.28	1.767
3.	70%	2.57	7.16	1.5
4.	90%	2.40	7.00	1.445

several parameters including the acid number value of 4.33 mgNaOH/g (efficiency 71.68%), value peroxide number was 7.48 mek O₂/kg (efficiency 31.65%) and color absorbance amounting to 2.759 (efficiency 8.03%).

Bleaching Process

The results of the analysis of used cooking oil at the beginning and after the bleaching treatment after the neutralization process with 19% NaOH treatment showed a significant decrease. The results of the analysis consisting of acid number, peroxide number and color number is shown in Table 5.

Effect of Bayah Natural Zeolite Mass to Acid Number

Used cooking oil without adsorption has an acid number value of 15.50 mg NaOH/g which indicates the amount of damage to the cooking oil, this value has been passing the threshold of cooking oil quality requirements stated in the quality standard Cooking Oil SNI 3741: 2013 where the maximum allowable acid number is 0.6 mg KOH/g.

Based on Table 5, it shows that the results of the acid number analysis after being carried out adsorption process with bayah natural zeolite, where the addition of zeolite mass gives linear results to decrease the acid number in used cooking oil. The greater the mass of zeolite used, the lower the value of the acid number obtained. The effect of the use of the zeolite mass used, this is it is possible that the greater the adsorbent ability the greater the surface area adsorbent for the adsorption process so that free fatty acids in the oil more and more waste is adsorbed by natural zeolite. The lowest acid number was obtained in the zeolite mass treatment of 90%, with 2.40 mg NaOH/g. The efficiency of the acid number obtained is 84.31%.

The ability of zeolite to reduce acid number is because zeolite contains a lot elements of SiO₂. The SiO₂ percentage of 75.35% identifies this zeolite hydrophobic (non-polar) so that it can be

used as an adsorbent for repair used cooking oil quality (non-polar) (Aswita, 2015).

Table 6. Effectiveness of Mass Natural Zeolite to Acid Number.

No	Zeolite Concentration Treatment	Effectiveness (%)
1.	30%	80.62
2.	50%	82.78
3.	70%	83.22
4.	90%	84.31

Effect of Bayah Natural Zeolite Mass to Peroxide Number

Used cooking oil without adsorption has a peroxide value of 10.42 mek O₂/kg which indicates the amount of deer damage degree to cooking oil, this value has been passing the threshold of cooking oil quality requirements stated in the quality standard cooking oil SNI 3741: 2013 where the maximum allowed acid number is 10 mek O₂/kg.

Based on Table 6 above, it can be seen the results of the analysis of the value of peroxide numbers after the adsorption process using natural zeolite bayah. More and more the greater the mass of zeolite used, the lower the value of the peroxide number. The smallest peroxide value was obtained by mass treatment of natural zeolite 90%, where the value of the peroxide number is 7.00 mekO₂/kg. The efficiency obtained amounted to 36.05%. The greater the zeolite mass used, the area the surface of the zeolite adsorbent is getting bigger to allow the process to occur adsorption on used cooking oil so that the unwanted impurities will be even more reduced.

Table 7. Effectiveness of Mass Natural Zeolite to Peroxide Number.

No	Zeolite Concentration Treatment	Effectiveness (%)
1.	30%	32.66
2.	50%	33.47
3.	70%	34.58
4.	90%	36.05

The ability of natural zeolite to reduce the amount of peroxide in the oil is due by the silanol (Si-OH) group. Zeolite provides considerable adsorption power because in zeolites, oxygen is the link between the two silica layers that flank one the bonded alumina layer is very weak, this makes the structure easy to expand so that the peroxide and water molecules easily move between the crystal units. Peroxides can enter into the structure and replace the loose hydrogen ions to neutralize cargo (Aswita, 2015).

Effect of Natural Bayah Zeolite Mass to Color Degradation

The color or clarity is a selling point factor for a cooking oil. Because the clarity of cooking oil is an aesthetic and benchmark value measure the purity of the cooking oil. Oil that is clear is not always better compared to oil that is thick yellow. Color is influenced by carotenoids and other components in oil. In some ways, carotenoids are very beneficial for health (Yustinah, 2014).

The presence of carotenoids causes a reddish yellow color. Very carotenoids are oil soluble and is a hydrocarbon with many saturated bonds. When hydrogenated oil will result in hydrogenation of carotenoids and a red color will occur reduced. Apart from that, the heating treatment will also reduce the pigment color, because carotenoids are unstable at high temperatures. This pigment is easily oxidized to oil will go rancid easily (Yustinah, 2014).

Based on Table 6, it can be seen the effect of using natural zeolite mass on the absorbance value of the oil analyzed by spectrophotometry. The greater the mass The zeolite used, the smaller the absorbance value obtained at oil. The smallest absorbance value was obtained by treating the zeolite mass 90% amounting to 1,445 abs. The efficiency of oil color degradation was 51.83%. More and more the greater the absorbance of a solution, the cloudier the solution is, and the more it is poor quality of the solution (Frima, 2015). At the stage of neutralization of cooking oil, the despicing results are mixed with 19% NaOH solution, the mixture will be formed a grain or brown sediment which can be called salt (soap). The salt formed may help the process of separating substances color of impurities in used cooking oil.

Table 8. Effectiveness of Mass Natural Zeolite to Color Degradation.

No	Zeolite Concentration Treatment	Effectiveness (%)
1.	30%	34.07
2.	50%	41.10
3.	70%	50.00
4.	90%	51.83

The next stage is bleaching with using natural zeolite adsorbent. At this stage the color degradation is experienced significant brightness level due to the presence of natural zeolite adsorbent. This can this is because natural zeolite is able to absorb more dye previous process. The greater the mass of natural zeolite used, the ability or surface welding which allows the adsorption process on used cooking oil the greater it is. The decrease in the absorbance number in oil is due to the physical adsorption process of natural zeolite which is composed of pores with a surface area that is able to absorb harmful compounds in the oil (Fauziah, 2019).

So it can be said that in this study the use of the natural zeolite mass of bayah the best was obtained at 90% treatment with the results of several parameter analysis including the acid number value of 2.4 mgNaOH/g (efficiency 84.31%), the number value peroxide 7.00 mekO₂/kg (32.83% efficiency), color absorbance of 1,445 abs (efficiency degradation is 51.83%).

CONCLUSION

Based on the experiments that have been carried out in refining used cooking oil with see some analysis parameters, then in the neutralization process, the concentration optimum NaOH is 19% with the acid number value of 4.3 mgNaOH/g, the peroxide number is 7.48 mekO₂/Kg and degradation color of 8,03%. Then in the bleaching process, the optimum percent mass of natural zeolite is 90%, namely the numerical value acid of 2.40 mgNaOH/g, the peroxide number of 7.00 mekO₂/Kg and degradation color of 51.83%.

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