

Microwave pyrolysis using self-generated pyrolysis gas as activating agent: An innovative single-step approach to convert waste palm shell into activated carbon

Peter Nai Yuh Yek^{1,2}, Rock Keey Liew², Mohammad Shahril Osman¹, Chee Chung Wong¹, and Su Shiung Lam^{2,*}

¹University College of Technology Sarawak, Department of Engineering, 96000, Sibu, Sarawak, Malaysia

²Pyrolysis Technology Research Group, Eastern Corridor Renewable Energy Group (ECRE), School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

Abstract. Waste palm shell (WPS) is a biomass residue largely available from palm oil industries. An innovative microwave pyrolysis method was developed to produce biochar from WPS while the pyrolysis gas generated as another product is simultaneously used as activating agent to transform the biochar into waste palm shell activated carbon (WPSAC), thus allowing carbonization and activation to be performed simultaneously in a single-step approach. The pyrolysis method was investigated over a range of process temperature and feedstock amount with emphasis on the yield and composition of the WPSAC obtained. The WPSAC was tested as dye adsorbent in removing methylene blue. This pyrolysis approach provided a fast heating rate (37.5°C/min) and short process time (20 min) in transforming WPS into WPSAC, recording a product yield of 40 wt%. The WPSAC was detected with high BET surface area ($\geq 1200 \text{ m}^2/\text{g}$), low ash content ($< 5 \text{ wt}\%$), and high pore volume ($\geq 0.54 \text{ cm}^3/\text{g}$), thus recording high adsorption efficiency of 440 mg of dye/g. The desirable process features (fast heating rate, short process time) and the recovery of WPSAC suggest the exceptional promise of the single-step microwave pyrolysis approach to produce high-grade WPSAC from WPS.

1 Introduction

Palm oil represents one of the main agriculture commodity in Malaysia, recording approximately 17 million tons of production in 2016 [1]. Consequently, nearly 53 million tons of wastes palm have been generated every year from the palm oil industry [2]. Each ton of oil palm wastes consists mainly of 22 wt% of empty fruit bunch (EFB), 6 wt% of waste palm shell (WPS) and 14 wt% of palm mesocarp fibre (PMF). These wastes are

* Corresponding author: lam@umt.edu.my

currently under-utilized and simply burned as solid fuel in boiler to generate steam for sterilization. The current practice emits undesirable fly ash and greenhouse gas to the atmosphere which in turn creates environmental pollution. Therefore, oil palm wastes should be converted into useful products such as activated carbon in order to maximize its economic value rather than using it as boiler fuels.

Waste palm shell activated carbon (WPSAC) is a carbonaceous material produced from controlled thermal process in order to increase the level of porosity by high internal surface area and pore volume. The performance of WPSAC is determined by pore size (e.g. microporous, mesoporous, or macroporous) and surface composition (e.g. the presence of oxygen or acidic functional group) influences the adsorption efficiency [3]. Due to these properties, WPSAC has widely been applied in removal or adsorption of carbon dioxide from the exhaust gas streams in power plant and the raw natural gas in agriculture industry [4], removal of phenol [5] and tetracycline [6] in chemical industry, or used as adsorbent to remove heavy metals such as lead (Pb) and cadmium (Cd) [7]. Recently, WPSAC was utilized in technological applications such as supercapacitor and protection from electromagnetic radiation [8, 9].

The present study attempts to utilize an innovative single step approach to produce WPSAC from waste palm shell by microwave pyrolysis using self generated CO₂ as activating agent. Microwave radiation as a heat source provide rapid and targeted heating to the inside waste palm shell by dipole rotation and ionic conduction [10]. The study also examined the influence from varying the amount of waste palm shell as feedstock and the pyrolysis temperature on the process features, the yield and composition of the WPSAC obtained, and its adsorption of methylene blue. These features are important to assess the feasibility of developing a single step method that is energy and cost efficient in producing WPSAC from oil palm waste. There have been limited studies on single step physical activation of WPSAC preparation, and no studies have been reported on the use of self-generated pyrolysis gas for WPSAC preparation via microwave pyrolysis technique.

2 Material and methods

2.1 Source and preparation of waste palm shell

Waste palm shell (WPS) was collected from a palm oil mill located in Sibul, Sarawak. The waste was washed with distilled water to remove dust and impurities. It was then dried in the oven at 110°C for 2 hours to remove moisture and ground to a desired size of 0.15 mm for further analysis.

2.2 Characterization of WPS

WPS was analysed using proximate and ultimate analyses. The proximate analysis was conducted according to the ASTM standards D5142 to determine the contents of moisture, fixed carbon, volatile matter, and ash. Elemental analysis was conducted using a FlashEA 1112 CHNS elemental analyser to determine the carbon, hydrogen, nitrogen and sulphur contents in the WPS, whereas the oxygen content was determined by mass difference.

2.3 Microwave pyrolysis of WPS

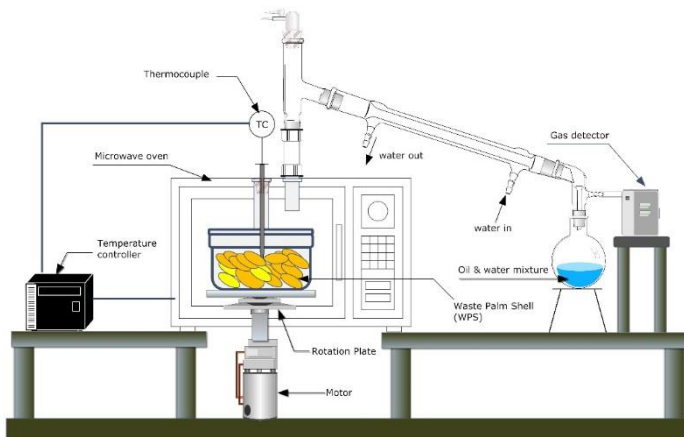


Fig. 1. Schematic diagram of microwave pyrolysis system used to produce activated carbon.

Fig. 1 shows the schematic diagram of the microwave pyrolysis system. Pyrolysis of WPS was performed in a modified microwave oven (Sharp R213CST) with a frequency of 2450 MHz. The microwave oven housed a porcelain reactor that can prevent combustion in the reactor. The pyrolysis experiments were performed in batch and closed operation, and a rotation plate was used to ensure even distribution of microwave irradiation. A Type-K thermocouple was used to measure the temperature and the readings were recorded by a data logger every 5 seconds throughout the pyrolysis process. A gas detector was placed near to the exhaust point to determine the presence of hydrocarbon, CO and CO₂ gases in the pyrolysis gas produced after the pyrolysis operation.

The experiment started by inserting different amounts of WPS into the reactor. Then, the microwave oven was turned on to heat and pyrolyze the WPS for 35 min at 900 W with a rotation speed of 10 rpm. The waste palm activated carbon (WPSAC) was produced as the main product of interest and it was cooled down inside the ceramics reactor. The product yield was calculated based on the equation 1, where Y is the mass yield, m_i and m_f refer to the initial mass and final mass respectively. WPSAC was washed using distilled water and dried in an oven at 105°C. The dried WPSAC was stored for analyses and future use.

$$Y = \frac{m_i}{m_f} \times 100\% \tag{1}$$

2.4 Single step activation



During carbonization stage, WPS was heated and pyrolyzed and this resulted in the release of volatile matter in the form of pyrolysis gas and the generation of pores on the surface of the solid char formed during the microwave pyrolysis process. The pyrolysis gas was remained in the reactor and this in turn contributed to activation of the solid char to produce

more pores on its surface, thus producing a highly porous solid char termed “activated carbon”. The WPS was converted into WPSAC via one step activation by self-generated pyrolysis gas in which the carbonization and activation occurred simultaneously. Heating in the closed system of ceramics reactor, the moisture (H₂O) content of WPS was likely to evaporate as hot gas and WPS has carbonized by microwave pyrolysis to become hot char. Reaction between hot char of WPS and hot gas generated hydrogen gas and carbon monoxide (Equation 2). Carbon monoxide as one of the product from Eqn. 2 was further reacted with H₂O to produce more hydrogen and carbon dioxide (Equation 3). Both products (i.e. CO₂ and H₂) obtained from Eqn. 3 were reacted with hot char to produce methane gas and carbon monoxide as shown in Equation 4 and 5, respectively. Activation process occurred during reaction between carbon dioxide with hot char as shown in Eqn 4.

2.5 Characterization of waste palm activated carbon

The WPSAC was analysed for their chemical functional group using a Perkin Elmer Spectrum 100 Fourier Transform Infrared (FTIR) spectrometer. A thin KBr (potassium bromide) disc method was used in the FTIR analysis. The analysis was then performed at wavenumber ranging from 400 to 4000 cm⁻¹ for each sample [11]. The infrared spectrum obtained was presented in a form of transmittance (%) against wavenumber (cm⁻¹).

Scanning electron microscopy (SEM) analysis of WPSAC was conducted using JEOL JCM6000 to study the surface morphology and porosity. The WPSAC was also characterized using an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics) to obtain N₂ adsorption-desorption isotherm for calculation of BET surface area, pore volume and pore size.

2.6 Adsorption test of methylene blue using WPSAC

The adsorption test of methylene blue (MB) was conducted using the WPSAC obtained. The adsorption test was performed in a beaker containing 0.5 g of WPSAC and 300 mL of methylene blue solution with an initial concentration of 10mg/L. The beaker was agitated at room temperature with a mixer speed of 200 rpm until the equilibrium was reached. The methylene blue solution was centrifuged and the residual concentration of MB in the supernatant solution was analysed using a UV-Vis spectrophotometer at 665 nm. The amount of MB adsorbed per unit mass of adsorbent at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (6)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution in litre, and W is the mass of adsorbent used in gram.

3 Results and discussions

3.1 Proximate and elemental analyses of waste palm shell

Table 1. Proximate analysis (wt%) and Elemental analysis (wt%)

Description	Waste palm shell (WPS)	Waste palm shell activated carbon (WPSAC)
Proximate analysis (wt%)		
Moisture ^a	4	2
Volatile matter ^b	58	10
Fixed carbon ^c	34	85
Ash ^d	4	3
Elemental analysis (wt%)		
Carbon	50.5	82.8
Hydrogen	6.9	4.1
Nitrogen	3.1	2.8
Sulfur	0.1	0.1
Oxygen ^c	39.4	10.2

^a Dry basis

^b Volatile matter produced from pyrolytic decomposition of hemicellulose, cellulose, and lignin

^c Calculated by difference

^d Obtained by combustion at 1000°C

Table 1 shows the proximate and elemental composition of WPS and WPSAC. The WPS was dominated by volatile matter (58 wt%) and fixed carbon (34 wt%) with small amounts of moisture (4 wt%) and ash (4 wt%). The high volatile content suggests that WPS is more likely to be reactive in creating more pores on the carbonaceous material formed from pyrolytic carbonization process [12]. The WPS can be pyrolyzed to produce carbon rich material such as biochar or activated carbon due to its considerable amount of fixed carbon. As shown in Table 1, the fixed carbon, volatiles, moisture and ash content for the resulting WPSAC was 85 wt%, 10 wt%, 2 wt% and 3 wt%, respectively. This indicates that the carbonization of WPS during microwave pyrolysis had reduced the volatile matter of WPSAC to 10% and increased the fixed carbon content to 85%. Relatively high fixed carbon and low ash contents make WPS more profitable if compare to other palm biomass to produce higher yield of WPSAC. It was also found from Table 1 that the carbon content of WPSAC was increased to 82.8 wt%, and the content of oxygen reduced to 10.2 wt% with small amount of hydrogen (6.9 wt%), nitrogen (3.1 wt%) and sulfur (0.1 wt%). Overall, the results from proximate and elemental analysis indicate that the microwave pyrolysis transformed WPS into a carbon rich material with properties comparable to biochar.

3.2 Chemical functional groups of waste palm shell activated carbon

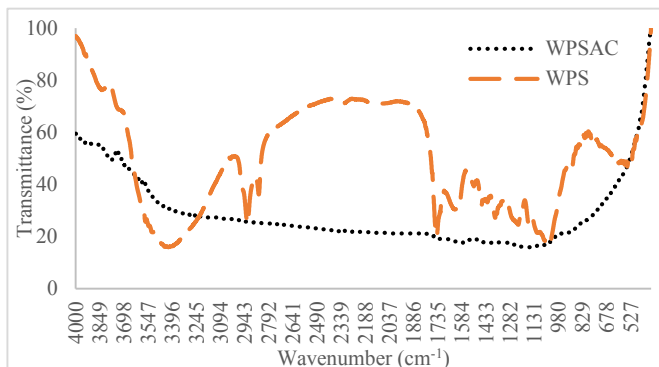


Fig. 2. FTIR spectrum of raw waste palm shell (WPS) and waste palm shell activated carbon (WPSAC).

The FTIR spectra of raw WPS and WPSAC are shown in Fig 2. The spectra of the WPS displayed the following bands 3200–3600 which correspond to O-H stretch in alcohols; 1400–1600 which is assigned to C=C stretch aromatics; the bands at 1000–1300 could be related to C-O groups. Raw WPS showing a wide range of transmittance peak, indicated that a large amount of organic and inorganic matters from cellulose, hemicellulose and lignin. Compare to the almost flat FTIR spectra of WPSAC, indicated that almost all the lignocellulose materials were completely decomposed during carbonization and activation process [13]. Spectra showed great difference at bands 3200–3600 which directly indicates that hydrogen was broadly removed to form graphitic structure; a typical activated carbon structure. However, WPSAC also showing transmittance peak at 1590 cm^{-1} related to functional group of aromatic with C=C stretch bending that cause higher reactions in the methylene blue absorption later.

3.3 Temperature profile of different feedstock amount

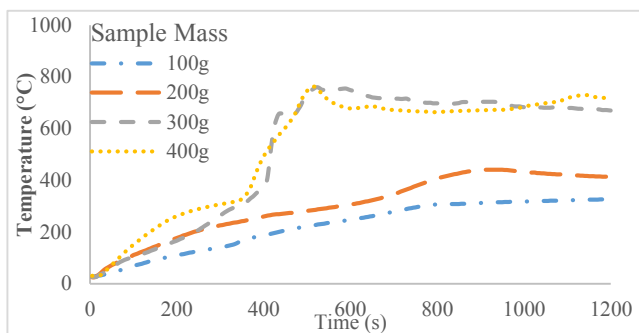


Fig. 3. Temperature profiles for pyrolysis of WPSAC obtained from different feedstock amount.

Fig. 3 shows temperature profiles recorded during pyrolysis of the waste palm shell with different sample mass. It can be observed that comparatively lower temperatures were achieved for 100 and 200 g of sample mass with maximum temperature recorded at 330°C and 450°C respectively. However, when sample mass was increased to 300 g and 400 g, the maximum temperature achieved was increased significantly to 750°C at around 500 s. This

was probably because more carbon monoxide and hydrogen generated from the exothermic reaction in Eq 3 and 4. Also, exothermic reaction in more feedstock (300 g and 400 g) is much larger than endothermic reaction (Eq. 2 and 5). Then, more heat energy released to cause rapid increasing of temperature from 300 to 750°C in 300 and 400 g feedstock amount.

Generally, pyrolysis of the biomass was observed to produce biochar, bio-oil vapours, steam, and incondensable gases as by-products. The incondensable gases could consist of high amounts CO and small amounts of H₂ and CO₂, which form pyrolysis gas [14]. In this research, it was thought that the pyrolysis gas produced within the reactor was trapped inside the ceramics reactor and forced to react with hot char and caused exothermic reaction. Besides that, hot char also carried out activation by carbon dioxide shown in Equation 5 as majority carbon monoxide and with minor gases of hydrogen and carbon dioxide were detected by gas alert at gas emission channel. When the pyrolysis temperature was further increased above 450°C, softening and decomposition of the high-molecular-weight compounds occurred that resulted from the depolymerisation of lignocellulosic components such as lignin [15].

3.4 Yields, surface area and adsorption performance of waste palm shell activated carbon

Table 2. Yields, surface area and adsorption performance of waste palm shell activated carbon.

Sample mass (g)	Maximum Temperature (°C)	Yields (wt %)	S _{BET} (m ² /g)	MB adsorption (mg/g)
100	330	43.0	750	160
200	450	35.5	890	250
300	750	31.5	1200	425
400	750	31.0	1252	440

Table 2 shows the yield of WPSAC obtained at different maximum temperature and feedstock amount. The reaction rate in pyrolysis can be expressed in terms of conversion from the raw waste palm shell to WPSAC. The conversion (C) of pyrolysis is defined as the ratio of weight loss to the initial raw material weight shown in the Eq. 7,

$$C = \frac{m_i - m_t}{m_i} \quad (7)$$

where m_i is the weight of the initial raw material (WPS) and m_t is the weight of char after pyrolysis. In this respect, the weight loss of the sample or the conversion is an indication of the thermal degradation occurring during pyrolysis. Higher pyrolysis temperature contributed immensely to the volatilization of cellulose, hemicelluloses and lignin which may be responsible for the low WPSAC yield [15].

The release of the volatiles from the carbon structures of the waste palm shell is dependent on the prevailing pyrolysis temperature. At about 450°C, low molecular - weight volatiles are released, thereby WPSAC yields with around 35.5% to 43.0 wt% (Table 1). Further increases in the pyrolysis temperature to 750°C, the small gradual decrease of yields to 31.0 wt% caused by the releasing of high-molecular-weight volatiles. Beyond that, the release of volatiles is almost complete and hence the conversion remains constant. The produced WPSAC had tested as absorbent for Methylene blue adsorption test. The removal of Methylene blue increased with prolonging the contact time to 24 hours and reached the equilibrium stage. The amount of MB adsorbed at the equilibrium time reflects the maximum adsorption uptake of WPSAC under operating conditions. In the present study,

adsorption equilibrium, q_e reached 440 mg/g with an initial concentration of 10 mg/L.

3.5 Textural and surface morphology

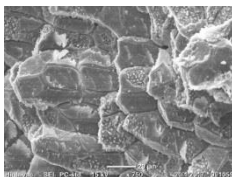


Fig. 4. Raw waste palm shell.

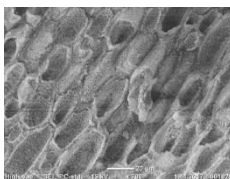


Fig. 5. Uniform pore in 100 g.

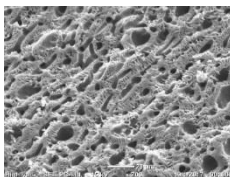


Fig. 6. Irregular pore sizes in 200 g.

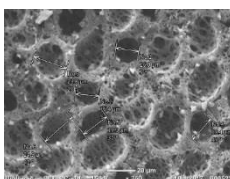


Fig. 7. Uniform macro pore in 300 g and 400 g.

The scanning electron micrograph shows the pores development on the surface of the WPS to WPSAC. WPS is covered with many globular silica bodies that contain sharp, conical agglomerations shown in Fig. 4 [16]. During microwave pyrolysis, silica body was removed from the carbon surface and create a macro pore shown in Fig. 5. With 100 gram of WPS loading and maximum temperature of 330°C, pores with less than 1 μm have been observed on waste palm biochar due to releasing globular silica body from the WPS surface. However, Fig. 6 observed some porous structure with non-regular pore sizes developed on the surface. This is probably due to decomposition of hemicellulose happen when maximum temperature reached 450°C in 200g WPS sample. Fig. 7 shown the effect of pyrolysis temperature appears on the larger pores generated and within it some smaller pores generated by pyrolysis gas activation. The pores on the surface of the WPSAC are well-developed with mainly 2 types of macrospore. Larger pores size range from 15–25 μm and within it some smaller pores ranging from 1–5 μm are generated with activation

process. Due to this, larger surface area generated and better for the adsorption.

4 Conclusion

In this study, waste palm shell-based activated carbons were produced successfully by self-generated pyrolysis gas as activating agent. From the experiment, quantity of WPS as one of the factor influence the generation of pyrolysis gas to perform the activation. Single-step approach reduced the production cost and time to convert waste palm shell into activated carbon. The results of the present investigation show that WPSAC prepared is potential useful adsorbent for the MB adsorption.

The authors gratefully acknowledge the financial support provided by University College of Technology Sarawak under Grant scheme (Project No. UCTS/RESEARCH/<1/2016/03>(01)).

References

1. C.Y. May, Overview of the Malaysian Oil Palm Industry, Malaysian Palm Oil Board, Economics & Industry Development Division, 2016
2. J.P. Tang, H.L. Lam, M.K. Abdul Aziz, N.A. Morad. *Energ.*
3. S. Sedghi, S.H. Madani, C. Hu, A. Silvestre-Albero, W. Skinner, P. Kwong, P. Pendleton, R.J. Smernik, F. Rodríguez-Reinoso, M.J. Biggs. *Carbon* **95**, 144–149 (2015)
4. M.K. Aroua, W.M.A.W. Daud, C.Y. Yin, D. Adinata. *Sep. Purif. Technol.* **62**, 609–613 (2008)
5. S. Mubarik, A. Saeed, M.M. Athar, M. Iqbal. *J. Ind. Eng. Chem.* **33**, 115–121 (2016)
6. P. Liu, W.-J. Liu, H. Jiang, J.-J. Chen, W.-W. Li, H.-Q. Yu. *Bioresour. Technol.* **121**, 235–240 (2012)
7. P. Xu, C.-X. Sun, X.-Z. Ye, W.-D. Xiao, Q. Zhang, Q. Wang. *Ecotoxicol. Environ. Saf.* **132**, 94–100 (2016)
8. R.K. Gupta, M. Dubey, P. Kharel, Z. Gu, Q.H. Fan. *J. Power Sources* **274**, 1300–1305 (2015)
9. M. Tripathi, J.N. Sahu, P. Ganesan, J. Jewaratnam. *Appl. Thermal Eng.* **105**, 605–612 (2016)
10. S.S. Lam, R.K. Liew, C.K. Cheng, H.A. Chase. *Appl. Catal. B-Environ.* **176–177**, 601–617 (2015)
11. S.S. Lam, R.K. Liew, X.Y. Lim, F.N. Ani, A. Jusoh. *Int. Biodeter. Biodeg.* **113**, 325–333 (2016)
12. S.S. Idris, N.A. Rahman, K. Ismail, A.B. Alias, Z.A. Rashid, M.J. Aris. *Bioresour. Technol.* **101**, 4584–4592 (2010)
13. A.F. Rugayah, A.A. Astimar, N. Norzita. *J. Oil Palm Res.* **26**, 251–264 (2014)
14. H. Guo, F. Peng, H. Zhang, L. Xiong, S. Li, C. Wang, B. Wang, X. Chen, Y. Chen. *Int. J. Hydrogen Energ.* **39**, 9200–9211 (2014)
15. Q. Jia, A.C. Lua. *J. Anal. Appl. Pyrol.* **83**, 175–179 (2008)
16. A.M. Abioye, F.N. Ani. *Appl. Mech. Mater.* **695**, 12–15 (2014)