Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

ARTICLE Received:18/07/2015, Accepted:15/09/2015

Effect of temperature on micropore of activated carbon from sticky rice straw by H_3PO_4 activation

Sumrit Mopoung [*, A], Supattra Inkum [B], Laddawan Anuwetch [C]

(A) Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, Thailand.
(B) Pu Duang Sueksalai School, Khon Sawan district, Chaiyaphum, Thailand.
(B) Yangwittayakhom school, Yang sub-district, Borabue district, Mahasarakham, Thailand.

*Corresponding author. E-mail address: sumritm@nu.ac.th

Abstract: Microporous activated carbon was prepared from sticky rice straw using activated phosphoric acid. The effects of carbonization temperature, activation temperature, and phosphoric acid on physical and chemical properties of charcoals and activated carbon were studied. The rice straw was carbonized between 300 °C and 700 °C and activated between 600 °C and 800 °C with phosphoric acid using a weight to volume ratio of 1:2 (charcoal:H_3PO_4). It was found that the suitable carbonization temperature for rice straw charcoal preparation is 600 °C. The micropore of activated carbon made from rice straw based charcoal increased with increasing activation temperature from 600 °C to 800 °C. This phenomenon was confirmed by the iodine number and SEM micrographs. The iodine number of activated carbons produced in this work was in the range from 1137 mg/g to 1762 mg/g.

Keywords: Microporous activated carbon, temperature, phosphoric acid, sticky rice straw

1. Introduction: About 38 million tons of rice straw is produced in Thailand every year [1]. It is an agricultural waste from rice harvest, which is often disposed of by burning. Rice straw has been utilized for the cultivation of *Phanerochaete chrysoporium* to produce cellobiose dehydrogenase [2], in reinforced polymer composites [3], as source of cellulose [4], feed ingredient for lactating dairy cows [5], for gasification [6], bioethanol production [7], syngas production [8], and manure processing [9]. An inexpensive and biodegradable thermoplastic has been developed through the acetylation of rice straw with acetic anhydride [10]. Pyrolysis of rice straw to produce biochar for improving soil fertility in large-scale application is increasing carbon storage and decreasing green house gas emissions. The rice straw-derived biochars had high alkalinity and cation exchange capacity, and high levels of available phosphorus and extractable cations [11]. The rice straw has been utilized for activated carbon preparation by a two-stage method of carbonization and KOH activation [12].

In this research, the microporous activated carbon was prepared from sticky rice straw. The effects of carbonization temperature from 300 °C to 700 °C for charcoal production and activation at temperature from 600 °C to 800 °C, and effect of phosphoric acid were studied. Charcoal and activated carbon were characterized by iodine number, FTIR, SEM, and XRD.

2. Materials and methods

2.1 Preparation of material: Straw (sticky rice RD6) was obtained from Khon Sawan District, Chaiyaphum Province, Thailand. It was chopped to pieces few millimeters long and dried in oven (SL Shel Lsb 1375 FX) at 110 °C for 24 h. It contained 7.43% ash, 77.30% volatile matter and 15.27% fixed carbon by dried weight.

2.2 Preparation of charcoal: The dried straws were carbonized in furnace (Fisher Scientific Isotemp) at 300, 400, 500, 600, and 700 °C for 1 h using a closed system in a porcelain crucible and then cooled down to room temperature. The percent yields of charcoals obtained at different carbonization temperatures were determined. The charcoal products at different carbonization temperatures were analyzed to find the optimal carbonization temperature.

2.3 Preparation of activated carbon: It was found that the suitable carbonization temperature for charcoal preparation from straw is 600 °C. So, the charcoal carbonized at 600 °C was selected for activated carbon preparation. It was grinded and sieved to 0.2-0.5 mm and then, impregnated with 0.25 N H_3PO_4 (UNIVAR, AR) at weight to volume ratio of 1:2 (charcoal:H_3PO_4). The slurries were left overnight at room temperature and then dried at 110 °C for 24 h. The samples were activated in a closed system with pyrolysis temperatures between 600 °C and 800 °C and soaked in furnace for 1 h. After cooling down, the activated carbons were leached 2-3 times with 5 N HCl (AR Merck) and 48% HF (Merck) then with distilled water until the pH became neutral. The washed samples were dried at 110 °C. The final activated carbons were weighed to calculate the percent yield.

2.4 Characterization of physical and chemical properties of materials: The dried straw, charcoals, and activated carbons were analyzed for proximate composition, including ash **[13]**, volatile mater **[14]**, and fixed carbon **[15]**. The iodine number parameters of the charcoal and activated carbon materials were determined by methods of AWWA B604-74 **[16]**. The charcoal and activated carbon were characterized by fourier transform infrared spectrometry (GX, Perkin Elmer), scanning electron microscopy (LEO 1455 VP), and X-ray diffraction (PW 3040/60, X' Pert Pro MPD).

3. Results and discussion

3.1 Proximate analysis: Volatile matter and percent yield of rice straw based charcoals decreased with increasing carbonization temperature from 300 °C to 700 °C (Table 1). In contrast, ash content and fixed carbon increased with increasing carbonization temperature. The volatile matter includes the labile components with rapid decay during thermal treatments. The decrease of volatile matter content with increasing carbonization temperature is mirrored in the increased contents of stable fractions fixed carbon and ash. Ash is a nonvolatile inorganic matter therefore its content increases with increasing carbonization temperature and concomitant decrease in the volatile matter content. The ash content of rice straw charcoal of sticky rice RD6 is lower than rice straw charcoal from *Oryza sativa* rice **[11]**. Fixed carbon content of sticky rice charcoal obtained at 700 °C is 5 times higher compared to normal rice straw. On the other hand, the volatile matter content decreased about 18 fold. These results indicate that normal rice straw has high content of volatile matter, which results in a low yield of charcoal.

The fixed carbon content of activated carbon obtained with activation at 600 °C to 800 °C shows an increasing trend with increasing activation temperature. The fixed carbon content was also higher than in the untreated charcoals. It was shown that the activated carbon is relatively stable. However, it may have lost some volatile matter through degradation in the phosphoric acid and burn off.

The ash content in activated carbons is very low. This may be due to the dissolution in phosphoric acid during the activation stage or during the HCl and HF washing steps.

3.2 Percent yield: Percent yield of charcoal and activated carbon materials at different carbonization and activation temperatures are shown in Table 1. It was showed that the percent yield of both decreases with increasing temperature. This is caused by evaporation of volatile matter and, to some extent, also by partial oxidation of carbon with oxygen in the atmosphere and phosphoric acid during the activation process. The percent yield of charcoal decreased more than that of activated carbon. Thus it can be concluded that the activated carbon is highly stable.

3.3 Iodine adsorption: The critical pore diameter for the adsorption of iodine is ca. 5 nm (micropore) [17]. The iodine numbers of rice straw charcoals increased from 300 °C to 500 °C, but decreased afterwards (Table 1). Arenas and Cheine [18] have described that evaporation of volatile matter is incomplete at low pyrolysis temperatures resulting in the micropores not being fully extended. The highest iodine adsorption was observed for charcoal prepared at 500 °C indicating that at this temperature the carbonization is complete. After this point, the surface area is reduced, which is due to the burn off of carbon. This results in increased pore size and a more porous wall. Therefore, the iodine adsorption on charcoal was reduced.

Activated carbon obtained at 600 °C to 800 °C showed increased iodine adsorption with increasing activation temperature. Iodine adsorption on activated carbons obtained at all activation temperatures is higher than for charcoal prepared by carbonization at 500 °C. This is because the phosphoric acid stimulates formation of more micropores during the activation process. Moreover, the very low ash contents in the activated carbon materials can be ascribed to its dissolution during the activation and washing steps. This can result in increased adsorption together with increased activation temperature. Given the higher iodine adsorptions of activated carbons after activation (from 1337 to 1762 mg/g) it can be concluded that their micropore content is very high. These micropores can be used to remove heavy metals.

3.4 FTIR spectra: FTIR spectra of rice straw based charcoals carbonized between 300 °C and 700 °C are shown in Figure 1. The broad band at about 3400 cm^{-1} is due to the O–H stretching of hydroxyl groups which decreases with increasing carbonization temperature. The very weak peak at 2924 cm^{-1} of charcoals prepared at 300 and 400 °C is due to the C–H stretching of aliphatic CH_x [19], which disappears after carbonization at 500 °C. The peak at 1580 cm^{-1} and very weak shoulder peak at about 1680 cm^{-1} are due to C=C stretching of aromatic components and to a smaller extent to C=O stretching in quinones and ketonic acids [19]. The very weak peak at 1380 cm^{-1} is due to the aliphatic deformation of CH_2 or CH_3 groups or O–H bending of phenolic–OH. This reveals that greater dehydration and increased aromatization occurred as the carbonization temperature increased from 300 °C to 700 °C as a result of the decomposition and condensation of volatile matter [11]. The peak at 1118 cm^{-1} is due to the Si–O–Si asymmetric stretching. The peaks at 800 cm^{-1} and 450 cm^{-1} assigned to the Si–O symmetric stretching and bending, respectively. It is characteristic of silica [20]. These peaks decreased with increasing carbonization temperature and disappeared completely at 600 °C. For charcoal prepared at 700 °C, bands for all of the functionalities were diminished and the FTIR spectrum resembled that of graphite [11]. In this study, the charcoal carbonized at 600 °C was selected for activation for activated carbon preparation.

Table 1 Percent yield, proximate analysis and iodine number of rice straw based materials.

Samples	Ash (wt%)	Volatile matter (dried wt%)	Fixed carbon (dried wt%)	Percent yield (wt%)	Iodine No. (mg/g)
Rice straw	7.43	77.30	15.27	-	-
Charcoal 300 °C	10.91	38.89	50.20	36.81	158
Charcoal 400 °C	12.25	24.93	62.82	33.56	498
Charcoal 500 °C	13.69	11.37	74.20	29.04	751
Charcoal 600 °C	14.32	7.74	77.94	**27.37**	246
Charcoal 700 °C	15.25	6.06	78.69	24.51	188
Activated carbon 600 °C	0.06	11.39	88.55	75.83	1337
Activated carbon 700 °C	0.05	6.24	93.71	64.46	1554
Activated carbon 800 °C	0.02	4.51	95.47	**58.70**	1762

The FTIR spectra of rice straw based activated carbon materials obtained with pyrolysis between 600 °C and 800 °C are shown in Figure 2. It was found that the FTIR peaks of activated carbon are very weak when compared to the charcoals prepared at 600 °C. This reveals that the

functionalities are further degraded during the activation process.

The peaks at 1380 cm^{-1}, 1118 cm^{-1}, 800 cm^{-1}, and 450 cm^{-1} of activated carbon have disappeared completely. It was shown that the phosphoric acid used for activation as well as HCl and HF used for washing are very high effective. However, the peaks at about 3400 cm^{-1}, 1580 cm^{-1}, and 1680 cm^{-1} of activated carbon are still albeit with very low intensity. The intensity of these peaks decreases with increasing pyrolysis temperature from 600 °C to 800 °C. The new peak at about 1200 cm^{-1} found in the activated carbon is due to the P–O–C linkage of phosphate ester and overlap of C–O bond [21]. These functional groups are created during the activation with phosphoric acid. These functional groups are attached to the surface of the activated carbon material and remain there despite the washing steps with strong acids.

3.5 SEM micrographs: Figure 3a shows SEM micrograph of rice straw based charcoal. It shows closed pores on the surface. However, after activation, the activated carbon showed open pores in its structure (Figure 3b). These results are consistent with results obtained with *japonica* rice straw derived activated carbon [12]. The pores become more open with increasing pyrolysis temperature. This is true especially for materials obtained through pyrolysis at 800 °C. This is due to better access of phosphoric acid to the charcoal at higher pyrolysis temperatures and enhanced degradation of charcoal surface [22]. A micrograph obtained with magnification of 10000 revealed a large number of disordered micropores (Figure 3c).

3.6 XRD patterns: The XRD pattern of the rice straw based charcoal carbonized at 600 °C is showed in Figure 4a. It indicates the presence of SiO_2 (peak at 21° and 27°) in the form of amorphous silica [21] and KO_2 (peak at 29° and 40°) [23]. Si assimilated from the soil and is deposited in inter- and intracellular spaces throughout the leaf and stems to form silicified structures leading to the formation of SiO_2 phase in the charcoal materials. K is immobilized in the mineralized silica during the precipitation of Si [23]. The peak at about 23° is assigned to diffuse graphite. It is attributed to graphite-like atomic order within a single plane. This indicated that the atomic order and crystallite size in the rice straw charcoal was developed at high carbonization temperature. The structure resembles that of the activated carbon obtained with H_2SO_4 activation [24]. However, the rice straw charcoal is also amorphous.

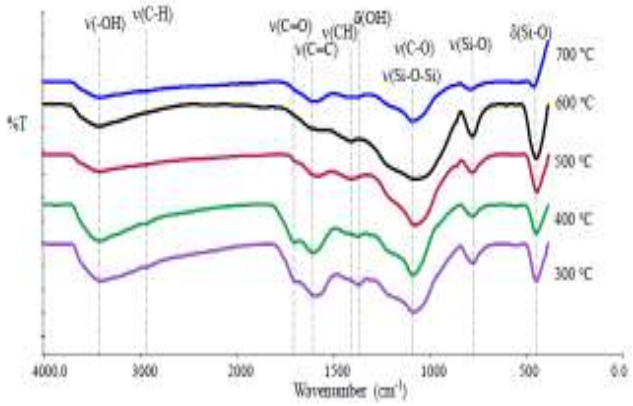

Figure (1): FTIR spectra of rice straw based charcoals carbonized between 300 °C and 700 °C.

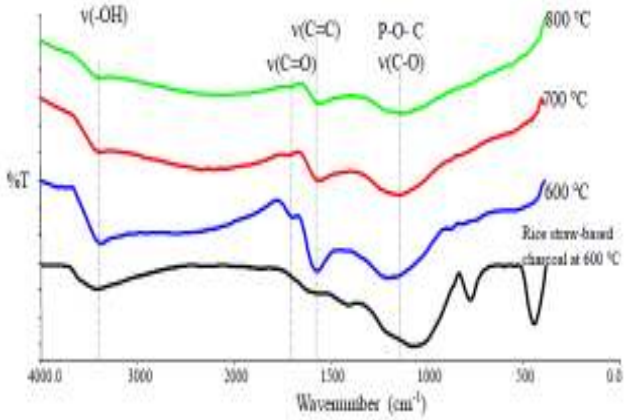

Figure (2): FTIR spectra of rice straw based activated carbons pyrolyzed between 600 °C and 800 °C.

The small peaks detected in the charcoal materials disappeared after the activation process (Figure 4b). This shows that the phosphoric acid activation and acid washing (HCl and HF) are highly efficient. It was also found that the activated carbons are more amorphous (broad bands with maximum at about 24 and 44° [25]). Furthermore, the crystal structure of charcoal was destroyed and micropores were created by the action phosphoric acid.

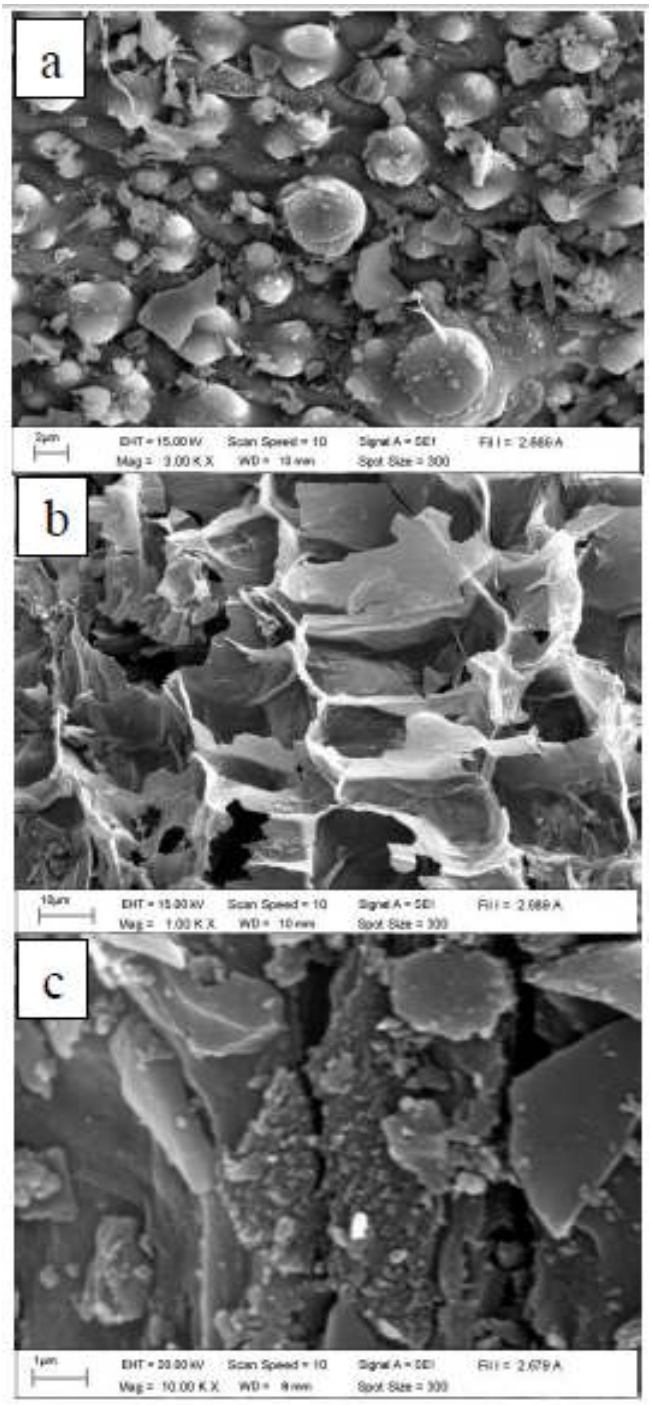

Figure (3): Scanning electron micrographs of rice straw base charcoal carbonized at 600 °C (a), rice straw based activated carbon activated at 800 °C, mag. 1000 X (b), and rice straw based activated carbon activated at 800 °C, mag. 10000 X (c)

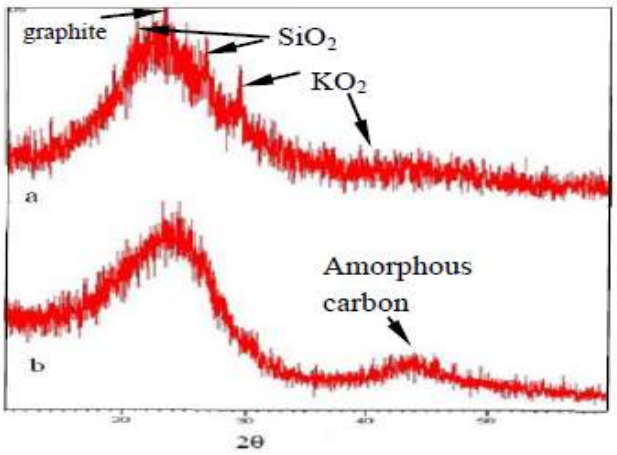

Figure **(4):** X-ray diffractograms of rice straw based charcoal carbonized at 600 °C (a) and rice straw based activated carbon activated at 800 °C (b).

4. Conclusions: In this study, it was found that the suitable carbonization temperature for charcoal production from rice straw is 600 °C. The micropore content of rice straw based activated carbon materials obtained after activation with phosphoric acid increased with increasing activation temperature from 600 °C to 800 °C. This result was confirmed by the outcomes of iodine adsorption and SEM micrograph experiments. The activated carbon materials obtained after washing with HCl and HF are highly pure. The iodine adsorption on rice straw based activated carbons increased from 1137 mg/g to 1762 mg/g as the activation temperature increased from 600 °C to 800 °C. It was shown that rice straw based activated carbons obtained with phosphoric acid activation in the temperature range from 600 °C to 800 °C are highly microporous. The results of this study indicate that the conditions used are suitable for the productions of microporous activated carbon materials from rice straw.

Acknowledgements: This research was supported by Faculty of Science, Naresuan University. The instruments used in this research were purchased with partial funding from Chemistry Department and Science Lab Centre, Faculty of Science, Naresuan University.

References:

[1] T. Silalertruksa, S. H. Gheewala, M. Sagisaka, K. Yamaguchi, Appl. Energ. 112 (2013) 560.

[2] S. B. Kim, E. Kim, H.Y. Yoo, M. Kang, S. W. Kang, C. Park, J. S. Kim, S. W. Kim, Renew. Energ. 53 (2013) 43.

[3] M. Bassyouni, S. Waheed Ul Hasan, The use of rice straw and husk fibers as reinforcements in composites. Biofiber Reinforcements in Composite Materials. Elsevier Ltd, (2015) 385-422.

[4] G. Fan, M. Wang, C. Liao, T. Fang, J. Li, R. Zhou, Carbohyd.Polym. 94 (2013) 71.

[5] P. J. Weimer, D. R. Mertens, R. Ponnampalam, B. F. Severin, B. E. Dale, Anim. Feed Sci. Tech. 103 (2003) 41.

[6] K. -Y. Chiang, Y. -X. Lin, C. -H. Lu, K. -L. Chien, M. -H. Lin, C. -C. Wu, S. -S. Ton, J. -L. Chen, Int. J. Hydrogen Energ. 38 (2013) 12318.

[7] H. A. –H. Ibrahim, Energ. Procedia 14 (2012) 542.

[8] Q. Li, S. Ji, J. Hu, S. Jiang, Chinese J. Catal. 34 (2013) 1462.

[9] Z. Hu, Y. Liu, G. Chen, X. Gui, T. Chen, X. Zhan, Bioresource Technol. 102 (2011) 7329.

[10] G. Zhang, K. Huang, X. Jiang, D. Huang, Y. Yang, Carbohyd. Polym. 96 (2013) 218.

[11] W. Wu, M. Yang, Q. Feng, K. McGrouther, H. Wang, H. Lu, Y. Chen, Biomass Bioenerg. 47 (2012) 268.

[12] K. L. Chang, C. -C., Chen, J. -H. Lin, J. -F., Hsien, Y. Wang, F. Zhao, Y. –H. Shih, Z. -J. Xing, S. -T. Chen, New Carbon Mater. 29 (2014) 47.

[13] American Standard of Testing Material. Standard Test Method for Total Ash content of Activate Carbon ASTM D 2866-94 (1996).

[14] American Standard of Testing Material. Standard Test Method for Volatile Matter Content of Activate Carbon ASTM D 5832-95 (1996).

[15] American Standard of Testing Material. Standard Test Method for Fixed Carbon in Activate Carbon ASTM D 3172-89 (1994).

[16] American Water Works Association. Standard Test for Determination of Iodine number of granular Activated Carbon AWWA B604-74 (1974).

[17] G. H. Oh, C. P. Park, Fuel 81 (2002) 327.

[18] E. Arenas, F. Cheine, Carbon 42 (2004) 2451.

[19] A. C. Lua, T. Yang, J. Colloid Interf. Sci. 274 (2004) 594.

[20] P. Lu, Y. L. Hsieh, Powder Technol. 225 (2012) 149.

[21] A. M. Puziy, O. I. Poddubnaya, A. Martinez-Alonso, F. Suárez-Garcia, J. M. D. Tascón, Carbon 40 (2002) 1493.

[22] C. Toles, S. Rimmer, J. C. Hower, Carbon 34 (1996) 1419.

[23] M. N. Nguyen, S. Dultz, F. Picardal, A. T. K. Bui, Q. V. Pham, J. Schieber, Chemosphere 119 (2015) 371.

[24] S. B. Kim, S. J. Lee, E. J. Jang, S. O. Han, C. Park, S. W. Kim, J. Ind. Eng. Chem. 18 (2012) 183.

[25] X. Ma, F. Ouyang, Appl. Surf. Sci. 268 (2013) 566.

*****