



# PALM KERNEL SHELL ACTIVATED CARBON USING PHOSPHORIC ACID FOR CRUDE PALM OIL CLARIFICATION: PROPERTIES AND APPLICATION

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**Abstract:** The application of oil palm kernel shell (PKS) as an activated carbon is lately known an alternative and cheap energy. Unfortunately, it needs to activate the surface areas in order to increase the adsorption process. For this, the addition of chemical activator i.e., phosphoric acid is a must. This work aims to determine the properties of palm oil shell activated charcoal and its application for clarification of crude palm oil. The palm shell charcoal was calcined at 500 °C for 1-5 hours. Then, it was grounded become powder and sieved at 200 mesh. The palm shell charcoal was then activated by adding H<sub>3</sub>PO<sub>4</sub> 10% wt with ratio 1:4. The obtained palm shell activated charcoal was then characterized by FTIR, XRD, BET and SEM. The charcoal was then applied for clarified of crude palm oil and rotated at 400 rpm for an hour. The structure of palm shell activated charcoal found mesoporous structure with pore size 1.69 Å and surface area 116.587 m<sup>2</sup>.g<sup>-1</sup>. The obtained activated charcoal was dominantly hemicellulose and lignin with monoclinic rectangular structures. It was found the optimum concentration of PKS activated carbon for clarification of CPO was 5 wt% calcined at 80 °C.

**Keywords:** Palm kernel shell (PKS), Activated charcoal, Surface areas, Crude palm oil (CPO) clarification.

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## INTRODUCTION

Activated charcoal is a solid adsorbent that has amorphous properties and can be produced from almost any carbonaceous material [1]. It is also fabricated by heating at high temperatures [2] which has a highly crystalline form and internal pore structure [3]. It contains 85-95% charcoal consists of free carbon atoms and an inner surface. It is also namely as an adsorbent [4]. The activated charcoal, which is a very porous absorbent [5], has a very large absorption capacity. It is bacteriostatic and allow to absorb toxins, gases, anti-nutrients, and removes various pollutants such as dyes, heavy, metals, pesticides [6].

Activated charcoal has very unique properties such as

high surface area and porosity, which increases the adsorption capacity [7]. It is used as an adsorbent for blanching oil. It can also absorb colloidal suspensions that produce undesirable odors and reduce the amount of peroxide [2]. In addition, it can be applied for many applications on an industrial scale including solvent recovery, technological purification, pollutant removal, desalination, medical applications, electrochemical devices, electrode materials and catalyst support [4]. It is also used as adsorbent to reduce gate gas pollutants and removal of dissolved impurities in drinking water, groundwater, sewage streams and other water [8]. Lately, the increasing demand for activated charcoal is due to the enormous benefits of activated carbon applied for water purification, domestic and industrial wastewater treatment [9], desalination [10–14], gas storage and gas purification and separation, removal of pollutants and odors, and as support for catalysis, as well as in medical applications.

Literally, activated charcoal enable to produce from all natural materials containing carbon, both organic carbon [15–17] and inorganic carbon [18–22] provided as long as the material is in porous structure [2]. The activated charcoal derived from palm shell waste is a promising raw material, besides being widely available, it also does not require high costs for the preparation of materials in the manufacture of activated charcoal [3]. The presence of lignocellulosic composition in waste oil palm has made it a good candidate for use as activated charcoal [23]. In addition, oil palm shells have good porosity and surface and high carbon content, and have a carbon content of 55.7 wt.% [1].

Avoiding the challenges posed by improper disposal of oil palm biomass, several studies have been carried out to convert this available and renewable biomass into value-added products with diverse applications [24][25]. Where is the oil palm biomass, indicating that it is an excellent precursor to prepare activated charcoal. So that, by reusing or recycling waste into activated charcoal, it will further minimize the cost of materials for activated carbon production. It means that this work is in line with the world program (the Sustainable Development Goals/SDGs) in order to anticipate the pollution caused by waste coming from industries.

Oil palm shell is a good material for the preparation of high quality activated charcoal because of its high density, relatively high carbon content, low ash content [26][27], high surface area, highly developed porosity and low price [1][28][7] and more sustainable [29]. Where the main surface functional groups in oil palm shells are carbonyl groups (such as ketones and quinones), ethers and phenols, where after carbonization, char displays surface functional groups of ketones, quinones, and aromatic rings. Oil palm shells are biomass from the palm oil industry [24][30]. This biomass is a cheap and abundant agricultural solid waste. It has a composition of 26.27% cellulose, 12.61% hemicellulose, 42.96% lignin, a higher density of 1.4 g/mL [31][32], carbon 49.75%, oxygen 44.86%, hydrogen 5.32%, nitrogen 0.08%, sulfur 0.16% [4]. On the other hand, palm shells is one of the disposals of palm oil mill industrial waste [33]. It contains a predominance of carbon, oxygen, and traces of impurities such as alumina, silica, potassium, and calcium [34]. It is also an excellent absorption capacity [35], hard but light and natural rocky endocarp [7], has a high surface area, porosity [1][36], high carbon content and low prices [7], and obtains economic benefits from value-added products [37].

During the manufacture of activated charcoal, an activation process is needed. This process aims to expand the carbon pores due to the molecules of the activating agent being adsorbed by the carbon material and dissolving the impurities in the carbon pores [38]. In addition, the activation of charcoal into activated charcoal tends to cause an increase in the number and diameter of pores. The formation of pores due to the evaporation of volatile substances from raw materials due to the cooking process [39]. The manufacture of activated charcoal involves two stages; (i) carbonization of the raw material in an inert atmosphere and (ii) subsequent activation of the carbonized charcoal in an oxidized environment [28][8]. Physical activation, also known as thermal activation. It is a dual-stage pyrolytic process involving carbonization and activation. Whereas chemical activation (known as wet oxidation) is a single-stage activation technique that involves the use of chemical additives as catalysts to impregnate and carbonize precursors at low temperatures (between 300 to 800°C) in an inert

atmosphere [23]. The activation process is very important in the production of activated charcoal. Where the shape and size of the activated charcoal pores are affected by chemical or physical activation. Chemical activation involves a one-step process by saturating the precursor with a chemical reagent followed by roasting or heating under non-reactive conditions. Chemical activation produces activated charcoal with a high yield, high surface area and lower use temperature. There is an inorganic chemical agents in the activation of activated charcoal is  $H_3PO_4$  [25]. The application of activated charcoal as an adsorbent is the best choice to improve oil quality. It reduces the number of free fatty acids, impurities, and water content. The purpose of this work is to investigate the characteristics and applications of palm kernel shell activated charcoal as an adsorbent derived from oil palm shells with  $H_3PO_4$  as a chemical activation to purify and improve the quality of crude palm oil. The optimum concentration of activated charcoal with the addition of  $H_3PO_4$  is important for the future application.

## **MATERIALS AND METHOD**

Palm kernel shell (PKS) and crude palm oil (CPO) were collected and taken from PT. Kayung Agro Lestari in Manjau Village, Muara Pawan District, Ketapang Regency, West Kalimantan, Indonesia. Phenolphthalein ( $C_{20}H_{14}O_4$ ) Merck, Sulfuric acid ( $H_2SO_4$ ) Merck, Potassium hydroxide (KOH) Merck, Phosphoric acid ( $H_3PO_4$ ) Merck (PA), demineralize water, methanol, ethanol 98% were purchased from local suppliers.

### **Adsorbent Preparation**

Palm kernel shell (PKS) adsorbent was washed and dried. Then the PKS was sintered using air muffle furnace at 500 °C for 3 and 5 hours. The sintered PKS was grounded into a fine powder and sieved by 200 mesh sieving.

### **Activation of Adsorbent by Addition of Chemical and Physical Activator**

The powder of PKS was activated using  $H_3PO_4$  10 wt.% (PA) with ratio 1:4 (w/v) of PKS:PA for 24 hours. The PKS powder was then filtered by Whatman 42 and subsequently washed using demineralize water until pH neutral (pH=7,  $\pm$  0.5). The PKS activated was dried again at 110 °C for 3-5 hours to reduce water content then placed at desiccator. Afterwards, the PKS activated was again activated by physical activator utilize furnace at 550 °C for an hour.

The PKS activated carbon characterization was carried out, including: water content, ash content, volatile matter content, bound carbon content, and the value of the iodine number.

The chemisorption of the  $H_3PO_4$  and physical activator on the PKS activated carbon was characterized using attenuated total reflectance method by Fourier

transform infrared (FTIR, ATR, Bruker). The intensity of PKS activated carbon was determined by x-ray diffraction (XRD) to phase identification of a crystalline material. Brunauer-Emmett-Teller (BET) analysis was used to determine the specific surface area properties of the PKS activated carbon sample. The total pore volume of the sample was taken from the last point of adsorption isotherm. The average pore diameter of materials was determined by Dubinin-Astakhov and Barrett-Joyner-Helenda methods. Morphological structure of the PKS activated carbon was examined using scanning electron microscope (SEM JEOL operating at 15 kV).

#### Experimental Procedure

One hundred grams of crude palm oil was degumming by its mixture with phosphate acid 10 wt % at varied temperature 60, 80 and 100 °C. Afterwards, the PKS activated carbon was added at multiple loading number of 1, 3 and 5 wt % and mixed for an hour at 400 rpm. The oil is put in a funnel or separatory flask, to separate the gum from the oil. Then the oil will be washed with warm water at a temperature of 60 °C until the pH of the waste water becomes neutral. The result of this process will get clear oil and free from gum.

Crude palm oil quality tests were carried out including: dirt content, free fatty acid number, acid number, water content, iodine number and saponification number.

## RESULTS AND DISCUSSION

### Characteristic and Morphology of PKS Activated Carbon

PKS Activated Carbon found decompose to become cellulose and hemicellulose [40]. Also, the activated carbon undergoes changes in properties, both physical and chemical, namely the larger the surface area and the effect on the adsorption power.

Figure 1 show the results of the analysis of the quality of PKS activated carbon at a temperature of 500°C with

the chemical activating agent  $H_3PO_4$ , the treatment of the length of time for heating charcoal gave the same results for all treatments. The heating treatment for 1, 3, and 5 hours met the quality standards on the parameters of water content, ash content, and iodine number. Meanwhile, the parameters of volatile matter content and bound carbon content did not meet the quality standards. Overall, the PKS activated carbon, treated at a temperature of 500°C with the chemical activating agent  $H_3PO_4$  at heating for 5 hours was the best PKS activated carbon.

The water content found 11.0604 and 11.7332 at heated for 1 and 3 hours, respectively. And it becomes less 4.3272 % when heated for 5 hours. The less water content contained in the PKS activated, the larger the pores produced, and the larger the pores of the activated charcoal, the larger the surface area. Thus, this character will increase in the adsorption ability of activated charcoal. An excellent of adsorption ability of activated charcoal shows the better the quality of the PKS activated carbon itself [2].

Analysis of the ash content of PKS activated carbon from oil palm shells was also performed. It basically aims to determine the metal oxide content [1][2]. Where according to [41], there are several factors may affect the ash content; the activation of the temperature factor, activation time, and also the combination for both temperature and activation time. High ash content may reduce the quality of PKS activated carbon because the higher the ash content, the more inorganic material put up in the material [2]. It may also reduce the overall activity of activated carbon and reactivation efficiency [1]. The results showed the PKS activated carbon has an ash content value in the range of 5.74-5.98 wt.%. PKS activated carbon also has higher inorganic compounds, thereby increasing the number of residues that cannot be ignited as residues from combustion products [1][25].

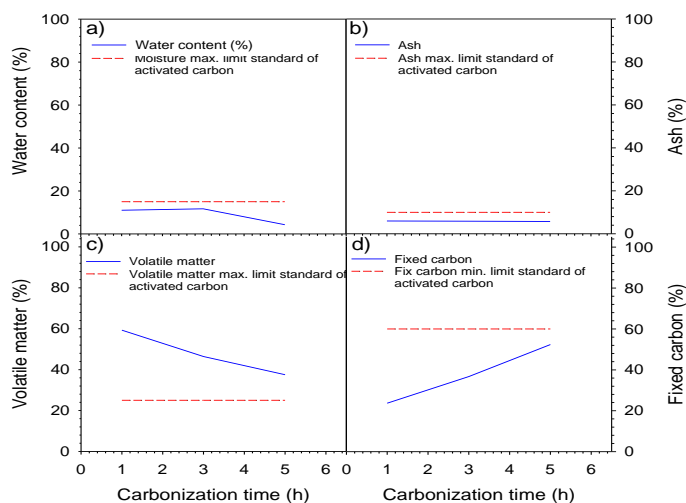
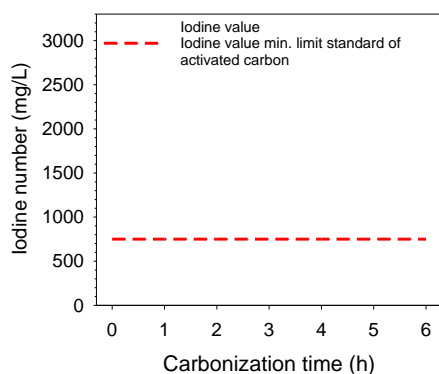


Fig. 1 (a) water content; (b) ash; (c) volatile matter; (d) fixed carbon of palm kernel shell activated carbon with the addition of  $H_3PO_4$  activator

Determination of volatile substances in PKS activated carbon basically aims to determine the amount of substances or compounds that have not evaporated in the carbonization and activation process. Where the volatile substance content is the content of volatile compounds other than water in PKS activated carbon [2]. According to [41], the high percentage of volatile substances in PKS activated carbon cannot be avoided because the compounds attached to the surface of PKS activated carbon can reduce the absorption of charcoal. The results show the volatile substance content was from 37.34 to 59.30 wt.%, where the heating treatment for 5 hours has the smallest value (37.34 wt.%). The good volatile substances create the reaction between carbon atoms and water vapor to form non-carbon volatile compounds such as CO, CO<sub>2</sub>, and H<sub>2</sub> during the activation process [41].

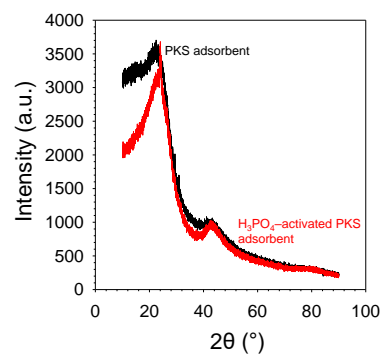
Determination of the carbon content bound in PKS activated carbon aims to determine the carbon content after the carbonization and activation process, where the carbon content refers to the percentage of char remaining after the volatile substance is removed [25]. The carbon in the charcoal is a substance found in the pyrolysis result fraction other than ash (organic substances) and volatile substances that are still present in the pores of the charcoal [2]. The results show the highest bonded carbon is sample sintered for 5 h (52.38 wt.%). It means that this result is less than 60 wt.% of good quality of PKS. The higher the carbon content in the palm shell activated charcoal, the better the quality of PKS itself. This is in accordance with previous research, where the greater the value of the volatile substance content, the lower the carbon stored in the charcoal [41]. The lower the value of volatile substances and the ash content of activated charcoal, the higher the value of the carbon content [2]. It is also supported by the content of cellulose and lignin inside materials [41].



**Fig. 2 Iodine number of palm kernel shell activated carbon quality by H<sub>3</sub>PO<sub>4</sub> activator at various sintering time**

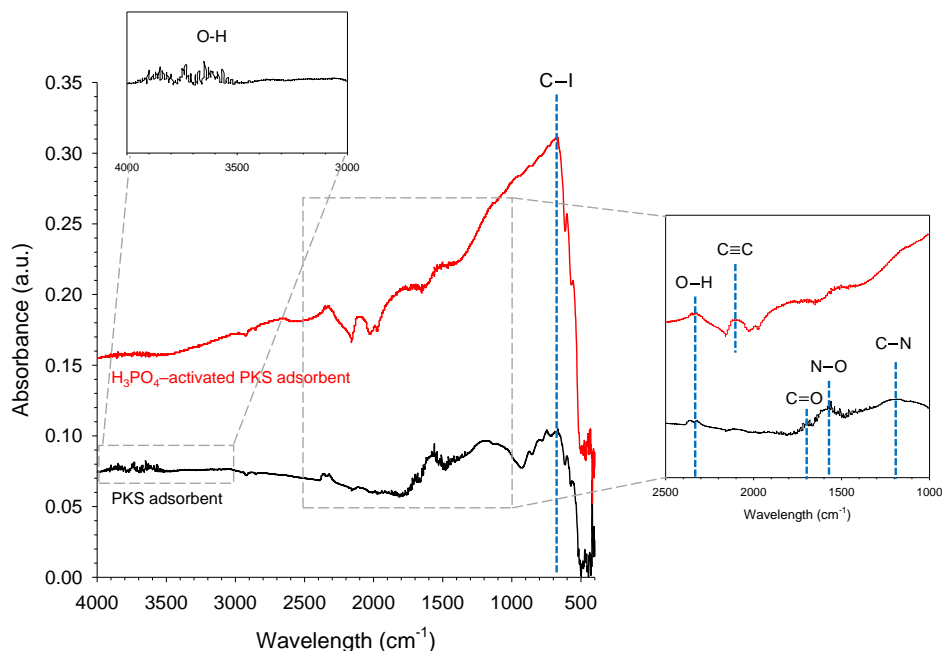
The iodine number is one of the main requirements for assessing the quality of activated charcoal. Where the iodine number itself is milligrams of iodine absorbed by the PKS activated carbon. The results show on Figure 2 clearly stated that at sintering for 5 h has a highest value (2,65 mg.g<sup>-1</sup>). A higher iodine number indicates a larger adsorption area compared to a lower iodine value [25]. The absorption of PKS activated carbon to iodine solution indicates the ability of activated carbon to adsorb components with low molecular weight, besides that the absorption of iodine indicates the ability of PKS activated carbon to absorb substances. In addition, activated carbon with a high ability to absorb iodine means that it has a larger surface area and has a larger microstructure, where the absorption of iodine is related to the formation of pores in activated carbon which increases with increasing activation time [42].

Figure 3 shows x-ray diffraction (XRD) curve of PKS activated carbon sintered at 500°C for 5 hours, and a size of 200 mesh without chemical activation. It shows that palm shell charcoal has a peak intensity of around 22° for hemicellulose and lignin and 42°, and has amorph properties.



**Fig. 3 XRD plot of PKS activated carbon from palm shell by phosphoric acid activation**

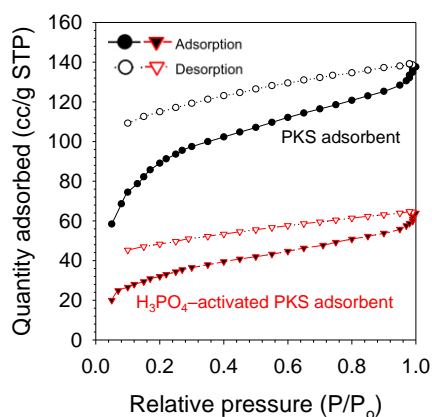
Fourier transform infra-red (FT-IR) is employed in order to analyze the surface of functional groups on carbon [25], where the characterization of activated carbon will be carried out using the FTIR. It identifies possible functional groups such as -OH, C=C, C=O and CO groups in PKS activated carbon. They show the polarity of PKS activated carbon as an absorber [43]. Figure 4. The FTIR of PKS activated carbon (sintered at 5 hours, 200 mesh, without chemical activation) with black line shows it has a functional group shell charcoal with water at = 1650-1630 cm<sup>-1</sup>, and the -CO ester group at = 2000-2300 cm<sup>-1</sup> wavelength.



**Fig. 4** FTIR spectra of activated carbon from palm kernel shell by phosphoric acid activation

PKS activated carbon (sintered at 5 hours, 200 mesh, without chemical activation) with red line shows the PKS activated carbon has a functional group shell charcoal catalyst, with bending vibrations of the siloxane groups at  $= 432-590\text{ cm}^{-1}$ , the carbonate group at  $1400-1500\text{ cm}^{-1}$ , and the absorbed  $\text{H}_2\text{O}$  at  $= 2800-3750\text{ cm}^{-1}$ . The previous research show that there are various types of wavelengths found at each peak, so that, it is found the microstructure of the palm shell carbon in each variation [31]. From the spectral information, it is found that the functional groups contained in PKS activated carbon in absorption bands of  $2853.69\text{ cm}^{-1}$ ,  $2853.97\text{ cm}^{-1}$ ,  $2853.74\text{ cm}^{-1}$  and  $2854.11\text{ cm}^{-1}$  are the vibrations from CH. And the absorption is  $1029.25\text{ cm}^{-1}$ ,  $1030.41\text{ cm}^{-1}$ ,  $1048.57\text{ cm}^{-1}$  and  $1034.00\text{ cm}^{-1}$  indicated the presence of aliphatic CO which indicated that the sample was activated charcoal. Most of the functional groups on the sample surface are mostly removed during the sintering process or activation process and those functional groups are volatile materials and impurities are released at high applied temperatures [25].

The Brunauer-Emmett-teller (BET) of PKS activated carbon result was shown on Figure 5. The PKS with no chemical activation showed palm shell charcoal has microporous structure due to pore size =  $1.36$  with surface area =  $312.543\text{ m}^2/\text{g}$ , with hysteresis loop type H3.

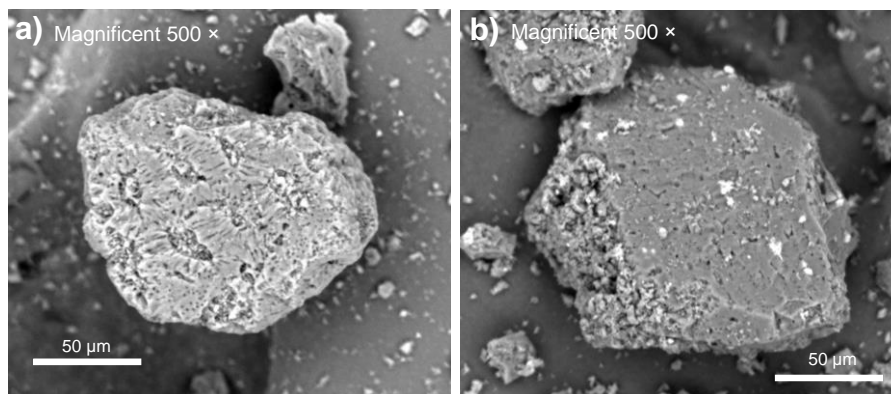


**Fig. 5**  $\text{N}_2$  physisorption of PKS activated carbon from palm shell by phosphoric acid activation

The PKS activated carbon BET with activation of the  $\text{H}_3\text{PO}_4$  shown on Figure 5, shows that PKS activated carbon is microporous (size pore =  $1.69\text{ nm}$ ) with surface area =  $116.587\text{ m}^2/\text{g}$  with hysteresis loop type H3. Research has also been carried out by [37], where BET and microporous surface area are quite high from activated carbon fabricated from palm shells, so that the material is suitable as an effective adsorbent, where in the study it was also stated that the maximum BET surface area of The produced palm shell activated carbon is  $1366\text{ m}^2/\text{g}$ . Meanwhile, other studies have shown that crude palm kernel shells have a BET surface area of only  $0.793\text{ m}^2/\text{g}$  and a pore volume of  $0.0014\text{ cm}^3/\text{g}$  [34], and the higher the carbon-activated pore surface area, the greater the pore capacity. absorb it. The increase in surface area as well as pore volume is considered to be due to chemical reactions between structural carbon and activating agents, apart from the dehydration process.

The morphology of surface PKS activated carbon was shown on Figure 6. It investigates the surface morphology of the catalyst before and after activation. As shown on Figure 6a the SEM of PKS activated carbon without chemical activation, shows that palm

shell charcoal shows the morphology of shell charcoal at a magnification of 500 times fold, where the shell charcoal particles in this sample are almost spherical in shape with a slightly rough surface.



**Fig. 6 Image of scanning electron microscopy test analysis on palm kernel shell activated carbon (a) without chemical activation (b) activated by H<sub>3</sub>PO<sub>4</sub>**

Figure 6b exhibits the SEM image morphology of PKS activated carbon with H<sub>3</sub>PO<sub>4</sub> activation. It shows the morphology of PKS activated carbon at 500-fold magnification, where the PKS activated carbon catalyst particles in this sample are in the form of a monoclinic rectangular structure with a slightly rough surface. The results of previous research also showed that the palm kernel shell charcoal powder used was to pass through a 200mesh sieve (particle size = 74 microns = 0.0740 mm). This is due to the uniform grinding effect, so that the difference in pressure during grinding causes different grain sizes [31].

#### Characteristics of Crude Palm Oil

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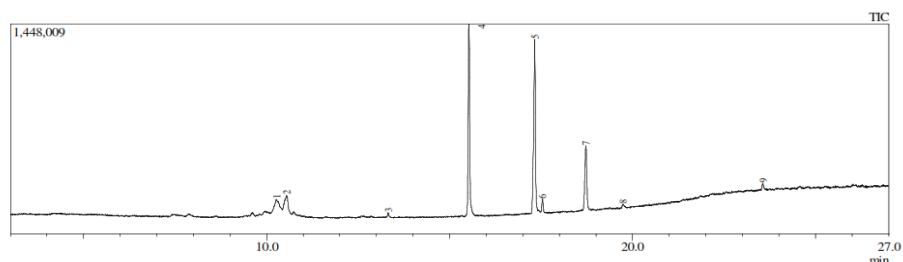
Crude palm oil is crude palm oil derived from the mesocarp or yellow palm fruit fiber, obtained by extraction and has not yet obtained for purification process [44]. It is because it usually contains dissolved and insoluble impurities in the oil [45]. In palm oil has the constituent components of palm oil, namely; triglycerides (95.62 wt.%), free fatty acids (4.00 wt.%), water (0.20 wt.%), phosphatides (0.07 wt.%), carotenes (0.03 wt.%), and aldehydes (0.07 wt.%) [44].

From results show that the oil has characteristic values of free fatty acids, water content, dirt content, saponification number, specific gravity, density, acid number and iodine number, as shown in Table 1.

**Table 1. Characteristics of crude palm oil**

Physical and chemical properties	CPO Quality	[46]	[1]	This work
Free fatty acids (%) w/w max.	5,0	4,0433	-	7,5139
Water content (%) w/w	0,5	0,2950	-	2,8700
Dirt content (%) w/w	0,5	0,0610	-	0,0049
Saponification number (mgKOH.g <sup>-1</sup> )	-	201,0379	195-205	124,21
Specific Gravity (g.ml <sup>-1</sup> )	-	0,9303	0,921-0,925	0,9400
Density at 50°C (kg.m <sup>-3</sup> )	-	-	891,00	114,0000
Acid number	-	-	-	19,71
Iodine number (mg.g <sup>-1</sup> )	50-55	-	-	36,05

In addition, analysis of crude palm oil was also carried out using Gas chromatography mass spectroscopy (GC-MS) in order to investigate the type and composition of fatty acids in crude palm oil. The following Figure 7 show the crude palm oil analysis results.



**Fig. 7** Free fatty acid of crude palm oil sample by GS-MS analysis

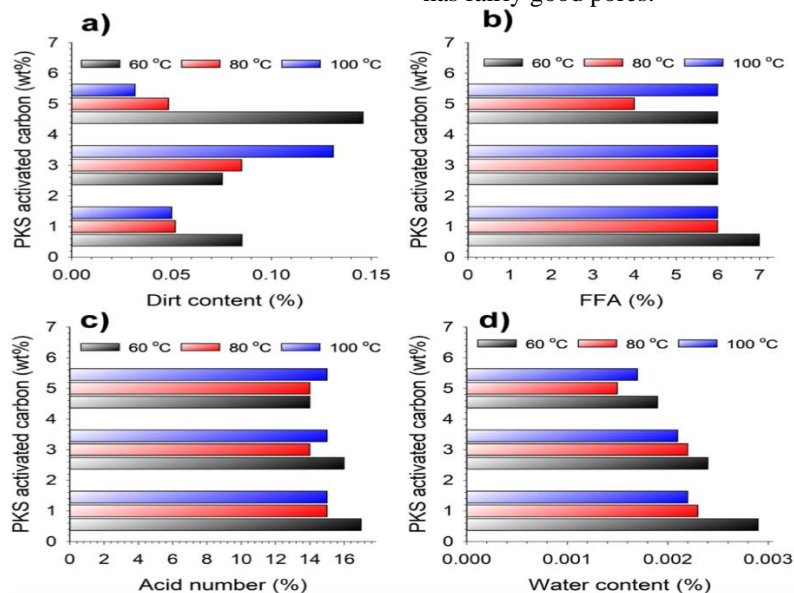
Figure 7 shows there are nine peaks found from left to right with different areas. These peaks are to investigate the composition of crude palm oil from sample. Peak 1 to 3 are free fatty acids with different composition as such: 3.65; 3.57; 74 wt.%. Then, peak 4 to 5 are triglycerides with 34.61 and 37.98 wt.%. Peak 6 to 9 are found as free fatty acids with various composition (2.11; 15.23; 0.93 and 1.18 wt.%).

#### Effect of PKS Activated Carbon Concentration Towards Temperature of CPO

Based on the results, the interaction between PKS activated carbon concentration and heating temperature significantly affected the FFA number and acid number parameters. However, it had no significant effect on the parameters of dirt content, water content, iodine number, and saponification number. Furthermore, test results of the interaction between PKS activated carbon concentration and heating temperature can be seen in Figure 8.

Based on the results of Duncan's follow-up test at 5%

level, the FFA number parameter interaction between treatments (1%, 60°C) and (5%, 80°C) were significantly different with all treatments. However, the treatment (1%, 80°C) was not significantly different from the treatment (1%, 100°C), (3%, 60°C), and (3%, 100°C). For treatments (1%, 100°C) was not significantly different from other treatments (3%, 80°C) and (5%, 60°C). But, the acid number parameter, the treatment (1%, 80°C) was not significantly different from the treatment (1%, 100°C), (3%, 60°C), (3%, 80°C), (3%, 60°C), (3%, 100°C), (5%, 60°C), (5%, 80°C) and (5%, 10C). The presence of the addition of activated charcoal from palm kernel shells in crude palm oil refining tends to show a decrease the values for both free fatty acid number and the acid number. The value of the free fatty acid quality parameter has a linear tendency with the acid value quality parameter. The addition of activated charcoal from palm oil shells has the ability to bind dirt and other components such as water in the oil. This is because activated charcoal has fairly good pores.



**Fig. 8** Crude palm oil after treatment by varied of PKS activated concentration in multiple parameters such as (a) dirt content; (b) free fatty acid; (c) acid number; and (d) water content

In this study of 10%  $H_3PO_4$  was also applied as an agent for the degumming process, which is one of the stages in the oil refining process. The degumming process is carried out to separate the sap or mucus consisting of phosphatides, proteins, residues, carbohydrates, water and resins. The addition of  $H_3PO_4$

shows a lower percentage of free fatty acids, acid numbers, and saponification numbers than using sulfuric acid. This is because phosphoric acid is a type of weak acid when compare to sulfuric acid. Also, phosphoric acid has only one phosphorus-oxygen double bond to delocalize the charge on the ion. It is

due to easier to bind phospholipid compounds contained in oil compared to sulfuric acid [47].

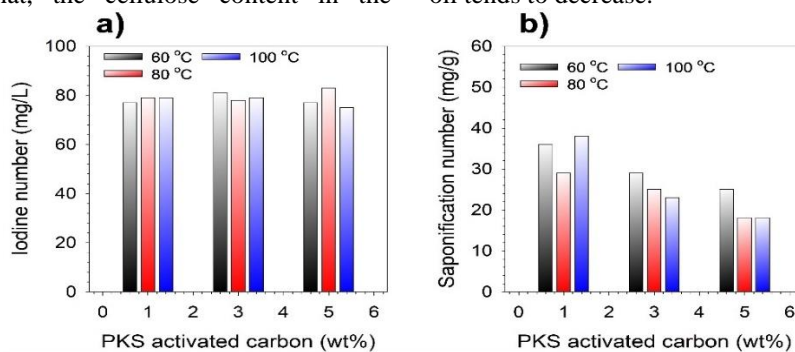
Free fatty acids are acids that are liberated on oil hydrolysis. The influence of high levels of free fatty acids on the quality of oil production cause rancidity in the oil ([48]). According to [49], basically, oil does not contain free fatty acids. However, it can indeed be formed by the presence of lipase enzymes and water that can hydrolyze triglycerides in the ingredients, including crude palm oil. The presence of these free fatty acids is an indicator of damage to the oil, which is caused by a hydrolysis reaction [50,51]; oxidation process, and enzyme hydrolysis [52]53], short chain organic acid content [54]. Thus later, the free fatty acids in the oil is easily oxidized into derivative products, namely aldehydes, ketones, alcohol compounds, esters and cyclic compounds, and are easily formed which causes the oil become rancid more easily [55].

Free fatty acids are important properties used to determine or control the quality of oils, including crude palm oil. The higher the value of free fatty acids in the oil, the lower the quality of the oil. Conversely, the lower the value of the free fatty acids in the oil, the better the quality of the oil [50] [40]. So, the free fatty acids will affect the chemical properties, physical properties and stability of the oil [56]. The results of the analysis of the number of free fatty acids, showed that the concentration of PKS activated carbon at the addition of 5 wt.% with a heating temperature of 80°C was able to provide the smallest free fatty acid number value (3.86 wt.%). This clearly shows that the PKS activated carbon of oil palm shells is able to play a role in reducing the value of free fatty acids. As an adsorbent, palm shell PKS activated carbon is able to reduce free fatty acid levels. This is due to the presence of compounds contained in PKS activated carbon and is able to neutralize or stabilize free fatty acid compounds contained in oil. It also has a surface area and pores that bind and absorb free fatty acid compounds on the surface. In addition, according to [52], adsorbents also have cellulose which adsorb fatty acids and oil dyes, where the cellulose content contained in the absorbent contains hydroxyl groups or  $\pm\text{OH}$  groups. While free fatty acids contain the compounds that binds to the  $\pm\text{OH}$  group of the adsorbent. So that, the cellulose content in the

adsorbent serves to absorb the dye in the oil. The higher the concentration of  $\text{H}_3\text{PO}_4$  activator used in palm shell PKS activated carbon added to the oil, the number of free fatty acids in the oil tends to decrease.

The acid number is an important parameter to determine the presence of free fatty acid values and other components in crude palm oil. The acid number is closely related to the amount of KOH added to neutralize 1 gram of oil. The value of the acid number of the oil is directly proportional to the value of the percentage of free fatty acids from the oil. If the acid number is higher according to the percentage of free fatty acids in the oil [55]. The results of the analysis on the acid number analysis of crude palm oil added with activated carbon of palm kernel shells, showed that the range of values for the acid number of crude palm oil was 13.84 to 16.63. The smallest acid number found was the addition of 5% concentration of PKS activated carbon heated at 80°C. This shows that the addition of PKS activated carbon has an effect on the value of the acid number. The level of free fatty acids contained in the oil including crude palm oil is one of the parameters determining the quality of the oil. The amount of free fatty acids in the oil is indicated by the value of the acid number [48]. The high acid number indicates that the free fatty acids in the oil are also high. So that the quality of the oil is getting lower.

Water content is an important parameter to investigate the quality of crude palm oil. The lower the water content, the better the oil resistance and oil quality [50]. The presence of water in oil accelerate oil damage such as the occurrence of hydrolysis reactions [49]. Then with the hydrolysis of oil into glycerol and free fatty acids, this process can accelerate the reaction in the presence of acids, alkalis, water vapor, high temperatures and enzymes [56]. Water content seems a function to break fat or oil into glycerol and free fatty acids, where the formation of these two compounds is due to the termination of the triglyceride chain in the oil. The results tend to show a decrease in the value of water content (0.0015 wt.%) with the addition of 5 wt.% of PKS activated carbon heated at 80°C. This shows that palm oil shell PKS activated carbon has the ability to absorb water in crude palm oil. The higher the concentration of  $\text{H}_3\text{PO}_4$  chemical activator used in PKS activated carbon added to oil, the water content in the oil tends to decrease.



**Fig. 9** Crude palm oil after treatment by varied of PKS activated concentration in multiple parameters such as (a) iodine number and (b) saponification number



The amount of saponification number depends on the molecular weight. Oil with a low molecular weight will have a higher saponification number than oil with a high molecular weight [46]. Oxidation occurs to form peroxide compounds and decompose into short chain organic acid compounds. It is causing the oil to decrease in quality, so that, it will increase the amount of saponification in palm oil when occurred continuously. In addition, the higher the concentration of  $H_3PO_4$  chemical activator employed in PKS activated carbon when added to oil, the tendency of the saponification number in the oil tend to increase.

## CONCLUSION

The PKS activated carbon sintered at a temperature of 500°C with the chemical activating agent  $H_3PO_4$  at heating for 5 hours was found the optimum result activated carbon from the palm kernel shells. The administration of PKS activated carbon with a concentration of 1% was significantly different with a concentration of 3 and 5 wt.% on the quality parameters of the FFA number and the saponification number parameter. The parameters of acid number and water content, the administration of PKS activated carbon with a concentration of 1% was not significantly different when compare to the addition of 3 wt.%. However, it is significantly different with 5 wt.%, and based on further test results, 5% PKS activated carbon concentration was the best treatment for all quality parameters. Heating at a temperature of 60 °C was significantly different from a temperature of 80 °C and a temperature of 100 °C for the FFA number quality parameter, on the acid number parameter and saponification number, the 60 °C temperature treatment was significantly different from the 80 °C temperature, but not significantly different from the 100 °C temperature treatment, while the water content parameter the 60 °C temperature treatment was significantly different from the 80 °C and 100 °C temperatures, but the 80°C temperature treatment was not significantly different from the 100 °C treatment.

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