



EFFECT OF ACTIVATION TEMPERATURE ON PROPERTIES OF ACTIVATED CARBON PREPARED FROM OIL PALM KERNEL SHELL (OPKS)

Marshahida Mat Yashim, Noraini Razali, Norkamruzita Saadon and Norazah Abdul Rahman

Faculty of Chemical Engineering, Universiti Teknologi Mara, Terengganu, Bukit Besi, Dungun, Malaysia

E-Mail: marsh5166@tganu.uitm.edu.my

ABSTRACT

The effect of carbonation temperature on thermal properties of the prepared activated carbon using oil palm kernel shell (OPKS) impregnated with phosphoric acid was studied. Porosity plays an important factor for activated carbon performance as a catalyst and it is developed from relatively high temperature during carbonation process. However, too high temperatures may result in widening of micropores and burning off the activated carbon. OPKS/H₃PO₄ activated carbons were prepared at 500 °C, 600 °C and 700 °C with high impregnation ratio by weight, 2.5:1. The thermal behaviour of these prepared activated carbon were analysed using Thermal Gravimetric Analysis (TGA) and the functional groups develop during the preparation were studied using Fourier Transform Infrared Spectroscopy (FTIR). Results FTIR indicate the changes in the surface functional groups were manipulated when they are impregnated with activation precursor and carbonized at high temperature as comparison made with un-impregnated activated carbon. TGA analysis shows major thermal decomposition occurred only after the sample was heated up to 750 °C. This indicates samples prepared are thermally stable.

Keywords: thermal analysis, functional groups, impregnation ratio, catalyst.

INTRODUCTION

Activated carbon is the lignocellulosic materials with highly developed surface area and porosity which are very useful for separation and purification processes. Abundance of lignocellulosic materials may be obtained from various sources potential for the feedstock to activated carbon. Research shows, activated carbon has been develop from various agricultural waste like corn cob, coconut shell, nuts kennel, rice hulls (Ioannidou and Zabaniotou, 2007). Agricultural waste like empty fruit bunch, oil palm kennel shell has gained many attention for the past decade (Abdul Khalil *et al*, 2013).

Malaysia is among the largest palm oil producer which contributes with 47% of the world production (Ismail A. *et al*, 2010) thus contribute to high density of oil palm production waste. Abdullah and Sulaiman (2013) reported that About 90 million tons of oil palm fruit production was recorded in 1998, consisting of empty fruit bunch, oil palm kennel shell and fruit frond. Currently, these waste are underutilized. Due to hard surface area structure make OPKS very less feasible for organic fertilizer.

Since the resource of hardwood are limited in recent days, the oil palm kennel shell can be a promising alternative in producing activated carbon thus utilizing them are desirable economically and environmentally. Adsorptive capacities are largely associated with internal porosity and other character such as pore volume and and the presence of functional groups (Ismadji, 2005). These special characters of activated carbon is develop through activation process physically or chemically.

Prior to carbonization, precursor has to be impregnated with dehydrating agent in chemical activation. The chemical is typically an acid, strong base,

or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). Phosphoric acid is preferable due to its environment concerns (El Qada, 2008). Then, the raw material is carbonized at lower temperatures (450-900°C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. The optimum temperatures have been reported to be between 400 °C to 500 °C by most the earlier researchers irrespective of the time of activation and impregnation ratio for different raw material (Srinivasakannan C. and Zailani A. B. M., 2004). However, increasing activation temperature reduces the yield of the activated carbon continuously. According to Guo, J. and Lua. (2000), this is expected since an increasing amount of volatiles is released at increasing temperature from 500 °C to 900 °C.

METHODOLOGY

Preparation of raw material

OPKS was collected directly from palm oil factory was washed several time and the unwanted residue of fibre was removed. The OPKS then dried in the oven at 70 °C for 24 hours to remove the moisture. The dried OPKS then placed in furnace at 400°C for 1 hour before it was ground and sieved into particle sizes between 0.5 mm to 2.0 mm. The study is focused on this particular particle size range.



The impregnation step

The OPKS was later immersed in 100 ml of H_3PO_4 (ortho-phosphoric acid) with the impregnated ratio (by weight) of 2.5:1 (weight of dried OPKS:weight of H_3PO_4). The prepared mixture were heated and stirred on the hot plate for 1 hours at $85^\circ C$ and left overnight at room temperature until it reach complete dryness.

Carbonation/Activation step

The impregnated OPKS was placed in the furnace at temperature $500^\circ C$ for 3 hours. This important step is called activation step during which high density pores are developed across its surface. Upon this stage, the OPKS prepared is called OPKS activated carbon. All the steps are repeated using different activation temperature of $600^\circ C$ and $700^\circ C$ within the same 3 hours period.

Neutralization step

Upon the activation process, the activated carbon was then cooled at room temperature and washed repeatedly with 0.1 M NaOH, warm and cool distillate water until it reaches 6.7 pH value. Finally, the activated carbon is dried in the oven at $100^\circ C$ for 24 hours to remove excess moisture.

Characterization of activation carbon

Prepared OPKS activated carbon and dried OPKS (not activated carbon) samples are tested with Fourier Transform Infrared Spectroscopy, FTIR and Thermogravimetric Analysis, TGA method for characterization and comparative analysis.

FINDINGS AND DISCUSSION

Fourier transform-infrared spectroscopy (FTIR)

The FTIR has been employed for the investigation of activated carbon surface area. The FT-IR spectra revealed complex surface has been develop upon carbonation process by the presence of several peaks.

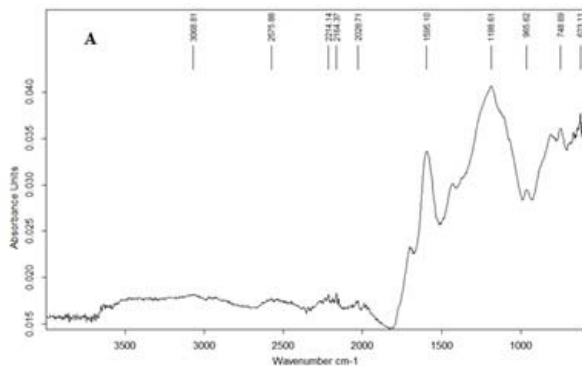


Figure-1. FTIR results for dried OPKS char carbonized at $700^\circ C$.

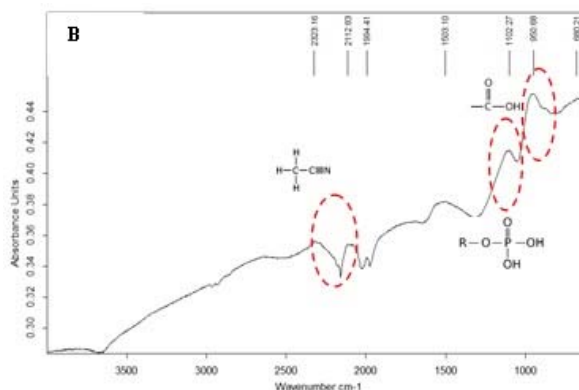


Figure-2. FTIR results for dried OPKS activated carbon impregnated by 2.5:1 (weight ratio) and activated at $700^\circ C$.

Table-1 & 2 below present the peaks wavelength and possible assignment functional groups develop during impregnation and activation step.

Table-1. FT-IR sample analysis for dried OPKS.

No	Adsorption Peak (cm^{-1})	Bond	Types of Functional Group
1	1595.10	C-C	Aromatics
2	1188.61	C-N	Amines
3	965.62	=C-H	Alkenes
4	748.69	C-Cl	Alkyl Halides

Table-1 shows major functional group exist on the surface of dried OPKS. The highest intensity adsorption peak is figured at $1188.61 cm^{-1}$ which is medium aliphatic compounds. Another functional group that can be found on the surface of dried OPKS are aromatics, amines, alkenes, alkyl halides and alkynes which all state at adsorption peak of $1595.10 cm^{-1}$, $965.62 cm^{-1}$ and $748.69 cm^{-1}$. However, these existed functional groups will be manipulated when they are impregnated with activation precursor and carbonized at high temperature. Table-2 shows the changes of the functional groups after impregnation and carbonation processes were done onto the OPKS.

Table-2. FTIR sample analysis for OPKS activated carbon with impregnation ratio of 2.5:1 activated at temperature of $700^\circ C$.

No.	Adsorption Peak (cm^{-1})	Bond	Types of Functional Group
1	2112.83	C≡N	Nitriles
2	1994.41	C=C	Alkynes
3	1503.10	C-C	Aromatics
4	1102.27	C=O P=O	Carbonyl, Ester group Phosphate ester
5	950.68	C-O	Carboxylic acids



Table-2 shows the major functional groups exist on the surface of OPKS activated carbon upon impregnation and carbonation processes. They consist of several functional groups that are different from the dried OPKS. Results FTIR shows some reorganization of the surface functional groups. The peak related for nitriles group is figured at 2112.83 cm^{-1} shows higher absorbance value which cannot be found on the dried OPKS. Results also shows the formation of more carboxylic groups onto the surface. Another functional group that can be found on the surface of treated sample are aromatics, phosphate ester and carboxylic acids which all allocated at adsorption peak of 1503.10 cm^{-1} , 1102.27 cm^{-1} and 950.68 cm^{-1} respectively.

Band at $1000\text{--}1300\text{ cm}^{-1}$ (maxima at $1190\text{--}1200\text{ cm}^{-1}$) is usually found with oxidized carbons and has been assigned to C=O stretching in acids, alcohols, phenols, ethers and/or esters groups (Zawadzki, 1989) and the presence of C=O stretching bands of carbonyl group on the OPKS activated carbon was believed to be introduced from the activation process. According to Puziey *et al.* (2002) it is also a characteristic of phosphorous and phosphor-carbonaceous compounds present in the phosphoric acid activated carbons. The formation of nitriles groups are expected from homolytic reaction during activation with phosphoric acid.

The significant difference between the two samples is the existence of esters group which representing the presence of phosphoric acid on the surface area of activated carbon. It indicates the new development of functional groups for activated carbon treated with phosphoric acid. The development of new functional group is useful for activated carbon to be used in separation application.

FT-IR has also been employed onto the OPKS activated carbon impregnated at the same weight ratio but activated at three different temperatures. The results are shown in Figure-3 below.

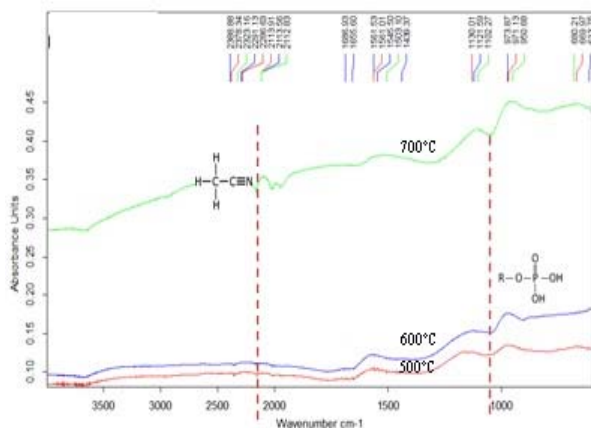


Figure-3. FTIR results for OPKS activated carbon activated at three different temperatures (500 °C, 600 °C and 700 °C).

Results show the similar functional group develop but at different absorbance units. It indicates different activation temperature had no significant effect on the surface functional groups. The difference is only on the amount of the functional group developed which is shown by the intensity of infrared radiation absorbed by a sample during the analysis done.

Thermogravimetric analysis

The thermogravimetric analysis of the produced activated carbon as a function of temperature is shown in Figure-4.

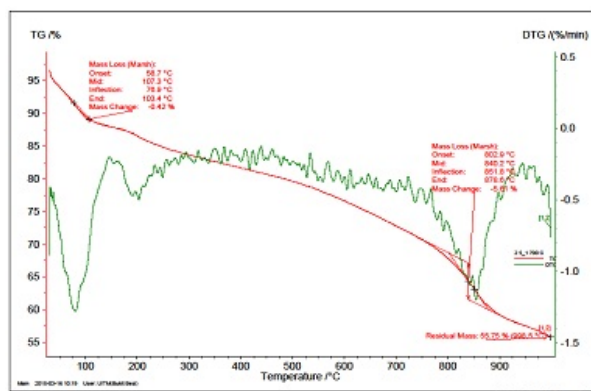


Figure-4. Thermogravimetric sample analysis results from left OPKS activated carbon impregnated at 2.5:1 and carbonized at temperature of 700 °C.

From Figure-4, relatively high mass loss occurred at temperature of range $60\text{--}100\text{ }^{\circ}\text{C}$. It is mainly attributed to the elimination of water absorbed in the pores of the carbon. In the range of $200\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ no considerable mass loss occurs for treated activated carbon but the decomposition of the material continues. It shows that OPKS are stable at relatively high heating temperature. This trend supports that OPKS activated carbon are feasible at high temperature application.

However, at the range at $750\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$ the samples of treated activated carbon start present another mass loss which is about 26%. Önal *et al.* (2007) suggested that such phenomenon was caused by conversion of residual lignin to carbon monoxide. However, residual mass of 55.75% shows support stability of the activated carbon across high temperature range.

Sample from different activation temperatures ($600\text{ }^{\circ}\text{C}$ & $500\text{ }^{\circ}\text{C}$) shows the same pattern for thermal gravimetric analysis. This shows, lower temperature prepared activated carbon are also feasible at high temperature application.

CONCLUSIONS

From these results it can be concluded that the synthesis process successfully enhance the relative carbon proportion of the Oil Palm Kernel Shell (OPKS) could be effectively used as the precursors of activated carbon



synthesis. Activated carbon prepared from the chemical activation using phosphoric acid has enhance the surface functional groups that make it plausible for separation process application. The synthesis process also effectively develop activated carbon that has satisfactory thermal stability. More characterization analysis are required to support its potential in various application.

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