

Preparation of Activated Carbon Using Bio-Oil Phenol-Formaldehyde Resin

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High-specific surface area activated carbon with distinct pore texture was prepared using bio-oil phenol-formaldehyde (BPF) resin as the raw material and KOH as the activator for chemical activation. The carbonization process was characterized with thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The pore texture was characterized with measurements obtained by N₂ adsorption analysis and scanning electron microscopy (SEM). It was found that adding bio-oil to phenol-formaldehyde resin can partly enhance the thermal stability and improve the textural properties of activated carbon. The functional groups of BPF resin gradually disappeared in the carbonization reaction with increasing temperature. The activated carbon prepared by BPF resin with 30%wt bio-oil exhibited the optimal performance.

Keywords: Bio-oil; PF resin; Activated carbon; KOH activation

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INTRODUCTION

Phenol-formaldehyde (PF) resin is widely used in the preparation of activated carbon because of its pure components and easy activation. Resol PF resin is prepared using a formaldehyde-to-phenol molar ratio above 1 and an alkali as catalyzer, which is a common material for activated carbon (Pizzi and Stephanou 1993). There are many activation methods to activate carbonized PF resin, but chemical methods still have a wide range of applications in industrial production. Chemical activation results in low reaction temperatures, simple reaction steps, and high efficiency compared with other methods.

With changing requirements, finding renewable-based materials and enhancing the percentages of mesopores are becoming new subjects in the production of activated carbon. Activated carbon made from PF resin by chemical activation has many micropores, but fewer mesopores, which limits its application (Balathanigaimani *et al.* 2008; Olivares *et al.* 2009). Because micropores are limited in carbonized PF resin, mesopores cannot be formed by activator-enlargement of micropores. Many efforts have been made to resolve this problem, for example by increasing the amount of activator or by reactivation after pre-activation (Juarez-Galan *et al.* 2009; Xing *et al.* 2009). However, considering the possibility for severe environmental contamination, serious equipment corrosion, and the high price of the above methods, there is an urgent need to explore new approaches.

Bio-oil obtained by fast pyrolysis of renewable biomass has abundant amounts of phenols (Kawser and Farid 2000; Oasmaa and Meier 2005). Extensive studies have been conducted concerning the preparation of bio-oil phenol-formaldehyde (BPF) resin (Amen-Chen *et al.* 2002a,b,c; Zheng and Chang 2007; Liu *et al.* 2014). Earlier literature indicates that using bio-oil as a phenol substitute in the synthesis of PF resin is feasible and that the chemical and physical properties of BPF resin are very similar to commercial PF resin, but with a lower cost (Kelley *et al.* 1997; Gagnon *et al.* 2004). Bio-oil contains a certain amount of small-molecule carbohydrates and tiny particle carbides, which contribute to the increasing number of micropores. In addition, the excellent thermostability of bio-oil is beneficial in enhancing the quantity of residual substances during the carbonization of PF resin.

The objective of this study was to develop a high-specific surface area activated carbon by chemical activation, using BPF resin as the raw material and KOH as an activator. The variation in quantity loss and functional groups of the resin during the carbonization process were examined by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR), while the pore structure and surface area of carbon were detected using N₂ adsorption analysis and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Bio-oil from fast pyrolysis of pine sawdust was supplied by the Institute of Wood Based Material, Beijing Forestry University, China. The bio-oil had a pH value of 3.5 and was composed of 22% phenolic compounds, 30% water, 15% organic acids, and 33% other compounds, including sugars, esters, and ketones (Fan *et al.* 2010).

Other raw materials used in the activated carbon preparation included the following: phenol (reagent-grade product supplied by Zhuoxin Chemical Industries, Beijing, China); formaldehyde aqueous solution (37% industrial-grade product supplied by Xilong Chemical Industries, Guangdong, China); sodium hydroxide (NaOH) (reagent-grade product supplied by Xilong Chemical Industries, Guangdong, China); potassium hydroxide (KOH) (reagent-grade product supplied by Xilong Chemical Industries, Guangdong, China); hydrochloric acid (1.19 g/mL reagent-grade product supplied by Guoyao Chemical Industries, Beijing, China); and distilled water (reagent-grade product supplied by Qianjing Chemical Industries, Guangdong, China).

Methods

Preparation of BPF resin

BPF resins, with bio-oil amounts of 0, 15, 30, and 45% wt. (% wt. of phenol), were synthesized using a special procedure, which called for adding the materials twice. The first batch of formaldehyde (80% of the total) and NaOH (80% of the total) was added to phenol in a four-necked flask and then blended for 10 min. The mixture was heated to 90 °C within 30 min, and the temperature was held for 30 min. Subsequently, bio-oil was added to the reaction system at 85 °C for 30min. After this, the second batch

of formaldehyde (20% of the total) and NaOH (20% of the total) was added. The reaction was maintained at 85 °C for 30 min, followed by a temperature decrease to 70 °C for 20 min. Finally, the prepared resin was cooled to room temperature.

All of the resins had a final formaldehyde-to-phenol (F/P) molar ratio of 2:1. The synthesized BPF resins were designated PF, BPF - 15%, BPF - 30%, and BPF - 45%.

Preparation of BPF resin-based activated carbon

The BPF resin was solidified at 150 °C and prepared for 1 to 1.5-mm-diameter particles. Subsequently, particles were pyrolysed at 600 °C in nitrogen gas for 40 min carbonization, with a heating rate of 5 °C per min. After carbonization, resin was cooled and mixed together with KOH at a ratio of 3:1. Then, the mixture was activated at 850 °C with a heating rate of 5 °C per min for 2 h under nitrogen gas flow of 200 mL per min. After cooling to room temperature, the pH value was adjusted to 6.5 to 7.5 using 1.19 g/mL hydrochloric acid. The activated carbon was obtained after the removal of impurities using a rinsing and drying process.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out with the TG-400 (PerkinElmer, Waltham, MA). Specimens were placed in alumina crucibles and heated to 800 °C at a heating rate of 10 °C per min. The atmosphere used for pyrolysis was nitrogen gas at a flow rate of 35 mL per min.

N₂ adsorption analysis

A Quadrasorb SI surface area analyzer (Quantachrome, Boynton Beach, FL) was used to measure the N₂ adsorption volume. Respectively, according to the adsorption isotherms, the specific surface area, mesopore surface area, and pore size distribution were calculated according to the BET, V-t, and BJH systems (Lowell and Shields 1991).

Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared spectroscopy, in absorbance mode, was used to characterize the functional groups in the resins, as affected by the carbonization reaction. A Bruker Vertex 70 Fourier transform IR spectrometer (Bruker, Karlsruhe, Baden Wurttemberg, Germany) was used to determine the spectra. The spectra that were obtained ranged from 4000 to 400 cm⁻¹, with a resolution of 4 cm⁻¹ and 32 scans.

Scanning electron microscope (SEM)

The microstructure of the activated carbons was observed using a QUANTA-200 SEM (FEI, Hillsboro, OR) at an accelerating voltage of 5000 V.

RESULTS AND DISCUSSION

TGA Analysis

The TGA curves of PF and BPF resins are displayed in Fig. 1. All the curves presented three separate degradation stages. The first stage was observed in the

temperature range of 40 to 300 °C. The loss of weight consisted of the loss of water and small molecular substances. The water was present either because of the quantity added during the synthesis of the resin or as a result of condensation reactions. Aldehydes and hydrocarbons constituted the major part of the small molecular substances (Xu *et al.* 2008). The second stage demonstrated a significant loss of weight, which occurred in the temperature range of 300 to 600 °C. A series of chemical and physical reactions took place that resulted in the removal of functional groups (*e.g.*, C=O and CH₃) and the release of gaseous substances (*e.g.*, CO, CH₄, and H₂) (Meng *et al.* 2006). The final stage produced further carbonization and structural rearrangement and was observed in the temperature range of 600 to 800 °C. There was less weight loss in this stage; however, during the carbonization process, many micropores were formed because of the release of thermal energy, which came from cracking and condensation reactions.

Compared to PF resins, the weight loss of BPF resins was higher in the first stage and lower in the later stages. The small molecule carbohydrates and tiny particle carbides, rich in bio-oil, were easily heated to volatilize in a low temperature range, which corresponded to the first stage. There was less weight loss of BPF resins in the later stages, as bio-oil caused the system to form more crosslinking structures. The crosslinking structures were able to improve the thermal stability of PF resin and increase the output of activated carbon.

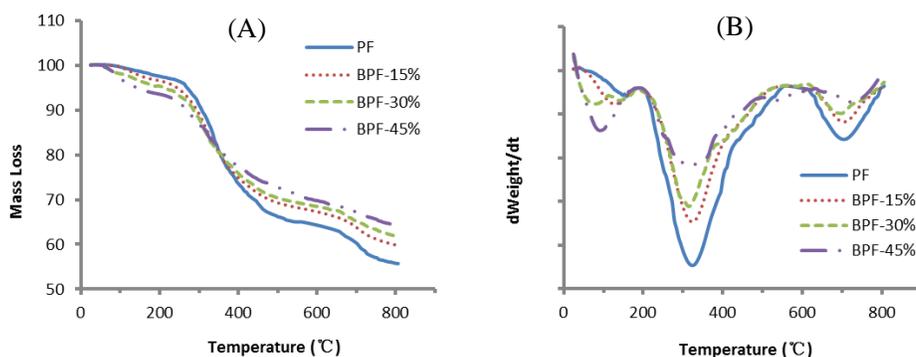


Fig. 1. (A) Thermogravimetric curves of BPF resins and (B) corresponding derivative curves

N₂ Adsorption Analysis

Figure 2 (A) shows different N₂ adsorption isotherms of BPF resin based on the activated carbons prepared using different concentrations of bio-oil. The four samples demonstrated the typical characteristics of I-type and IV-type adsorption isotherms. The adsorption isotherms of all samples exhibited a large amount of adsorption, which indicated that there were numerous micropores in the activated carbons at a low relative pressure. With increasing relative pressure, the increasing trend of the adsorption isotherms gradually slowed and tended to level out. When the relative pressure was high, the adsorption isotherms of the samples, especially BPF-30%, exhibited a sharply upturned appearance, which indicated the existence of mesopores. The figure also showed a trend whereby the adsorption capacity of the samples first increased and then decreased with increasing ratio of bio-oil. This means that adding bio-oil to PF resin is

beneficial for forming pores in the preparation process. On the other hand, excess bio-oil will result in a decrease in the number of pores. When the ratio of bio-oil increased to 30%, the adsorption capacity was larger than it was with the other ratios.

The pore size distribution is shown in Fig. 2 (B). According to IUPAC classification, pores can be divided by diameter into micropores (pore diameter less than 2 nm), mesopores (pore diameter between 2 and 50 nm), and macropores (pore diameter greater than 50 nm). The mesopore distribution first increased and then decreased with increasing ratio of bio-oil; however, the micropore distribution showed an inverse trend. The number of mesopores reached a maximum when the ratio of bio-oil was 30%. It can be inferred that adding bio-oil had a direct impact on the pore size distribution. More noteworthy was the appearance of a large number of mesopores, which provided the exact conditions necessary for this kind of activated carbon to have applications in adsorbing material, catalyst carrier, template, and nanoreactor.

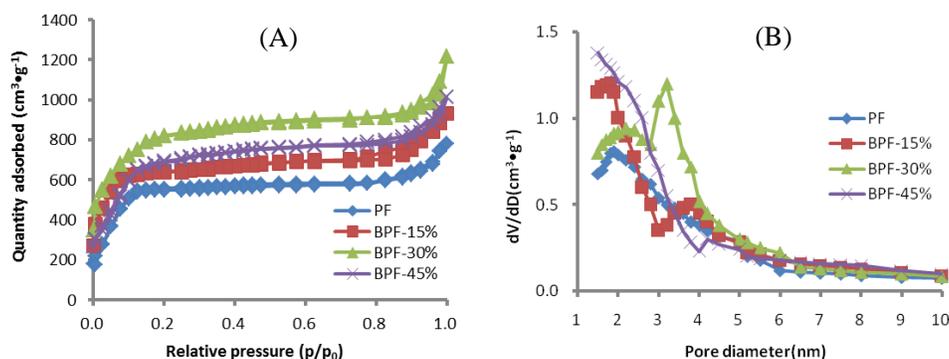


Fig. 2. (A) N₂ adsorption-desorption isotherms and (B) pore size distribution of the samples

Textural parameters of activated carbon according to different ratios of bio-oil are shown in Table 1. Bio-oil has a strong effect on the structural properties of activated carbons. As shown in the table, specific surface area, mesopore surface, and volume of samples exhibited a trend that first increased and then decreased with increasing ratio of bio-oil. The parameters reached a maximum when activated carbon was prepared using BPF-30% resin. The result coincides exactly with the adsorption isotherms and pore size distribution.

Table 1. Textural Parameters of Activated Carbon Prepared with BPF Resin

Samples	S_{BET} (m ² /g)	S_{meso} (m ² /g)	V_{tot} (cm ³ /g)	V_{meso} (cm ³ /g)	$V_{\text{meso}}/V_{\text{tot}}$ (%)	D (nm)
PF	1685.3	213.5	0.95	0.13	0.14	1.89
BPF-15%	2042.6	624.7	1.31	0.29	0.22	2.31
BPF-30%	2335.4	948.3	1.58	0.52	0.33	2.92
BPF-45%	1983.2	735.5	1.18	0.21	0.18	2.12

The small molecule carbohydrates and tiny particle carbides, rich in bio-oil, are easily heated to volatilize in carbonization reactions, which favors the formation of micropores in resin. During the activation reaction, KOH not only activates micropores; it also enlarges them. As a consequence, mesopores are formed and the surface area is enhanced. However, the ratio phenol/formaldehyde has been altered by bio-oil in BPF resin. If too much bio-oil is added, the composition of the resultant resin starts to harm the activation process. That is why an excess ratio of bio-oil decreases the number of pores.

FTIR Analysis

FTIR spectroscopy was used to show the change in functional groups in the BPF-30% resins during the carbonization process (Fig. 3). The absorption peak at 3020 to 3671 cm^{-1} can be assigned to the OH stretching modes (Hernandez-Padron *et al.* 2003; Monni *et al.* 2008). The characteristic absorption peaks in this region were sharp, demonstrating the presence of numerous OH groups in the BPF-30% resin. The absorption bands appearing at 2900 cm^{-1} were because of the asymmetric and symmetric stretching vibration of CH_2 groups. The absorption bands at 1600 to 1450 cm^{-1} were because of the vibration of $\text{C}=\text{C}$ groups in benzene rings, which indicated that phenols were richer in the BPF-30% resin. The absorption bands at 1166 to 1230 cm^{-1} resulted from the stretching vibrations of C-OH groups. The absorption peaks at 1060 cm^{-1} can be attributed to the vibrations of CH_2 -OH groups. The absorption peaks at 779 cm^{-1} resulted from the bending vibrations of C-H groups in benzene rings.

When the carbonization temperature reached 300 °C, an obvious reduction in the absorption bands at 1000 to 1800 cm^{-1} caused by the loss of C-OH and $\text{C}=\text{C}$ groups was evident. This result agreed well with the TGA analysis; the weight loss consisted of water and small molecular substances in the range of 40 to 300 °C.

After reaching 600 °C, almost all the absorption peaks were weak, especially for groups of OH and CH_2 . Methylenes had begun to break away from benzene rings, and gaseous substances (*e.g.*, CO, CH_4 , and H_2) were released. This result also corresponded with the TGA analysis.

At 700 °C or above, the absorption peaks practically vanished. This suggests that the functional groups in the resin had disappeared. At this temperature, KOH reacted with the functional groups to form or enlarge pores; however, it is harmful for the activation reaction if the carbonization temperature becomes exceedingly high.

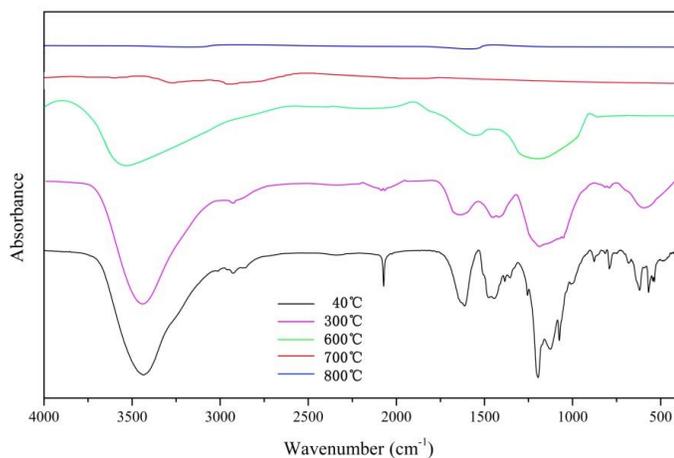


Fig. 3. FTIR spectra of BPF-30% resins

SEM Analysis

Figure 4 shows SEM images of the activated carbon prepared from PF resin and BPF-30% resin. The surface shape of PF-based activated carbon was uneven, and a few pores were discovered. Relatively more pores were seen in BPF-30% based activated carbon, and even a honeycomb structure was visualized. These results mean that BPF-30% based activated carbon may cause more efficient adsorption; by adding bio-oil, the pore texture of PF-based activated carbon can be improved.

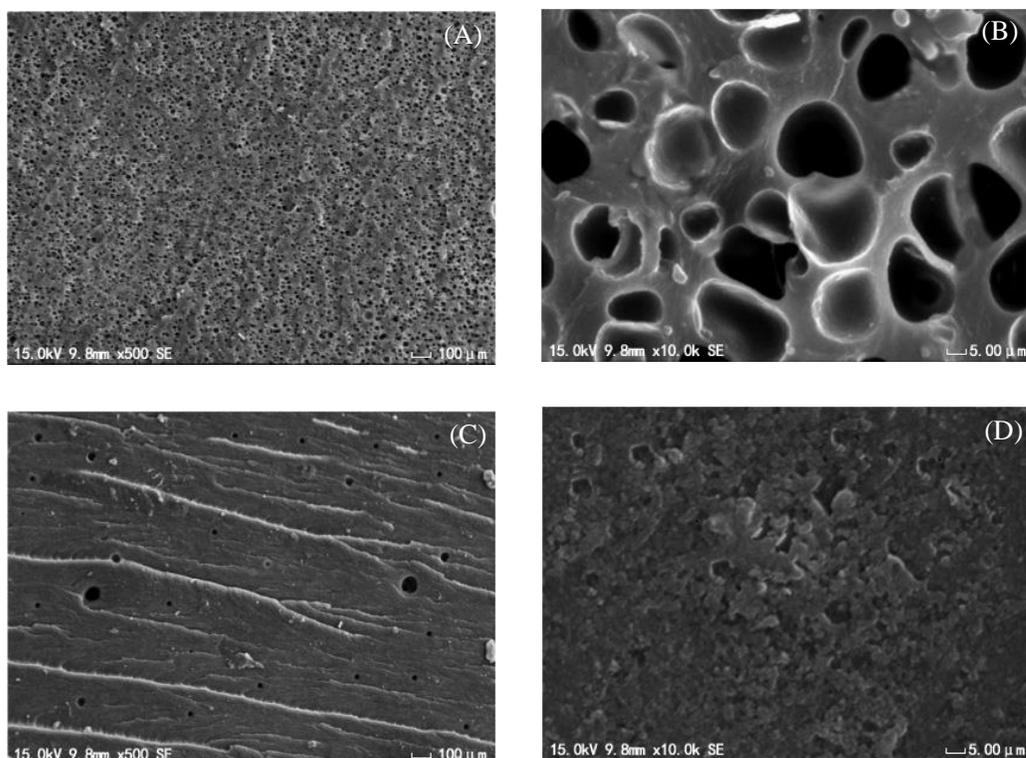


Fig. 4. (A,B) SEM images of porous carbon prepared from BPF resin and (C,D) porous carbon from PF resin

CONCLUSIONS

1. BPF resin can be used to prepare activated carbon by KOH activation. Adding bio-oil to PF resin can partly enhance the thermal stability of resins and improve the textural properties of activated carbon.
2. The textural parameters of activated carbon prepared by BPF resin first increase and then decrease with increasing ratio of bio-oil. More mesopores were formed as a result of using bio-oil.
3. With the carbonization temperature rising, the absorption peaks of functional groups in BPF resin gradually vanished. Carbonization temperatures that are too high can negatively affect the activation reaction.

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