PALM KERNEL SHELL ASH: THE EFFECT OF WEIGHT AND STIRRING DURATION ON WASTE PALM COOKING OIL QUALITY

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Abstract

This study aims to investigate the effect of variations Palm Kernel Shell Ash (PKSA) in weight and stirring duration on the quality of waste palm cooking oil (WPCO). PKSA is waste from the use of Palm Kernel Shell (PKS) as fuel in palm oil factories. The method used in this study is a laboratory experiment with variations in the weight of PKSA and variations in stirring duration to improve WPCO quality. PKSA was characterized using XRF, FTIR, and XRD. The parameters of WPCO analyzed were color, water content, and free fatty acid (FFA). The standard used for comparison was the SNI for palm cooking oil 7709-2019. The results showed that the treatment category of S3, where PKSA was 20 g and stirring duration was 90 min, decreased the parameter value of WPCO according to SNI requirements. The improved quality of WPCO can be used for various purposes, including biodiesel, fertilizer and poultry feed.

***Keywords**: PKSA, stirring duration, weight variation,WPCO*

Introduction

Palm kernel shells (PKS) are a major waste of the palm oil industry, accounting for 60% of oil production (Novita and Idris, 2022). PKS is generally used as a fuel in the palm oil industry. In addition, another waste produced from the use of PKS as fuel is palm kernel shell ash or PKSA. PKSA accounted for 50% of the total PKS burned. Edmund et al. (2014) used PKSA to purify water. In that study, SEM showed a large pore size of 51.8µm x 30.56µm so that it made PKSA can be used as an adsorbent. The high silica content of PKSA is estimated to be effective as an adsorbent.

Waste palm cooking oil (WPCO) is generally used for household needs and restaurant businesses (Novita et al., 2021; Miskah et al., 2019). Based on its chemical composition, WPCO contains compounds that are carcinogenic and occur during frying. The sustainable use of WPCO can impair human health, cause cancer, and reduce the intelligence of the next generation (Kembaren et al., 2018; Yahya et al., 2019). Proper handling is needed so that this WPCO can be useful and cannot harm human health or the environment (Olalekan et al., 2016; Mardina et al., 2012).

Several studies have conducted chemical analysis on WPCO, showing that the quality of the oil used repeatedly decreased, especially in terms of the peroxide value and acid number compared to the required quality standard. The quality standard for palm cooking oil in Indonesia 7709-2019 (BSN, 2019). Zein et al. (2016) used rice husk ash to improve the quality of used cooking oil, with variations in RHA weight and contact time of soaking RHA with used cooking oil. Regeneration of used cooking oil using coir and coconut shells was performed by (Rahayu et al., 2014). Putra et al. (2014) improved the quality of used cooking oil using activated carbon and clay as biodiesel feedstock was carried out by Putra et al., (2014). Olalekan et al. (2016) used oyster shells to improve the quality of vegetable oils. Bonassa et al. (2016) used sugarcane bagasse ash to reduce the pollutant parameters in waste cooking oil using a batch method. However, this study differs from previous studies in that it utilized palm oil waste to improve the quality of WPCO. PKSA has the potential to be used as an adsorbent to improve the quality of used cooking oils. This study explored the effect of variations in PKSA weight and stirring duration on the increase in several parameters of WPCO according to SNI 7709-2019. WPCO with certain parameter values can be used for other purposes, such as the manufacture of biodiesel, fertilizer and poultry feed.

Research Methods

Materials

Ethanol and sodium hydroxide were analytical grade (Merck, Germany).

Instrumentation

Analytical Balance (Kern & Sohn, GmbH) to accurately weigh the PKSA. A magnetic hot-plate stirrer (CRS 22H, CAPP) was used to ensure an appropriate stirring duration for the mixture of WCO and PKSA. FTIR (Fourier transform (FTIR)Infra Red; Nicolet iS 10 with KBR) and X-ray fluorescence (XRF; PANalytical Epsilon 3) were used for PKSA characterization.

Procedure

1) Waste palm cooking oil (WPCO)
   WPCO was obtained from a restaurant in Pekanbaru City. WPCO was deposited for several hours to separate the remaining solids from the food fried in WPCO.
2) PKSA preparation
   The Palm Kernel Shell Ash (PKSA) was reserved from a palm oil factory in Riau. PKSA was sieved 100 mesh and immersed in hydrochloric acid to remove the trace metals, then neutralized with aquadest, dried in 120 ºC for 5 h to evaporated water molecules (Novita et al., 2020).
3) PKSA characterization
   PKSA characterization includes functional group representation by FTIR, oxide content by XRF, and crystalline phase by XRD.
4) PKSA weight variation and stirring duration
   Weight variation of PKSA as 5 g, 10 g, 15 g and 20 g were employed in each Erlenmeyer flask containing 100 mL of WPCO. Each mixture was then stirred using a magnetic stirrer at 500 rpm at room temperature of 27 °C. The stirring duration of each mixture was 30, 60, and 90 min. The WPCO after treatment was then filtered to separate the oil and PKSA, and the oil parameters were analyzed according to SNI 7709-2019. Table 1 lists the treatment categories for WPCO according to PKSA.
5) WPCO analysis
   a. Color analysis
      Color analysis was conducted by panelists using the sense of sight (eyes) for testing conditions. An adequate sample was placed in a clean and dry container. The panelists then carefully assessed the color of the sample (Novita et al., 2021; BSN, 2019).
   b. Water content analysis
      Weigh 5 g of WPCO. The samples were then placed in an air oven and dried for 30 min at 130 ^{0}C. After drying, the samples were cooled to room temperature in a desiccator and carefully weighed. A recurrence procedure was required to ensure that the weight loss of WPCO did not exceed 0.05% per 30 min during the drying period (BSN, 2019; Novita et al., 2021). The percentage of moisture content

was calculated using Equation (1).

c. Free fatty acid (FFA)
WPCO (28 g) was added to 75 mL of hot neutral ethanol and 2 mL of phenolphthalein. The mixture was titrated with 0.1 N NaOH until a pale pinkish color appeared and remained constant for 30 s. FFA was counted as % FFA (BSN, 2019) according to equation (2).

Table 1. WPCO treatment category

Stirring duration (minutes)	PKSA weight variation (gram)			
	5	**10**	**15**	**20**
30	P1	Q1	R1	S1
60	P2	Q2	R2	S2
90	P3	Q3	R3	S3

$$\text{Moisture Content }\% = \frac{\text{loss in mass (g)}}{\text{mass of the test portion (g)}} \times 100 \quad (1)$$

$$\%\text{ FFA as palmitic} = \frac{\text{mL NaOH} \times \text{N NaOH } \times 25{,}6}{\text{Sample weight}} \quad (2)$$

Results and Discussion

WPCO before treatment characteristic compare to SNI 7709-2019

Table 2 listed various parameter of WPCO before treatment with PKSA compare to SNI 7709-2019. From Table 2, it can be inferred that the colour, FFA and water content of WPCO did not meet the requirements of SNI (BSN, 2019) of palm cooking oil. Brownish-orange colour of WPCO described the quality of oil had decreased. The high level of FFA and water content indicated deterioration of WPCO.

Table 2. WPCO before treatment characteristic compare to SNI 7709-2019

No.	Parameter	Unit	Value	SNI 7709-2019
1	Colour	-	Brownish-orange	Yellow - orange
2	FFA	%	0.402	Max 0.3
3	Water content	%	0.22	Max 0.1

FTIR Analysis of PKSA

FTIR spectra provide a description of the functional groups that exist in PKSA. Fig 1 shows the FTIR spectra of PKSA. The bands located at 528,29 cm^{-1}, 782,23 cm^{-1} and 1002,07 cm^{-1} arouse from the stretching of the Si-O-Si (siloxane group) bonds. The same description was reported by Chen et al. (2013), in which Si-O-Si bands appeared at 611-1057 cm^{-1}. The other slight bands were attributed to oxide vibrations that already exist in PKSA. The other oxides in PKSA are listed in table 3. Furthermore, no absorption was observed at 1400 – 4000 cm^{-1}, revealing the absence of residual organic compounds in PKSA. The siloxane functional group is responsible for the adsorbent properties of PKSA.

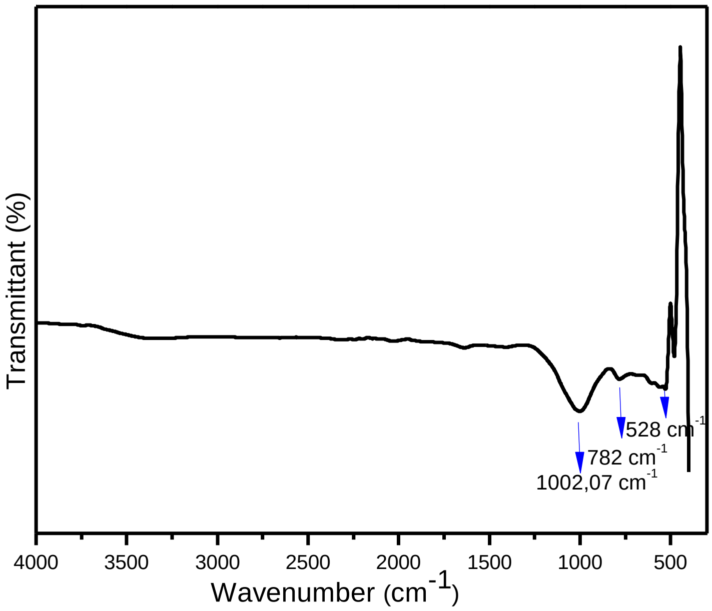

Figure 1. FTIR Analysis of PKSA

XRD Analysis of PKSA

XRD analysis revealed the solid structure of SiO_2 contained in PKSA. The calcination temperature of PKSA affected the formation of the crystalline phase of SiO_2. Chen et al., (2013) reported that the calcination temperature of SiO_2 in the range of 400-700 ^{0}C can trigger the formation of a crystalline phase of SiO_2. As illustrated in fig. 2, the strongest peak was observed at $2\theta = 27^o$ indicating the formation of a crystalline phase of silica in PKSA.

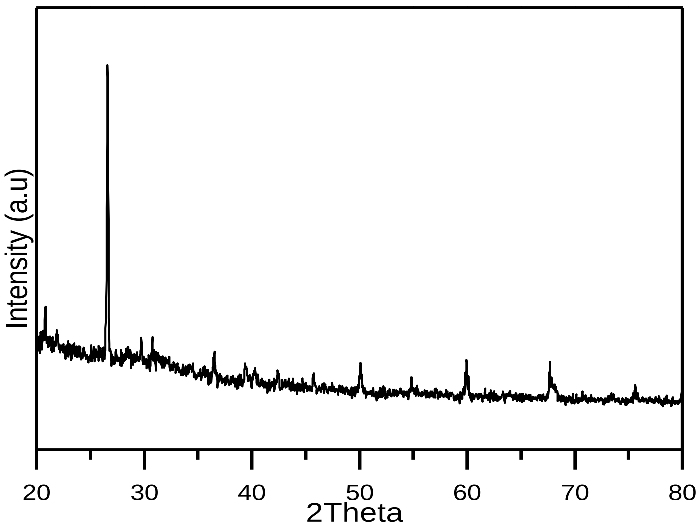

Figure 2. Diffractogram of PKSA

XRF Analysis of PKSA

XRF is a technique that shows the oxide or metal content in PKSA. Table 3 revealed the content of SiO_2 in PKSA after being soaked with HCl. SiO_2 is an oxide that plays a major role in the adsorption properties of PKSA. These properties help reduce the pollutant parameters of the used cooking oil.

The effect of PKSA weight and stirring duration to colour of WPCO

The color of WPCO after treatment with PKSA is listed in table 4. Table 4 shows that by increasing the PKSA weight and stirring duration, there was an increase in the WPCO color closer to the SNI requirement for palm cooking oil (BSN, 2019). Employing as much as 15 g of PKSA with a stirring duration of 90 min, the color of WPCO became orange, developed by treatment with PKSA of 20 g for all three stirring durations. The quality requirements for the color of palm cooking oil according to table 4 range from yellow to orange. Therefore, the treatments of R3-S3 can be a recommendation for the use of PKSA to improve the color quality of WPCO.

Table 3. Oxide content of PKSA

Oxide	Percentage
SiO_2	85,65
P_2O_5	4,12
CaO	3,71
K_2O	2,63
Fe_2O_3	2,13
other	1,76

Table 4. Color of WPCO after treatment with PKSA

Treatment Categories	Color
P1	Brownish-orange
P2	Brownish-orange
P3	Brownish-orange
Q1	Brownish-orange
Q2	Dark orange
Q3	Dark orange
R1	Dark orange
R2	Dark orange
R3	Orange
S1	Orange
S2	Orange
S3	Orange

Tarmizi et al. (2016) stated that the continuous heating of cooking oil and the content of fried ingredients affect the color quality of cooking oil. Oil deterioration can be caused by oxidation of nutrients in food, which is fried in palm oil. This process can trigger a change in the color of the oil to darker. Metals from food that are dissolved in oil during the frying process are another trigger for oil discoloration (Ramírez et al., 2022). In addition, oil discoloration indicates that the oil has experienced some reactions such as polymerization and the formation of carbonyl compounds (Ndé et al., 2019). On the other hand, PKSA has a sufficiently high adsorbent content that can enhance oil color clearness. Silica has an enormous surface area, which allows it to absorb polar and nonpolar impurities in oil. This property can increase the clarity of WPCO after treatment with PKSA.

Effect of PKSA weight and stirring duration to water content of WPCO

A series of experiments was conducted to analyze the reducing water content in the WPCO. Fig 3 illustrates the effect of PKSA weight and stirring duration on the water content of WPCO. From table 2, we can see that the water content of WPCO before treatment is 0,22%, while SNI (BSN, 2019) denotes that the water content of palm cooking oil is max 0,1%. Employing PKSA in WPCO in all treatment categories led to a decrease in the water content of WPCO. The highest percentage of WPCO water content decrease was in the S3 category with a 12,08% water content reduction level and a water content value of 0,193%.

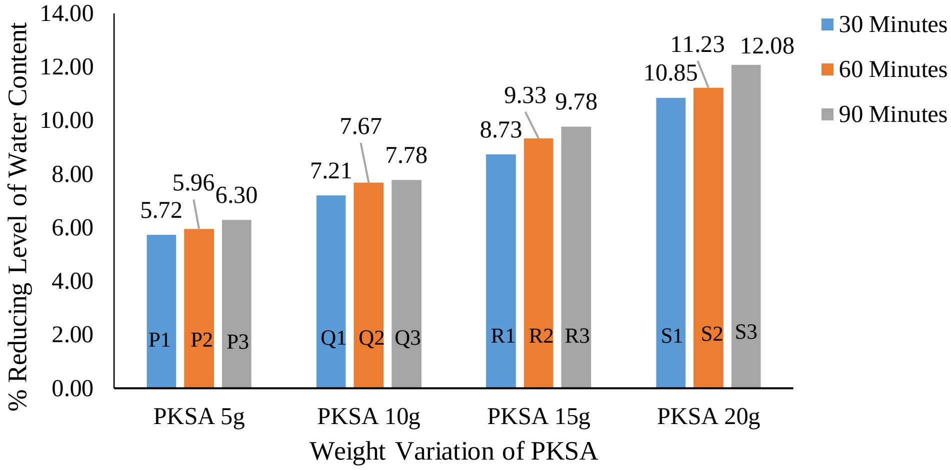

Figure 3. The effect of PKSA weight and stirring duration to water content of WPCO

The mechanism of H_2O absorption by PKSA involves the formation of bonds between SiO_2 in PKSA and the oxygen part of the water molecule through hydrogen bonds (Novita et al., 2020; Petchsoongsakul et al., 2020). The nature of PKSA as an adsorbent is influenced by the presence of functional groups and porosity of PKSA. The main functional group in PKSA is the silanol group (Si−OH). The silanol group can bind water molecules via hydrogen bonds (Petchsoongsakul et al., 2020). Therefore, the water level in WPCO decreased after treatment with PKSA.

The effect of PKSA weight and stirring duration to FFA content of WPCO

SNI (BSN, 2019) indicates that the FFA level in palm cooking oil is max 0,3%, while table 2 shows that the FFA level in WPCO before treatment is 0,402%. Fig 4 shows the effect of PKSA weight and stirring duration on the FFA content of WPCO.

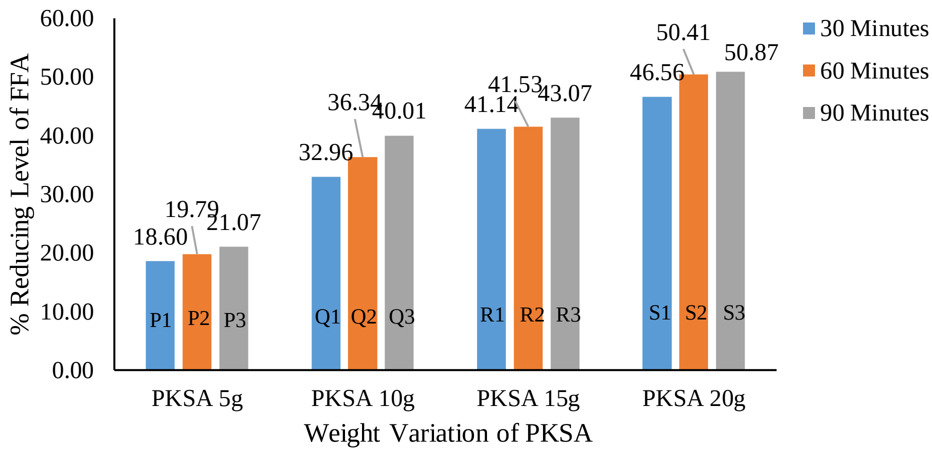

Figure 4. The effect of PKSA weight and stirring duration to FFA content of WPCO

The highest reducing level of FFA was in the S3 treatment category, which was 50,87%. However, from the Q3-S3 treatment categories, there was a decrease in the value of FFA in accordance with the SNI requirement of palm cooking oil;

therefore, it can be concluded that the Q3 treatment can be a recommendation for decreasing the FFA content in WPCO. However, the highest percentage of FFA decline was certainly more desirable, namely in the S3 treatment category. PKSA has the ability to reduce the FFA level, which can be inferred from the characterization that exhibits the levels of SiO_2 and is supported by the crystallinity of PKSA. The crystallinity properties provide a rich pore structure in PKSA, thereby increasing the adsorbent properties of PKSA.

The FFA content in the oil is formed by hydrolysis and oxidation processes during frying and storage (Fadhil et al., 2012). This condition is enhanced by the presence of heat, water content, acidity, and catalysts (enzymes). The longer this reaction lasts, the higher is the level of FFA formed in the oil. In addition, the high level of FFA in palm oil contributes to off-flavors and odors (hydrolytic rancidity) in the food that is fried in palm oil (Alshuiael and Al-Ghouti, 2020; Nitsae *et al.*, 2021).

Conclusions

The use of PKSA as a WPCO treatment proved to be effective in reducing several pollutant parameters in WPCO analysis. Of all treatment categories, the S3 treatment category was found to be the best treatment for improving the clarity of color, decreasing water content, and FFA of WPCO. WPCO, which has decreased the value of pollutant parameters, can be reused for various purposes, including as a material for making biodiesel, fertilizer, and poultry feed.

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Conflict of Interest

The authors declare no conflicts of interest.

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