Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1042068

57 (2016) 7999–8006
April

Taylor & Francis
Taylor & Francis Group

Characteristics of oil palm shell biochar and activated carbon prepared at different carbonization times

Usman D. Hamza[a,b,c], Noor S. Nasri[a,d,*], NorAishah S. Amin[b], Jibril Mohammed[a,b,c], Husna M. Zain[a,d]

[a]*Sustainability Waste-To-Wealth Unit, UTM-MPRC Oil and Gas Institute, Energy Research Alliance, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia, Tel. +60 192651147; email: usmandhamza@yahoo.com (U.D. Hamza), Tel. +60 137728200; email: noorshaw@petroleum.utm.my (N.S. Nasri), Tel. +60 167657458; email: jibrilmuhammad@gmail.com (J. Mohammed), Tel. +60 148086599; email: husnamdzain@gmail.com (H.M. Zain)*
[b]*Faculty of Chemical Engineering, Chemical Engineering Department, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia, Tel. +60 127165490; email: noraishah@cheme.utm.my (N.S. Amin)*
[c]*Chemical Engineering Department, School of Engineering, Abubakar Tafawa Balewa University, Tafawa Balewa Way, PMB 0248 Bauchi state, Nigeria*
[d]*Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia*

Received 30 December 2014; Accepted 15 March 2015

ABSTRACT

Palm shells, which are agricultural by-products from palm oil processing, were used to produce low-cost activated carbons. Effect of different carbonization times (1–4 h) on the biochar and activated carbon properties was investigated. The carbonization was carried out at 700˚C followed by CO_2 activation. Carbons were characterized using Fourier transform infrared spectroscopy, ultimate analysis, scanning electron microscopy (SEM), proximate analysis and nitrogen adsorption. The proximate analysis of the palm shell showed low moisture content (5.5%), high percentage of volatile matter (70%), average contents of fixed carbon (23%) and ash content (4.28%). Carbonization times (1–4 h) within the range investigated have little influence on the char yield, thermal and chemical properties of the material but had more effect on the textural properties. SEM micrographs revealed that more pore networks and cavities were formed after carbonization and activation of the palm shells. The textural characteristics of the biochars and activated carbon reveal that the pore size is predominantly mesoporous. The properties of the palm shell activated carbon prepared at 700˚C for 2 h indicated its ability to be used in volatile organics removal from wastewater and in gas-related adsorption applications.

Keywords: Palm shell; Biochar; Activated carbon; Characterization; Carbonization time

---

*Corresponding author.

Presented at the 7th International Conference on Challenges in Environmental Science and Engineering (CESE 2014) 12–16 October 2014, Johor Bahru, Malaysia

1. Introduction

Activated carbon is the most widely used adsorbent in separation and purification applications due to its high adsorption abilities for a large number of organic compounds. It is used in contaminants removal from water [1,2] and gases [3,4]. Nevertheless, the prices of commercially available activated carbons are relatively high and hence limit their usage. This prompted a growing research interest in the production of activated carbons from abundant and low-cost precursors which are mainly industrial and agricultural by-products, such as date pits [1], coconut shell [5], palm oil waste [6], olive stones [7], saw dust [8], bamboo [9], cashew nut shells [10], rice straw [2], apricot shell [11], waste tea and almond shells [12] which have been successfully used in activated carbon preparation.

Oil palm is a major source of vegetable oil, which is extracted from its flesh and kernel. It is produced mainly in South-East Asian countries like Indonesia, Malaysia and Thailand [6]. In addition to palm oil, large quantities of oil palm biomass wastes, including trunks, fronds, fibres, shells and empty fruit bunches are generated [13]. In Malaysia alone, the palm oil industry generates huge amount of solid wastes during the palm fruits processing. About 4.3 million tonnes of shell are produced annually in oil mills [14]. Oil palm shell has been proven to be a good precursor for activated carbon production [6,15].

Manufacture of activated carbon involved two stages: carbonization of the raw material in an inert atmosphere and subsequent activation of the carbonized char in oxidized environment. The carbonization involves thermal decomposition aimed at removing the volatiles and producing fixed carbon (FC) with rudimentary pores [16,17]. The activation duration has a significant effect on the development of the carbons' porous networks [17]. The aim of this work was to synthesize and characterize porous carbons from low-cost precursor, i.e. oil palm kernel shell (PKS). Effect of carbonization time on the yield and properties of the biochar and activated carbon was given more attention. The precursor and the activated carbon produced were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), proximate analysis, ultimate analysis, thermogravimetric (TG) and derivative thermogravimetric (DTG) test, and nitrogen adsorption analysis.

2. Experimental

2.1. Materials and preparation

Palm kernel shell (PKS) obtained from Koperasi Kampung Jawi Johor Bahru Berhad, Malaysia, was washed thoroughly with deionized water. It was then dried at 105℃ for 24 h, grinded and sieved to particle size of 0.85–1.7 mm. It was then carbonized in a well-lagged vertical tube furnace under inert atmosphere. The material was then heated from room temperature to carbonization temperature of 700℃, heating rate of 10℃/min with nitrogen flow of 100 cm^3/min. It was held at that temperature for different times (1–4 h) before being cooled down to room temperature under nitrogen flow. The resulting chars were labelled PKC1, PKC2, PKC3 and PKC4 which denote palm kernel char carbonized at 1, 2, 3 and 4 h, respectively. The palm kernel chars, PKC2 and PKC4, were subsequently activated using CO_2. The chars were heated under nitrogen flow of 100 cm^3/min to attain the activation temperature of 800℃. The flow was then switched over to CO_2 at a flow rate of 100 cm^3/min, heating rate of 10℃/min and temperature of 800℃. After the activation period of 1 h, the material was allowed to cool down to room temperature under nitrogen flow. The resultant activated carbons were labelled PAC2 and PAC4 which denote palm activated carbon formed from chars carbonized at 2 and 4 h, respectively.

The yield of the chars obtained is given by Eq. (1)

$$\text{Yield} = W_1/W_0 \tag{1}$$

where W_0 is the weight of raw kernel shell and W_1 is the weight of dried char.

2.2. Characterization of samples

Proximate analysis with the aid of TGA was used to determine the moisture, volatile matter (VM), FC and ash content. The surface chemistry of the samples were analysed by identifying the surface functional groups of the samples using Fourier transform infrared spectroscope (FTIR-2000, Perkin Elmer). The spectra were recorded from 4,000 to 400 cm^{-1}. Ultimate analysis was carried out using PerkinElmer CHNS/O elemental analyzer. Elements covered in the analysis are carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) obtained as a difference. A scanning electron microscope (Karl Zeiss, EVO50 XVPSEM, and Germany) was used to observe the morphology of the samples to study the presence and nature of porosities. The textural characteristics of the samples were further determined by nitrogen adsorption at −196℃ with an accelerated surface area and porosimeter (ASAP-2010, Micromeritics). The surface area was calculated by the BET method from the adsorption data. The total pore volumes (V_{tot}) were found from the amount of nitrogen adsorbed at relative pressure of 0.99. The micropore volume (pore size <20 Å) was obtained by *t*-plot analysis. The thermal decomposition properties of the material were studied using TG analysis in Mettler Toledo TGA/DSC1 thermogravimetric analyzer.

3. Results and discussion

3.1. Characterization of the activated carbon

3.1.1. Proximate analysis of oil palm shell and weight loss of chars

The effect of carbonization time on the weight loss of the porous carbons prepared from oil palm shell is shown in Table 1. The weight loss was defined in terms of the initial weight of the raw material. As the carbonization time was increased beyond one hour, the weight loss increases. The weight loss was nearly constant beyond 2 h carbonization time. The weight loss was due to the release of VMs and carbon burn-off [18].

The proximate analysis involves the determination of FC, moisture, ash and volatiles of the palm shell and the porous carbons produced. The result of the proximate analysis of the palm kernel shell is shown in Table 2. Low moisture content (5.5%), high percentage of VM (70.00%), average contents of FC (23%) and low ash content (4.28%) were recorded for the palm kernel shells. The percentage weight loss is about 68% after 2 h carbonization which could be due to the release of these volatiles indicated in the proximate analysis. The results from the proximate analysis are within the range of the literature values (Table 2).

3.1.2. Fourier transform infrared spectroscopy

The FTIR spectra of the raw palm kernel, chars and activated carbon produced are depicted in Fig. 1. The raw palm shell chars (PKCs) and activated carbons all displayed bands at 3,500–3,300 cm^{-1} which correspond to O–H stretch in alcohols, phenols and OH stretching. The presence of this group in raw palm shell and activated carbon was reported in the previous literature [19]. The peak at 2,300–2,400 cm^{-1} in the PKS and PKCs could be related to the presences of –COOH functional groups, and it was absent in PAC2 and PAC4 samples (Fig. 1(b)). The spectrum at 1,600–1,400 which is assigned to C=C stretch aromatics is also present in all samples (Fig. 1). This shows that the raw palm shell (PKS), char (PKCs) and activated porous carbons (PACs) contain some similar functional groups like O–H stretch, C=C stretch in aromatics and C–O bonds.

After carbonization and activation, there are some changes in the surface chemistry of the char and activated carbon. The bands at 1,740–1,720 cm^{-1} which correspond to C=O stretch in aldehydes, saturated aliphatic is only present in the raw PKS, this is due to thermal instability of aldehyde and ketonic groups at high temperature [18]. The transmittance at 1,300–1,000 cm^{-1} observed for PKS only, is associated with C–O stretch vibrations in ethers. The disappearance of C=O stretch in aldehydes and ketones and C–O stretch in ethers in the palm shell after carbonization and activation was also reported previously [20]. It was stated that at high activation temperature, C–O and C=O groups were destroyed, forming some poly aromatic structures [21]. Researchers also reported that pyrolysis in the presence of base destroyed the lignin structure containing the ester and ether linkages after the activation [21]. In addition, disappearance of the aforementioned functional groups at a higher temperature is an indication of hemicellulose and cellulose decompositions.

3.1.3. Ultimate analysis

The ultimate analysis of palm shell indicated a carbon, hydrogen, nitrogen, sulphur and oxygen contents of 47.77, 5.98, 0.90, 0.03 and 45.31%, respectively (Table 3). These values reported are close to those previously determined for palm shell [22]. The carbon content of PKS increased tremendously with concomitant decrease in H and O contents after carbonization, to form PKCs and subsequently activated to form

Table 1
Effect of carbonization time on weight loss of chars

Sample	Carbonization time (h)	Yield (%)	Weight loss (%)
PKC1	1	0.359	0.641
PKC2	2	0.313	0.687
PKC3	3	0.314	0.686
PKC4	4	0.311	0.689

Table 2
Proximate analysis of PKS

Proximate analysis (W%)	Sample	
	Palm shell (this study)	Palm shell [13]
Fixed carbon	23.00	18.37
Moisture	5.50	5.73
Ash	4.28	2.21
Volatiles	70.00	73.74

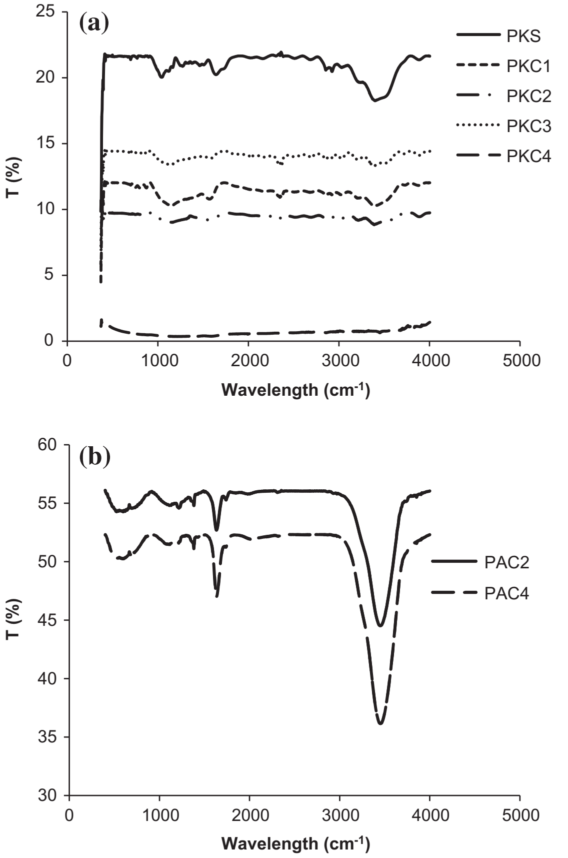

Fig. 1. The FTIR spectra of (a) raw palm kernel shell and chars and (b) activated carbons.

PACs (Table 3). Similar observations were reported in previous studies [23] about preparation of activated carbon from agro-wastes. This is associated with release of volatiles in the material, leaving a FC mass. There is a noticeable increase in carbon and nitrogen contents from PKC2 and PKC4 to PAC2 and PAC4 with concomitant decrease in H and oxygen contents. Activated carbon sample prepared from PKC2 biochar had higher C with low O content than the one prepared from PKC4 biochar.

Table 3
Ultimate analysis results for palm shell (PKS), biochars (PKCs) and activated carbons (PACs)

	Elemental composition (wt%)				
Sample	C	H	N	S	O
PKS	47.770	5.98	0.90	0.03	45.31
PKC1	88.020	2.45	1.12	0.01	8.41
PKC2	82.600	2.84	1.18	0.05	13.33
PKC3	89.410	2.36	1.14	0.02	7.07
PKC4	85.850	2.47	0.88	0.01	10.80
PAC2	89.481	2.341	1.643	0.0245	6.5105
PAC4	88.590	1.889	1.471	0.0105	8.0395

3.1.4. Scanning electron microscopy

SEM micrographs of raw palm kernel shell (PKS), palm kernel chars (PKC2 and PKC4) and the palm activated carbons (PAC2 and PAC4) produced are depicted in Fig. 2. It can be observed that there are little pores on the surface of the raw kernel shell (Fig. 2(a)). More cleared surface with better pore formation was observed on the PKCs biochar samples (Fig. 2(b) and (c)). During the carbonization, volatiles are removed, producing a FC mass with only rudimentary pores as shown in Fig. 2(b) and (c). The pores created are restricted or too small to adsorb molecules. Widening of pore diameters and creation of new ones are achieved after activation of the samples [24]. Additional cavities were formed over the surface with more widening and pore network observed in the PAC2 (Fig. 2(d)) and PAC4 activated samples (Fig. 2(e)).

3.1.5. N_2 adsorption

The textural properties of the palm shell biochar and activated carbons were analysed by means of nitrogen adsorption. The summary of the textural properties are presented in Table 4. The biochars had BET in the range of 11.537–133.19 m^2/g with pore

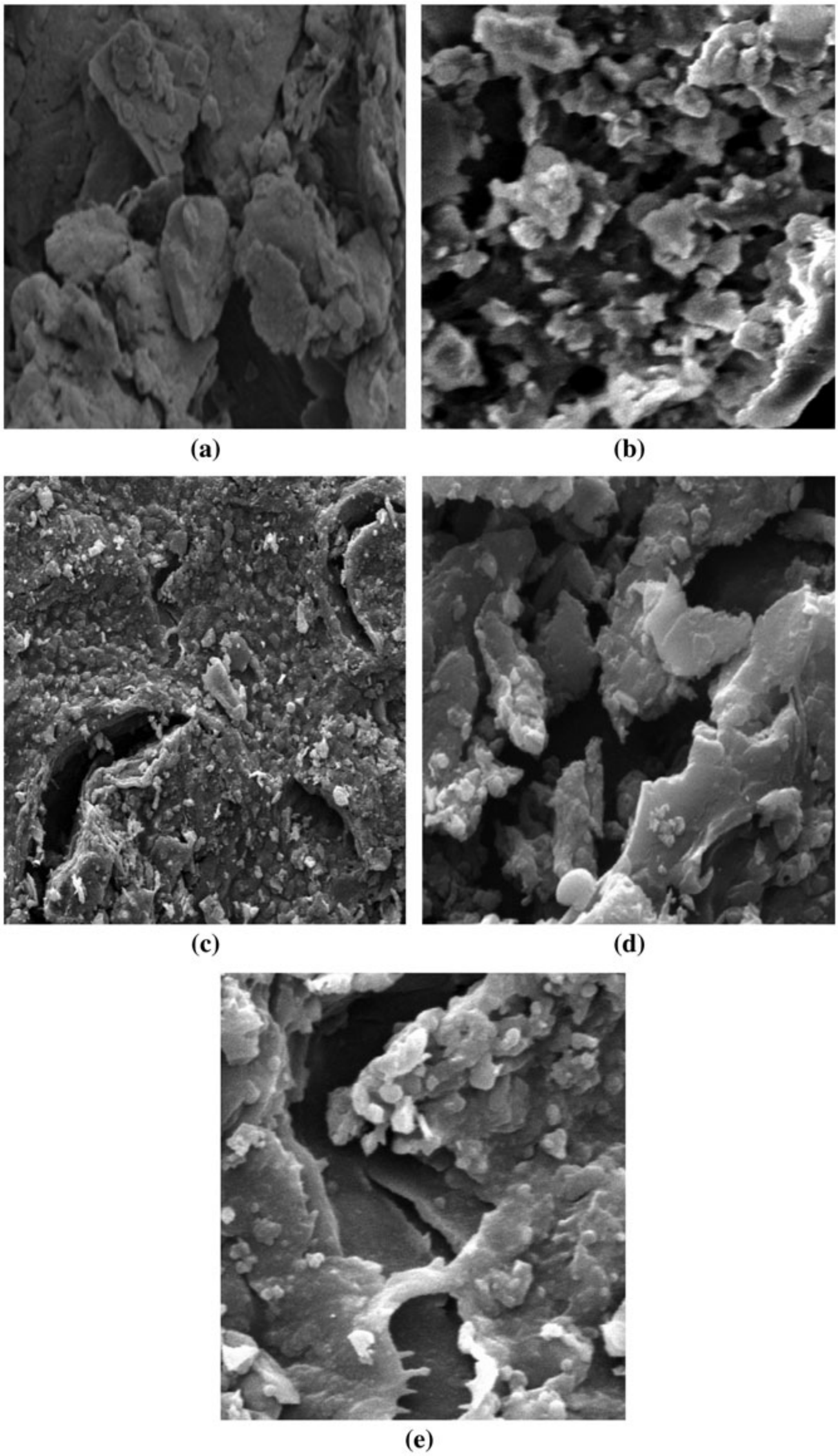

Fig. 2. SEM micrographs of (a) raw PKS, (b) palm kernel char (PKC2), (c) palm kernel char (PKC4), (d) palm activated carbon (PAC2), and (e) palm activated carbon (PAC4).

volume in the range of 0.010351–0.06989 cm^3/g. The PAC2 and PAC4 activated carbons had BET of 167.08 and 138.23 m^2/g, and pore volume of 0.0897 and 0.0987 cm^3/g, respectively (Table 4). Effects of carbonization time on the BET and pore volume are not regular. The surface area seems to increase with

Table 4
Textural properties of chars and activated carbons derived from palm shell

Sample	BET SSA (m^2/g)	V_{tot} (Cm^3/g)	V_{micro} (Cm^3/g)	% V_{micro} (Cm^3/g)	Avg. pore size (Å)
PKC1	133.190	0.06989	0.061942	88.62784	43.311
PKC2	11.537	0.010351	0.001198	11.57376	35.8868
PKC3	90.0238	0.053191	0.028006	52.65176	23.6342
PKC4	45.589	0.042949	0.003726	8.675406	37.6835
PAC2	167.080	0.0897	0.08032	89.540	21.474
PAC4	138.230	0.0987	0.0453	45.89666	28.56109

carbonization time, while the pore volume decreases. The observed increase in pore size with increase in carbonization time (Table 4) could be attributed to more residence time for the carbon–CO_2 reaction at the reaction temperature which brings about evolution of more pore structures. Generally, pores in activated carbon and porous matter are classified based on pore diameter as micropores (<20 Å), mesopores (20–500 Å) and macropores (>500 Å). Gas pollutant molecules vary from about 4–9 Å in diameter. Therefore, micropore activated carbons are more applied in gas-phase applications, while mesopores activated carbons are more useful in liquid applications due to large size of liquid molecules [18]. The biochars with the activated carbons produced in this work are predominantly mesoporous; therefore, they could be more applicable

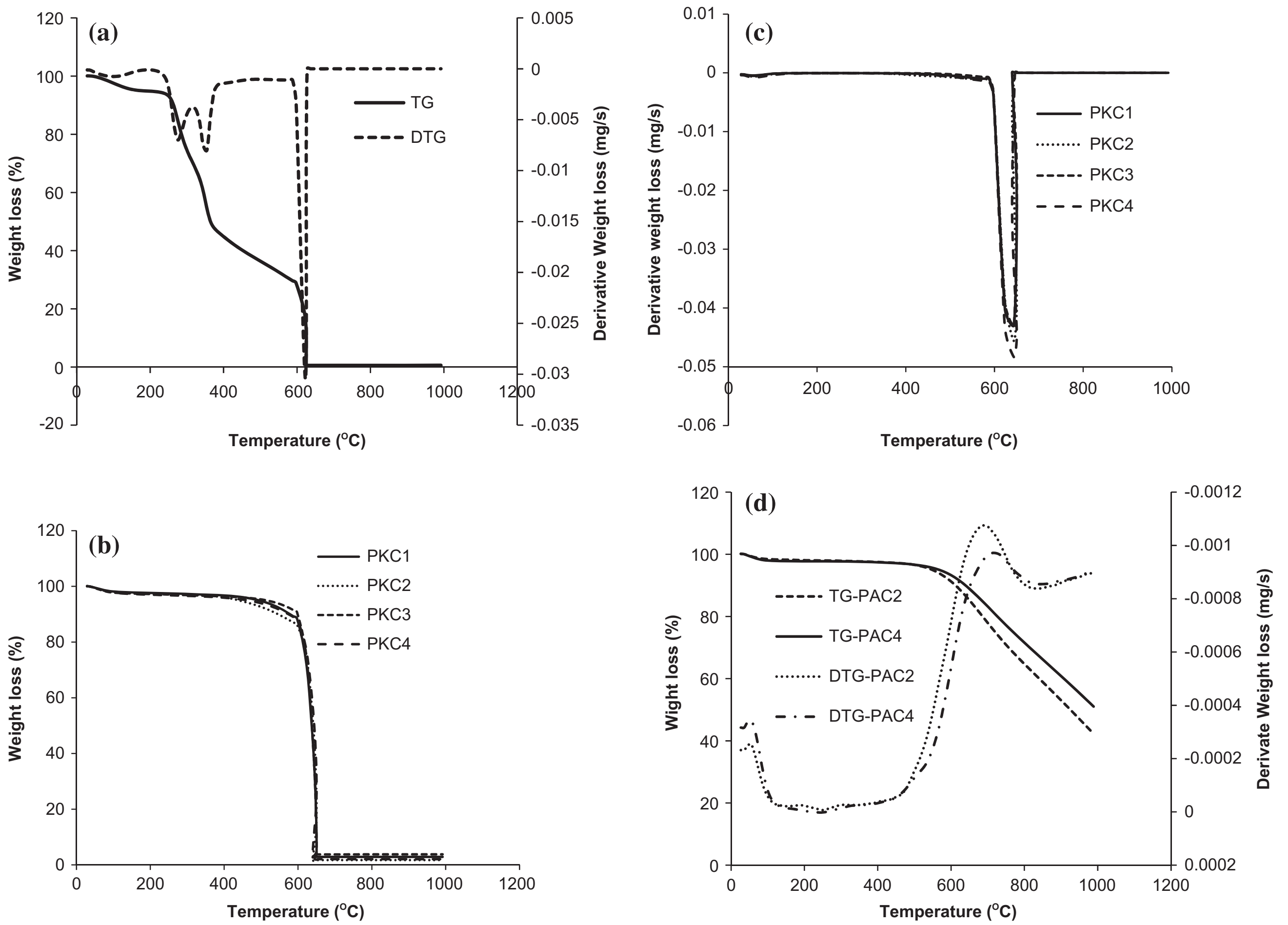

Fig. 3. (a) TG/DTG curves for raw palm shell, PKS; (b) TG for palm shell char, PKC; (c) DTG curves for biochar; and (d) TG/DTG for activated carbons produced.

to liquid applications. However, PAC2 have high micropore volume with average pore size close to the micropore range; therefore, it could as well be applied to gaseous and volatile organic (VOC) contaminants removal.

3.1.6. Thermogravimetric analysis (TGA)

The TG curve shows change in mass with increase in temperature. From TG and DTG evolution profiles, the peak derivative temperature (t_p) is 605˚C (Fig. 3(a)). This shows that the carbonization temperature for the PKS used in this research should be above 600˚C. The first segment of the TG/DTG curve could be attributed to moisture removal at temperature below 150˚C [25]. In the temperature range of 230–380˚C, decomposition occurs and there were two DTA peaks. The first peak to the left could be due to hemicellulose decomposition with corresponding weight loss of about 24%. The second peak could be attributed to cellulose/lignin decomposition. The TG/DTG curves flatten at higher temperature above 610˚C due to aromatization of the lignin fraction, leading to very little additional weight loss. The peak derivative temperature for PKS carbonized at 1–4 h (Fig. 3(c)) is within the range of 605–610˚C. Therefore, carbonization time has little or no effect on the peak derivative temperature.

Thermal decomposition curves of biochar samples PKC1, PKC2, PKC3 and PKC4 are shown in Fig. 3(b). The TG and DTG curves for the activated carbon samples PAC2 and PAC4 are shown in Fig. 3(c) and (d). The TG and DTG of the char samples look very similar. The little change below 120˚C is associated with moisture removal (Fig. 3(b)). All the char samples show maximum weight loss and decomposition near 600˚C (Fig. 3(b)). This indicated that carbonization beyond 1–2 h had little effect in bringing any noticeable change to the biochar properties. At higher temperature above 650˚C, there was no appreciable weight loss for the biochars. The weight loss of chars at around 700˚C was 97.13, 98.27, 96.22 and 97.95% wt for PKC1, PKC2, PKC3 and PKC4 (Fig. 3(b)). The mass loss of the PACs is slower at higher temperature. For the activated carbon samples, the mass loss of PAC2 and PAC4 was 57.74 and 48.96 wt % at 700˚C (Fig. 3(d)).

4. Conclusions

Activated carbon was prepared from palm kernel shell at temperature of 700˚C, carbonization times of 1–4 h under CO_2 activation. The TGA/DTA of biochar prepared at different carbonization times look very similar with little or no difference. This indicated that carbonization beyond 1–2 h had little effect on the thermal and chemical properties of the material. The peak derivative temperature was 605˚C; therefore, carbonization of this material should only be carried out above this temperature. Weight loss beyond 2 h carbonization time is very minimal. Proximate analysis reveals that there is increase in carbon and nitrogen contents from conversion of biochar to activated carbon with concomitant decrease in H and oxygen contents. SEM results show that more cavities and widening of pore network are achieved after carbonization and activation. The biochars with the activated carbons produced in this work are predominantly mesoporous, which are more applicable to liquid applications. However, PAC2 have average pore size close to the micropore range which also have high micropore volume; therefore, it could as well be applied to gaseous and VOC contaminants removal. The results of this work show that biochar and activated carbons with different pore sizes for different applications could be produced by varying the carbonization time.

Acknowledgment

The authors acknowledge and appreciate the financial support provided by the ministry of education Malaysia through University Teknologi Malaysia (UTM), Johor, Malaysia, to fully undertake this research under the University Research Grant (URG) Q.J130000.2509.06H79.

References

[1] Z. Merzougui, Y. Azoudj, N. Bouchemel, F. Addoun, Effect of activation method on the pore structure of activated carbon from date pits application to the treatment of water, Desalin. Water Treat. 29 (2011) 236–240.

[2] M.E. Ossman, M. Abdel Fatah, Nahla A. Taha, Fe(III) removal by activated carbon produced from Egyptian rice straw by chemical activation, Desalin. Water Treat. 52 (2014) 3159–3168.

[3] C.S. Lee, Y.L. Ong, M.K. Aroua, W.M.A.W. Daud, Impregnation of palm shell-based activated carbon with sterically hindered amines for CO_2 adsorption, Chem. Eng. J. 219 (2013) 558–564.

[4] N.S. Nasri, U.D. Hamza, S.N. Ismail, M.M. Ahmed, R. Mohsin, Assessment of porous carbons derived from sustainable palm solid waste for carbon dioxide capture, J. Clean. Prod. 71 (2014) 148–157.

[5] N.S. Nasri, M. Jibril, M.A.A. Zaini, R. Mohsin, U.D. Hamza, A.M. Musa, Synthesis and characterization of green porous carbons with large surface area by two

step chemical activation with KOH, J. Teknologi (Sci. & Eng.) 67(4) (2014) 25–28.

[6] J. Guo, B. Gui, S. Xiang, X. Bao, H. Zhang, A.C. Lua, Preparation of activated carbons by utilizing solid wastes from palm oil processing mills, J. Porous Mater. 15 (2008) 535–540.

[7] L. Temdrara, A. Addoun, A. Khelifi, Development of olivestones-activated carbons by physical, chemical and physicochemical methods for phenol removal: A comparative study, Desalin. Water Treat. 53(2) (2013) 452–461.

[8] M. Sevilla, A.B. Fuertes, Sustainable porous carbons with a superior performance for CO_2 capture, Energy Environ. Sci. 4 (2011) 1765–1771.

[9] A. Boonpoke, S. Chirakorn, N. Laosiripojana, S. Towprayon, A. Chidthaisong, Synthesis of activated carbon and MCM-41 from bagasse and rice husk and their carbon dioxide adsorption capacity, J. Sustain. Energy Environ. 2 (2011) 77–81.

[10] A.J. Tsamba, W.H. Yang, W. Blasiak, Pyrolysis characteristics and global kinetics of coconut and cashew nut shells, Fuel Process. Technol. 87 (2006) 523–530.

[11] B. Xu, Y. Chen, G. Wei, G. Cao, H. Zhang, Y. Yang, Activated carbon with high capacitance prepared by NaOH activation for supercapacitors, Mater. Chem. Phys. 124 (2010) 504–509.

[12] E. Yagmur, Preparation of low cost activated carbons from various biomasses with microwave energy, J. Porous Mater. 19 (2012) 995–1002.

[13] M.A.A. Mohammed, A. Salmiaton, W.A.K.G. Wan Azlina, M.S. Mohamad Amran, Gasification of oil palm empty fruit bunches: A characterization and kinetic study, Bioresour. Technol. 110 (2012) 628–636.

[14] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Enhancement of basic dye adsorption uptake from aqueous solutions using chemically modified oil palm shell activated carbon, Colloids Surf., A 318 (2008) 88–96.

[15] S. Sumathi, S. Bhatia, K.T. Lee, A.R. Mohamed, Adsorption isotherm models and properties of SO2 and NO removal by palm shell activated carbon supported with cerium (Ce/PSAC), Chem. Eng. J. 162(1) (2010) 194–200.

[16] C.H. Yun, Y.H. Park, C.R. Park, Effects of pre-carbonization on porosity development of activated carbons from rice straw, Carbon 39 (2001) 559–567.

[17] A.A. Ahmad, A. Idris, Preparation and characterization of activated carbons derived from bio-solid: A review, Desalin. Water Treat. 52 (2014) 4848–4862.

[18] J. Guo, A.C. Lua, Characterization of adsorbent prepared from oil-palm shell by CO_2 activation for removal of gaseous pollutants, Mater. Lett. 55 (2002) 334–339.

[19] S. Sumathi, S. Bhatia, K.T. Lee, A.R. Mohamed, Selection of best impregnated palm shell activated carbon (PSAC) for simultaneous removal of SO_2 and NO_x, J. Hazard. Mater. 176 (2010) 1093–1096.

[20] J. Guo, A.C. Lua, Preparation and characterization of adsorbents from oil palm fruit solid wastes, J. Oil Palm Res. 12 (2000) 64–70.

[21] S.B. Abdul Hamid, Z.Z. Chowdhury, S.M. Zain. Base catalytic approach: A promising technique for the activation of biochar for equilibrium sorption studies of copper, Cu(II) ions in single solute system, Materials, 7 (2014) 2815–2832.

[22] M.Sukiran, Pyrolysis of Empty Oil Palm Fruit Bunch Using the Quartz Fluidized-fixed Bed Reactor, Master dissertation, University of Malaya, Malaysia, 2008.

[23] I. Ozdemier, M. Sahin R. Orhan, M. Erdem, Preparation and characterization of activated carbon from grape stalk by zinc chloride activation, Fuel Process. Technol. 125 (2014) 200–206.

[24] Z. HuM.P. Srinivasan, Y. Ni, Novel activation process for preparing highly microporous and mesoporous activated carbons, Carbon 39 (2001) 877–886.

[25] W. Li, K. Yang, J. Peng, L. Zhang, S. Guo, H. Xia, Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars, Ind. Crops. Prod. 28 (2008) 190–198.