Utilization of Palm Kernel Shell Ash to Improve Used Palm Cooking Oil Quality

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ABSTRACT

Palm kernel shell ash (PKSA) is a waste from the use of palm kernel shell as fuel which is very abundant, especially in Riau, Indonesia. The objective of this study utilized the PKSA to improve the quality of used palm cooking oil. The characteristics of PKSA were analyzed using FTIR to determine the presence of Si-O-Si and XRF to determine the amount of SiO_2 that functions as an adsorbent. This study determined the optimization of PKSA weight variations in reducing pollutant parameters in used palm cooking oil followed by optimum contact time variations. PKSA weight variations were 5g, 10g, 15g, and 20g, while the variations of contact time were 1, 2, 3 and 4 weeks. The parameters tested included color, water content, free fatty acids (FFA) and peroxide value (PV) in used palm cooking oil to be compared with the quality requirements for palm cooking oil in SNI 01-3741-2002. The results showed that the optimum weight of PKSA is 20 g with a contact time of 2 weeks. These conditions can reduce the red content of used palm cooking oil by 76.47%, moisture content 81.21%, FFA 59.01% and the PV 61.40%. The parameters of color, moisture content and FFA in these conditions are in accordance with the requirements for palm cooking oil quality according to SNI, while the PV parameter does not meet the SNI but still experiences a decrease.

Keywords: palm kernel shell ash, used palm cooking oil, optimum weight, optimum contact time

1. INTRODUCTION

Waste disposal problems continue to increase and to endanger environmental preservation. Recycling used frying oils not only could reduce disposal problems but, more importantly, would increase the effective usage of food and agricultural resources [1]. Used cooking oil is derived from several repetitions cooking, during the frying process, the oil will experience degradation reactions caused by heat, air, and water resulting in oxidation, hydrolysis, and polymerization.

Degradation reaction products contained in this oil will reduce the quality of the oil and cause adverse effects for human health [2]. Repeated use of oil is not good for health such as narrowing of the arteries that can lead to stroke, and hypertension [3].

Recycling used cooking oil using adsorbents such as silica gel, magnesium oxide, aluminum hydroxide gel, activated clay, and bagasse adsorbent has been studied (1,4,5) for improving the quality parameter of used cooking oil. The indicators of poor oil quality include elevated FFA, change the color, peroxide value, low smoke point, low iodine value, total polar material, high foaming properties and increased viscosity [6].

Yustinah [7] studied about coconut shell ash as an adsorbent for improving quality used palm cooking oil, this study using variation weight 2, 4, 6, 8, 10 and 12 g of coconut shell ash. The result was obtained when using 10 g coconut shell ash with a reduction of PV as 10,88

$meqH_2O_2$/Kg. The Reduction of color absorbance value was obtained when using 12 g of coconut shell ash.

The aim of this research was to study the ability of palm kernel shell ash (PKSA) as an adsorbent for improving the quality of used palm cooking oil by reducing FFA, PV, moisture content and refinery the color. Adsorbent weight variation and contact time variation will be used in this study to know the effective time and level of adsorbent that should be used in the used palm cooking oil refining process. Recycling of disposed oils and waste products from palm kernel shell (PKS) as a solid fuel into purified cooking oil and PKSA as adsorbent are expected to reduce waste disposal problems that are consistent to be hot issued discussion today. Zarina [8] reported about mineral content of PKSA, the results showed that SiO_2 51,18%, Al_2O_3 4,61%, Fe_2O_3 3,42%, CaO 6,93% dan MgO 4,02% contained in PKSA. Okoroigwe [9] used PKSA as an adsorbent to purified wastewater and conducted characterization of PKSA first by X-ray photoelectron and SEM. The results showed that the carbon content of PKSA by X-ray photoelectron was 49,79% and the pore size of PKSA by SEM was 51,8μm x 30,56μm, it could be concluded that PKSA is very effective as an adsorbent.

2. METHOD

2.1. Chemicals and Equipments

All chemicals used in this experiment were analytical grade brand Merck (Germany). Analytical balance (Kern

& Sohn, GmbH), FTIR (Nicolet iS 10 with KBr), XRF, Lovibond tintometer.

2.2. Used Palm Cooking Oil

Used palm cooking oil was prepared from a restaurant in Pekanbaru City.

2.3. Adsorbent of PKSA

Palm Kernel Shell (PKS) taken from a crude palm oil factory in Riau. PKS washed with water to remove littering sand and soil. PKS milled with a grinder into powder and sifted to obtain a diameter of $\pm < 600$ μm. PKS that have been dried then burn in the furnace at 800 ^{0}C temperature, to make palm kernel shell ash (PKSA). PKSA has to be activated first, it was immersed in hydrochloric acid to remove the trace metal, PKSA then neutralized with NaOH and washed with aqua dest, dried in 120 ^{0}C for 5 h to evaporated water molecules.

2.4. Determination of Optimum Condition

2.4.1. Weight Variation of PKSA

50 mL of used palm cooking oil was used to soak the PKSA weight 5, 10, 15, and 20 g in a closed glass vial. Soaking was done for 2 weeks. Soaked oil was filtered with filter paper. Oil parameters quality analysis was for color, moisture content, FFA and PV.

2.4.2. Contact Time Variation of PKSA

50 mL of used palm cooking oil was used to soak the PKSA with the optimum weight condition obtained from the previous treatment. Soaking contact time variations were 1, 2, 3 and 4 weeks. Soaked oil was filtered with filter paper. Oil parameters quality analysis was for color, moisture content, FFA and PV.

2.5. Oil Quality Testing
2.5.1. Colour Analysis

Pour the prepared test sample into 25.4 mm glass cell, ensure that the cell is thoroughly clean and dry. Place the cell containing the test portion in the lighting cabinet, immediately determine the color of the test portion, initially by using the color racks in the ratio of 10 yellow to 1 red [10].

2.5.2. Moisture Content (%)

Weigh accurately 5 g of test sample into a tared moisture dish that has been dried and cooled previously in a desiccator. Place in an air oven and dry for 30 min at 130 ^{0}C. Remove from the oven, cool to room temperature in a desiccator and weigh. Repeat procedure until the loss in weight does not exceed 0.05% per 30 min drying period [10].

$$\text{Moisture Content } \% = \frac{\text{loss in mass (g)}}{\text{mass of the test portion (g)}} x100$$

2.5.3. FFA (%)

7 g of oil sample was weighted in flask 250 mL. Added 75 mL hot neutral ethanol and 2 mL pp indicator then was titrated with 0.1 N NaOH which was standardized until the pink color and constant for 30 seconds. FFA was measured as % FFA [10].

$$\% \text{ FFA as palmitic} = \frac{\text{mL NaOH x N NaOH x 25,6}}{\text{Sample weight}}$$

2.5.4. PV (meq/kg)

5 g of oil was weighted into 250 mL Erlenmeyer flask with a glass stopper and add 50 mL of the 3:2 acetic acid isooctane solution. Swirl to dissolve the test portion. Add 0.5 mL of saturated KI solution using a suitable volumetric pipet. Allow the solution to stand for exactly 1 min, thoroughly shaking the solution at least three times during the 1 min, and then immediately add 30 mL of distilled water. Titrate with 0.1 M sodium thiosulfate, adding it gradually and with constant and vigorous agitation. Continue the titration until the yellow iodine color has almost disappeared. Add 0.5 mL of 10% SDS, and then add about 0.5 mL of starch indicator solution. Continue the titration with constant agitation, especially near the endpoint, to liberate all of the iodine from the solvent layer. Add the thiosulfate solution dropwise until the blue color just disappears. Conduct a blank determination of the reagent daily. The blank titration must not exceed 0.1 mL of the 0.1 M sodium thiosulfate solution [10].

$$\text{PV} = \frac{(S - B)\text{mL x M thiosulfate x 1000}}{\text{sample weight (g)}}$$

2.5.5. FTIR and XRF analysis

FTIR and XRF were used to analyze PKSA before and after soaked with the used palm cooking oil.

3. RESULTS AND DISCUSSION

3.1. Results

3.1.1. Analysis of Used Palm Cooking Oil Parameters

The analysis results of various parameters of used palm cooking oil before treated with PKSA compared to the Indonesian National Standard (SNI) 01-3741-2002 are available in Table 1 below:

Table 1. Used Palm Cooking Oil Compared to SNI 01-3741-2002

No	Parameters	Unit	Value	SNI 01-3741-2002
1	Color	-	(6,8) Red-Brown	Pale yellow to yellow
2	Moisture Content	%	0,44	Max 0,30
3	Free Fatty Acid	%	0,48	Max 0,30
4	Peroxide Value	Meq/Kg	29,87	Max 1,00

From table 1 can be concluded the color of used palm cooking oil had a high red-brown color level of 6,8. SNI set the color standard of palm cooking oil in range of pale yellow to yellow. The higher the red-brown content of palm cooking oil indicated the quality of oil had decreased. The red-brown color was due to compound degradation of used palm cooking oil and the suspended substances derived by the food components that were fried. Moisture content, FFA and PV of the used palm cooking oil did not meet the standard palm cooking oil of SNI 01-3741-2002. The continuous heated and repeated use of used palm cooking oil altered the chemical composition of the oil. These changes caused by the process of oxidation, polymerization, hydrolysis, and caramelization occurred in the oil [11].

3.1.2. *The efficiency of PKSA to Improve Quality of Used Palm Cooking Oil*
3.1.2.1. *Effect of PKSA Weight Variation*

Figure 1 below shows the efficiency of weight variation of PKSA in improving the quality of used palm cooking oil:
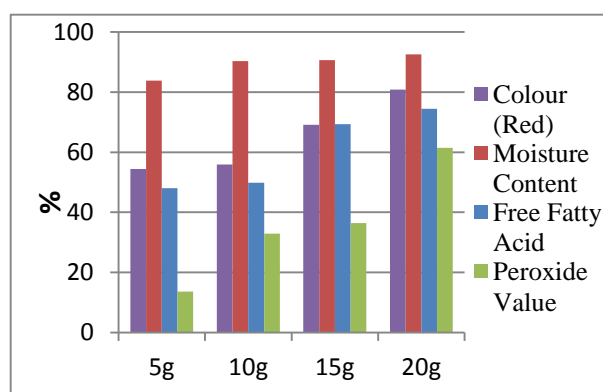

Figure 1. Effect of PKSA weight variation with 50 mL of used palm cooking oil and contact time for 2 weeks

Figure 1 detailed about the optimum condition of PKSA weight variation was 20 g of PKSA soaking in 50 mL used palm cooking oil. In this condition, the red-brown color in used palm cooking oil decreased from value of 6,8 to 1,30 with an efficiency of 80.88%, moisture content of used palm cooking oil decreased from 0.44% to 0.03% with an efficiency of 92.53%, FFA decreased from 0.48% to 0.12% with an efficiency of 74.47%, PV decreased from 29.87 meq/Kg to 11.53 meq/Kg with an efficiency of 61.40%.

The parameters analysis obtained with the optimum condition of 20 g PKSA, were included in the standard range of palm cooking oil quality requirements according to SNI 01-3741-2002 exception for the PV parameter. The tendency of the results of PV analysis continues to decline even though it did not meet the standard range of quality requirements according to SNI. The optimum condition of PKSA contact time variation was determined by PKSA optimum weight with the highest efficiency in lowering parameters of used palm cooking oil with the weight of PKSA was 20 g.

3.1.2.2. *Effect of PKSA Contact Time Variation*

Figure 2 below shows the efficiency of contact time variation of PKSA in improving the quality of used palm cooking oil:
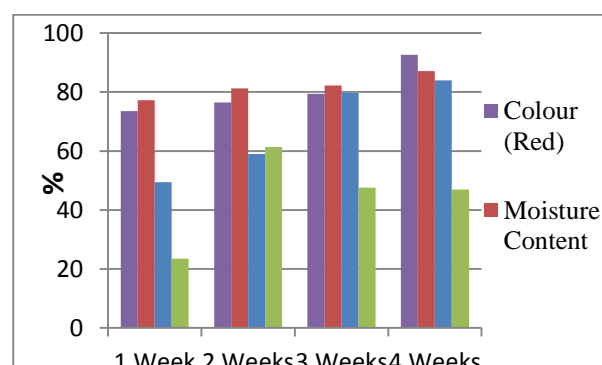

Figure 2. Effect of PKSA contact time variation with 50 mL of used palm cooking oil and PKSA weight 20 g

The highest efficiency of PKSA for the PV parameter was at the contact time of 2 weeks at 61.40%. As for the parameters of color, moisture content and FFA, the efficiency of PKSA increases with longer contact time although the contact time of 2 weeks each of it had exceeded 50% with parameter values that were in accordance with SNI 01-3741- 2002. It can be concluded that the optimum conditions of soaking of PKSA with used palm cooking oil were at a weight of 20 g and contact time for 2 weeks.

3.2. *Discussion*

3.2.1. *Color Analysis*

Oxidation process (i.e tocopherol and carotenoids) in the oil will cause degradation that continues to make a dark color in the oil. Metals such as Fe, Cu, and Mn that can be derived from foodstuffs will cause unwanted color in the

oil [12]. The more dark color in the used palm cooking oil indicates that the oil has undergone oxidation, polymerization and the formation of carbonyl compounds [11]. Heating temperature and long-warming influenced this process [12].

In this study, the greater use of PKSA weight and the longer contact time, making the level of clarity of used palm cooking oil also better. Lovibond analysis showed that the use of 20 g PKSA and 4 weeks contact time, the red content of the oil decreased with an efficiency of 92.65%, even though the contact time of 2 and 3 weeks had shown good clarity. The optimum condition of PKSA as weight and contact time for improved quality of used palm cooking oil has started from 2 weeks soaking and did meet with the standard range of quality requirements according to SNI.

The ability of PKSA to improve the clarity of used palm cooking oil is caused by the nature of PKSA as an adsorbent. The silica content in PKSA acts as an adsorbent. Silica has a large surface area that is capable of absorbing various polar or non-polar impurities. The effectiveness of an adsorbent depends on polarity, active side, surface area, porosity, particle size, pH and humidity [13].

3.2.2. Effect to FFA

The FFA content is one of the most important indicators of cooking oil deterioration. The oxidized products of fatty acids give the off-flavors and odors (hydrolytic rancidity) to the frying medium and fried foods [14]. During frying, the frying oil is exposed to elevated temperatures of the order of 160 to 180 ^{0}C in the presence of air and moisture. As a result, hundreds of complex chemical reactions take place in the oil and it gets chemically altered during frying [12].

The presence of FFA in cooking oil is caused by the hydrolysis reaction in oil, it is triggered by the moisture content in food that during fried in oil, this reaction is accelerated by the heating, acidity and catalyst. The results of palm oil hydrolysis are FFA and glycerol. The high content of FFA causes the oil yield as triglycerides reduced [15].

In this study, the efficiency of PKSA in lowering the FFA level of used palm cooking oil increased by increasing the contact time. Starting from contact time for 1 week the level of FFA of used palm cooking oil meets with a standard range of quality requirements according to SNI. Efficiency PKSA in lowering the FFA value of used palm cooking oil continues to increase (figure 2) until the contact time for 4 weeks, but the oil was exposed to oxygen longer.

The efficiency of PKSA in lowering the FFA levels in used palm cooking oil, related to the presence of silanol clusters on silica surfaces. Oxygen in the fatty acid carbonyl group can be bound to the surface of silica through the silanol group. The bond that occurs is the hydrogen bond between the oxygen atoms in the fatty acid carbonyl group with the hydrogen atom in the silanol group [16].

3.2.3. Effect to Moisture Content

The presence of water in the oil is not desirable because it can hydrolyze the oil produces free fatty acids which cause rancidity in the oil. This reaction was accelerated by the presence of bases, acids or enzymes. Moisture content in the oil also triggering the growth of microorganisms. The presence of water in oil as a whole can decrease the quality of oil [17].

The silica content in PKSA acts as an adsorbent that can bind water so that the siloxane groups turn into silanol groups. The highest efficiency of PKSA in reducing the moisture content of used palm cooking oil at contact time for 4 weeks (figure 2), even though all contact time variations meet with the standard range of quality requirements according to SNI 01-3741-2002. The siloxane group in the form of a polymer can bind water molecules to form a silanol group (Si-OH) through the hydrolysis process. The silanol group can be removed when the silica-containing material is heated through a condensation process to form a siloxane polymeric molecule.

3.2.4. Effect to PV

PV is the number of moles of active oxygen equivalent contained in 1000 g of oil or fat. PV indicates the damage level of oil or fat that occurs due to oxidation. Unsaturated fatty acids are triglyceride constituents that can bind oxygen to the double bonds contained therein, which can form peroxides [11]. PV is a useful biomarker that indicates the initial stages of oxidation [18]. At high temperatures in frying, the atmospheric oxygen reacts with the oil at the oil surface, causing oxidative alterations [12]. The hydrolysis of triglycerides and decomposition of hydroperoxide at high temperature in the presence of moisture and air forms FFA [19].

The highest efficiency of PKSA in reducing the PV level of used palm cooking oil was obtained in the contact time for 2 weeks soaked which was 61.40% (figure 2). At soaking for 3 and 4 weeks, efficiency PKSA decreased. This was due to contact with air oxygen experienced by oil for longer. Efficiency PKSA in reducing the level PV used palm cooking oil becomes the main determining the optimum condition of PKSA to improve used palm cooking oil quality. Contact time longer than 2 weeks does not further improve the quality of used palm cooking oil as a whole.

3.2.5. FTIR Analysis

FTIR analysis of PKSA before and after soaking with used palm cooking oil can be seen in Figure 3 below:
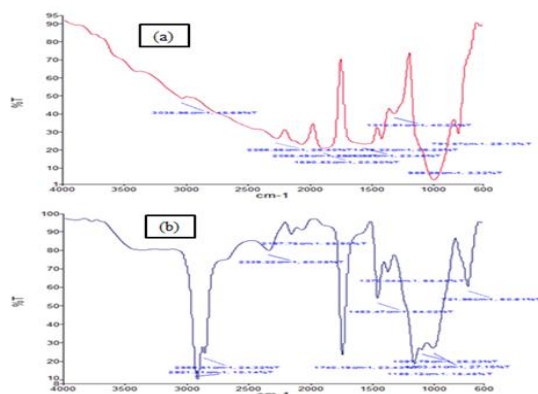
Figure 3. FTIR PKSA (a) before soaking; (b) after soaking with used palm cooking oil

FTIR analysis of PKSA as shown in Figure 3, the peak of Si-O-Si was detected both in PKSA before and after soaking with used palm cooking oil in the wavelength range of 1000 cm^{-1} to 1200 cm^{-1}. The presence of siloxane groups (Si-O-Si) in PKSA has a function as an adsorbent that can absorb organic or inorganic substances physically or chemically. The presence of silanol (Si-OH) groups in PKSA after treatment was detected at a wavelength of 2900 cm^{-1}. The silanol group indicates the process of adsorption of water molecules in the siloxane group. Both of those groups are responsible as an active site of silica gel which can be modified [20].

3.2.6. XRF Analysis

XRF or X-Ray Fluorescence was an analysis technique that can analyze the elements that build a material. This technique can also be used to determine elemental concentrations based on wavelengths and the number of X-rays re-emitted after a material was shooted on high-energy X-rays.

The results of XRF analysis of PKSA before and after soaking with used palm cooking oil are given in table 2 below:

Table 2. XRF analysis of PKSA

Before Soaking	SiO_2 55,2%
After Soaking	SiO_2 43,1%

The content of silica (SiO_2) in PKSA after soaking is lower than before soaking with used palm cooking oil. This shows that some SiO_2 has bound a water molecule to form a Si-OH silanol group.

The optimum condition of PKSA in lowering parameter of color, FFA, moisture content and PV of used palm cooking oil is 20 g of PKSA in weight for 2 weeks soaking. These conditions can reduce the red content of used palm cooking oil by 76.47%, moisture content 81.21%, FFA 59.01% and the PV 61.40%. The parameters of color, moisture content and free fatty acids in these conditions are in accordance with the requirements for palm cooking

oil quality according to SNI, while the PV parameter does not meet the SNI but still experiences a decrease. This study still requires advanced toxicity and metal content analysis of the oil-soaked with PKSA.

4. CONCLUSION

The optimum condition of PKSA in lowering parameter of color, FFA, moisture content and PV of used palm cooking oil is 20 g of PKSA in weight for 2 weeks soaking. These conditions can reduce the red content of used palm cooking oil by 76.47%, moisture content 81.21%, FFA 59.01% and the PV 61.40%. The parameters of color, moisture content and free fatty acids in these conditions are in accordance with the requirements for palm cooking oil quality according to SNI, while the PV parameter does not meet the SNI but still experiences a decrease. This study still requires advanced toxicity and metal content analysis of the oil-soaked with PKSA.

ACKNOWLEDGMENT

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