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Promoting Effect of PKS Ash on Activated Carbon Preparation from Cypress Sawdust

Liuyun Li[+] , Yuka Sato and Tadaaki Shimizu

Department of Chemistry and Chemical Engineering, Niigata University, 2-8050, Ikarashi, Niigata, 950-2181, Japan

Abstract. Activated carbon preparation from sawdust of Japanese cypress mixed with palm kernel shell (PKS) ash was studied. The PKS was used as an activation agent. Effects of PKS ash, its mixing ratio to sawdust, carbonization temperature and introduced gases were discussed. PKS ash shows a higher promoting effect on activated carbon production because of its high content of K. 1:1 (w/w) mixing ratio of PKS ash to sawdust produced a high surface area cypress char. Also, specific surface areas of the carbonized char showed strong temperature dependence. The 700 ℃, 750 ℃ chars, showed as high as 1618 and 1678 m^2g^{-1}, respectively, in N_2 gas ambient. CO_2 and steam activation for the PKS ash mixed cypress char was operated at relatively low temperature of 600 ℃ because of complete gasification by the gasifying agents at 750 ℃. Textural structure cypress char of 1668 m^2g^{-1} surface area was achieved under steam addition at 600 ℃, micro pores of 0.3－0.6 nm were generated profusely.

Keywords: activated carbon, activation agent, palm kernel shell ASH

1. Introduction

Regarding biomass waste-to-energy research, various technologies have been developed. Palm kernel shell (PKS) has a HHV of 4000-4500 Kcal kg^{-1}, which is between that of high and low rank coals and about twice of woody biomasses. Therefore, much attention is paying to PKS as an excellent fuel in power plant, considering reducing the dependence on fossil fuels as well as decreasing greenhouse gas emissions. In this study, we focus on the high K content in PKS ash, which can be considered as an activation agent for activated carbon preparation.

Typically, activated carbon is produced by chemical activation or physical activation. The chemical activation method requires proper chemical reagents. KOH, $ZnCl_2$, H_2SO_4, NaOH and K_2CO_3 are used as activation agents. To reduce environmental contamination, natural activation agents from agricultural wastes are researched [1], [2]. Unfortunately, plenty of agricultural wastes, such as rice straw, wheat straw, pine and olive tree, have SiO_2 as its main component (40 to 95%) [3]. Therefore, properly choosing the agricultural waste is required.

In his study, we focus on PKS ash as a natural activation agent instead of synthesized chemicals. The effects of various parameters including the ash/biomass weight ratio, effect of CO_2 or steam addition and the treatment temperature were investigated.

2. Experiment Methods

2.1. Materials

Commercial PKS ash with K of 31wt%, Mg of 1.8wt% and P of 2.5wt% was used as a natural activation agent. For reference, ash of waste mushroom culture ("Enokitake", Flammulina velutipes), containing P, K, Mg and Si [4], and a chemical reagent, K_2CO_3, were used. Cypress sawdust was used as a carbonization material to produce activated carbon.Sample preparation

[+] Corresponding author.
E-mail address: liliuyun@eng.niigata-u.ac.jpv.

Cypress sawdust was mixed with PKS ash or two other activation agents. PKS ash powder or its water-solution was mixed to cypress sawdust, and the effect of mixing method on textural structure of activated carbon was discussed. Weight ratios of PKS ash to cypress were varied from 0.5 to 2.0. Carbonization operation was carried out in a horizontal reactor. Carbonization was conducted by a slow pyrolysis, 15 ℃ min^{-1}, up to 600－1000 ℃, and holding at the final temperature for 60 min. Pure N_2, N_2/CO_2 and N_2/steam were introduced.

The char samples were washed in 0.5M HCl solution and stirred for 2 hrs to remove the ash components. After that, the samples were rinsed with deionized water and filtered until the solution pH is near to 7.0. After drying, activated carbon was produced.

2.2. Characterization of the Activated Carbons

Nitrogen adsorption isotherm was characterized by nitrogen adsorption and desorption at -196 ℃ using Brunauer-Emmett-Teller (BET) and micropore analysis methods. It should be noted that all samples were degassed at 300 ℃ for 3 hrs before the adsorption analysis in N_2 gas ambient. Scanning electron microscope (SEM) images were taken to discuss the sample's textural feature.The adsorption capacity of activated carbons was determined employing iodine number.

3. Results and Discussion

3.1. Effect of PKS Ash and the Mixing Methods on Pore Structure of Cypress Char

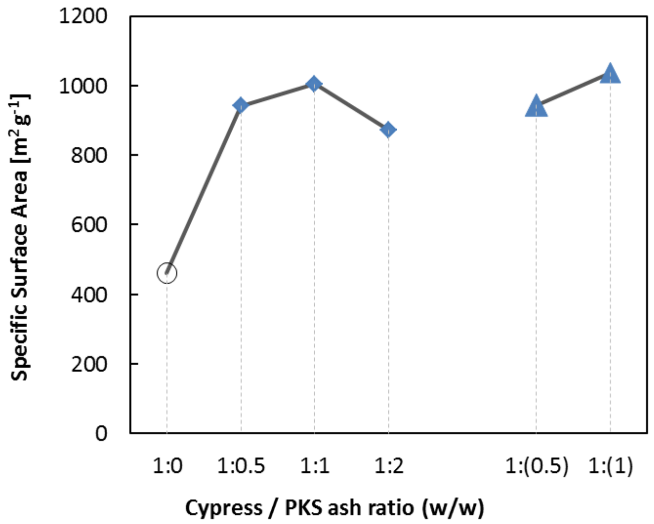

Fig. 1: Specific surface area of cypress char obtained from cypress /PKS ash mixture at different weight ratios. The ratios presented in ( ) note cypress mixed with the PSK ash water-solution, the others mixed with PSK ash powder (carbonized in N_2 stream, up to 900 ℃).

Figure 1 compares specific surface areas of the cypress chars carbonized up to 900 ℃ in N_2 stream. The PKS ash powder or water-solution was mixed with cypress sawdust at different weight ratios. PKS ash gives a great promotion on the porous char production, nearly twice specific surface areas are achieved comparing to that cypress char without PKS ash mixing. The mixing ratio 1:1 of cypress to PKS ash produces more porous char than 1:0.5 and 1:2. The mixing method gives some effect on the char structure. The same dosage of PKS ash water-solution promoted 8~14% higher specific surface area char generation than its powder. Additionally, in order to reduce water-insoluble components introduction into biomass sample and simplify the char after-treatment procedure, water solution of PKS ash was mixed with cypress in the following preparation.

3.2. Effect of Carbonization Temperature on Pore Structure of the Cypress Char

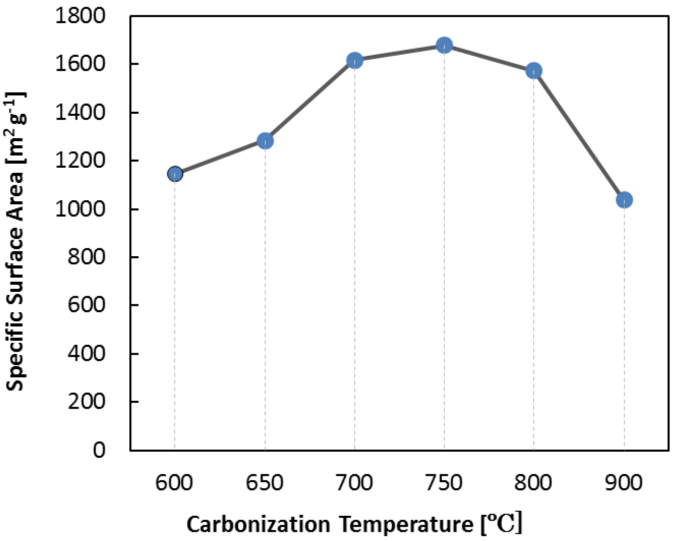

Fig. 2: Specific surface areas of cypress char obtained at different carbonization temperatures. (cypress mixed with the PSK ash water-solution by 1:1, carbonized in N_2 stream)

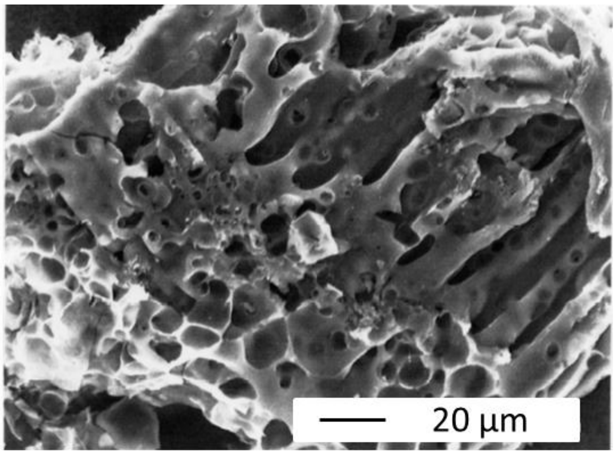

Fig. 3: SEM image of 750 ℃ cypress char (with PSK ash water-solution by 1:1, carbonized in N_2 stream)

Figure 2 shows the specific surface area of cypress char obtained from 1:1 cypress sawdust and PSK ash mixture, at various carbonization temperatures and in N_2 gas stream. When the carbonization temperature increases from 600 to 900 ℃, the areas increase firstly and reach a peak value of, 1678 m^2g^{-1} at 750 ℃, and then decreased with the carbonized temperature decreasing. Carbonization (devolativation) is a complex reaction process that includes decomposition of organic matters and elimination of volatile matters from remaining products. During devolativation process, volatile matters start to accumulate and particles undergo the first cracking, which can generate pores and increase particle surface area. When the carbonization temperature increases, the volatile matters start to escapes and the particles undergo the secondary cracking. It may form carbon to deposit on the char thus blocking the developed pore and leads to decrease the surface area of microspore [5]. Also continuous of secondary cracking and carbon activation by chemical agents at higher temperature may collapse or generate the micropore structure, to affect the char pore structure. On the other hand, the dependence of specific surface area on temperature can be explained by burn off mechanism. The products burn off at low carbonization temperature is lesser than higher carbonization temperature. Various amount of volatile matters revolution and the further burn off of the residues char influent material's porous structure. Namely, these reactions progression was related to the high surface areas [6], [7]. Figure 3 shows SEM micrograph of porous cypress char obtained at 750 ℃ in N_2 stream.

Additionally, cypress char prepared mixed with chemical reagent of K_2CO_3 solution, as a reference. The sample was heat-treated at 700 ℃ in N_2. The obtained char shows a specific surface area of 1079.7 m^2 g^{-1} and a pore volume of 0.429 cm^3 g^{-1}, which are about two thirds of those of cypress char obtained with PSK ash. It is considered as the distributions of the complex components in PSK ash, including K, Ca, Mg and P etc. Fig. 4 compares the pore size distributions of cypress char obtained by PSK ash and K_2CO_3 reagent, carbonized in N_2 at 700 ℃. Both of the samples have micro pore distribution and sharp peaks were measured between 0.2 and 0.4 nm. PSK ash promoted bigger pore generation, which results in higher surface area and more porous structure than the char with K_2CO_3 reagent.

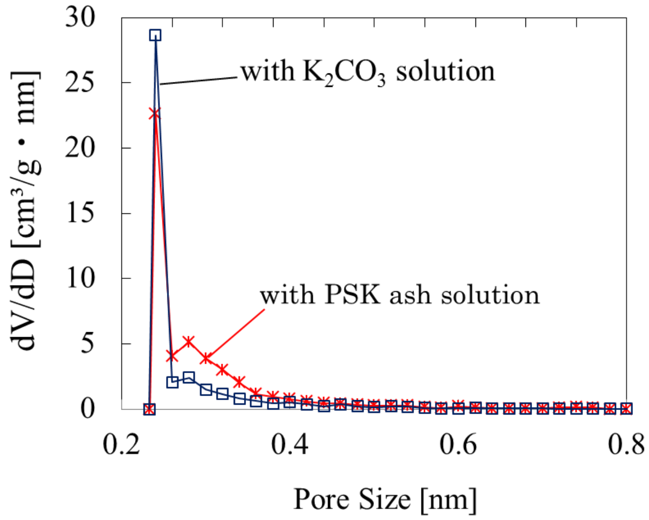

Fig. 4: Comparison of pore size distribution of cypress char mixed with K_2CO_3 solution and PSK ash solution, carbonized in N_2 stream at 700 ℃

3.3. Effect of CO_2 and Steam Addition on Cypress Char Structure

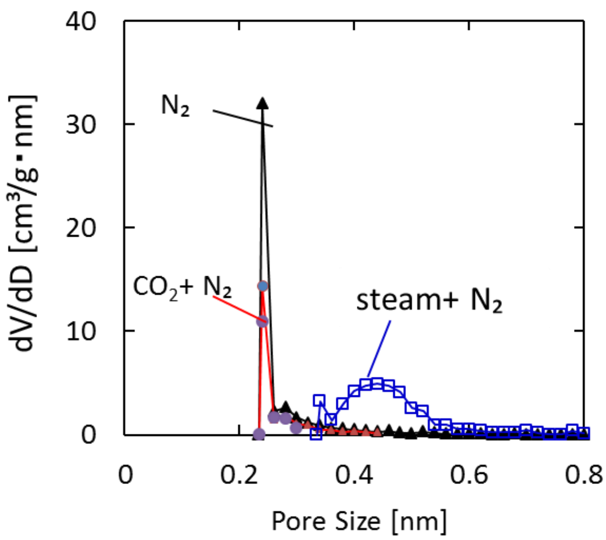

Fig. 5: Comparison of pore size distribution of cypress char carbonized in different gas streams at 600 ℃ (cypress was mixed with PSK ash solution by 1:1).

Steam and CO_2 (10 vol. % + N_2) were introduced into the activation process. It was firstly found that CO_2 gasified the cypress char completely at 750 ℃, with the PSK ash existence. Activation at lower temperature of 600 ℃ was conducted. At this condition, activation of CO_2 was not confirmed; the specific surface area was as small as 56% of that obtained in pure N_2 stream. The micro pore distribution also shows a relatively low level in Fig. 5. The contrastive image of hollow structure was also confirmed by SEM. It is considered that rather than activation, CO_2 gas reacts with a part of char micro structure, so that lower surface area and lower pore distribution in the CO_2 treated char [8]-[10]. Further research is required to investigate the optimum activation conditions. By contrast, steam gave a remarked promotion on the char porous structure formation. Higher surface area of 1668.1 m^2 g^{-1} was achieved, which is as much as 1.46 times of the 600 ℃ cypress char under N_2. Micro pores larger than 0.3 nm were greatly generated by steam, in Fig.5.

3.4. Effect of Carbonization Temperature on the Pore Structure of Cypress Char

Adsorption capacity for the produced cypress char samples was measured via the adsorption of iodine (I_2) from its aqueous solution, based on Japan Industry Standard method (JIS K-1474). The prepared 750 ℃ char (with a specific surface area of 1678 m^2g^{-1}) was confirmed having a high I_2 adsorption capacity of 1443 mg-I_2 /g-char. That is a high level adsorption for activated carbon.

4. Conclusions

PSK ash promoted cypress carbonation and high specific surface area chars were obtained. The char activation depended on the carbonation temperature and 750 ℃ was confirmed as an optimum temperature in nitrogen stream. Activation gases of CO_2 and steam introduction decreased the optimum activation temperature. Porous char was obtained at 600 ℃ with steam activation. By contract, CO_2 reacted with carbon and lower specific surface area structure was confirmed under the condition in this study. The produced cypress char also showed an excellent adsorptive capacity for I_2 from the I_2 aqueous solution

5. References

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