Catalytic Upgrading of Coal Pyrolysis Volatiles by Porous Carbon Materials Derived from the Blend of Biochar and Coal

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ABSTRACT: A suite of carbon materials is prepared from biochar and coal at three different blending ratios with 10, 20, and 30% biochar by mass. These carbon materials are activated by steam to obtain porous structures. The effect of the inactivated and activated carbon materials on the cracking of coal pyrolysis volatiles is evaluated. The results indicate that the inactivated carbon materials are beneficial to improve the yield of light oil with a boiling point below 170 °C. The steam-activated carbon materials are more conducive to cracking tar pitch than the inactivated carbon materials due to the increased defects in carbon structure. However, it is also easy to form more coke deposits. More components rich in hydrogen are cracked to generate radicals that could combine with the phenols' precursor over carbon materials, and the content of phenols in tar is increased. The carbon materials prepared from biochar and coal using this method show distinct advantages as filter media in the granular bed duster. It can improve the quality of tar along with reducing the dust content in tar.

1. INTRODUCTION

Low-rank coal contains a high content of volatiles that can be easily decomposed and released in the form of tar and gas during pyrolysis. Low-temperature pyrolysis of low-rank coal can extract tar that can be converted into high value-added liquid fuels and chemicals. Thus, the development of low-temperature coal pyrolysis technology is a key for the efficient conversion and utilization of low-rank coal. In practice, a volatile is easy to entrain along with dust during low-temperature pyrolysis, which is believed to cause blockade of the pipelines and increase the dust content in tar. For example, when the pulverized coal is used as the raw material, the fine coke powder and coal ash particles will precipitate out with the pyrolysis volatiles, which thus results in higher dust content in the tar. A solid material such as ash or char is used as a heat carrier to provide sensible heat in the Garrett, Lurgi—Ruhrgas (L-R), and Dalian University of Technology (DG) pyrolysis system. The solid heat carrier can be easily carried out by volatiles during pyrolysis, which also increases the dust content in tar. Furthermore, the pitch in tar is easy to condense to form coke in the pipeline, and it will also increase the difficulty of separating the dust from the tar. These factors will potentially increase the blockage of the product line and affect the stable operation of the pyrolysis system. To reduce the impact of dust and tar pitch in the pipeline, one of the promising methods is to employ the granular bed duster. The carbon material can be applied as the filter media in the granular bed duster, which can significantly affect the efficiency of dust removal. Qu et al. suggested that char can effectively control the content of fine particles in tar. Furthermore, the carbon material also plays a significant role in the catalytic upgrading of coal pyrolysis volatiles. Jin et al. studied the in situ catalysis of two carbon-based catalysts on coal pyrolysis volatiles, one char was prepared by pyrolysis of Shennu coal in a fixed bed reactor, and the other was a commercial activated carbon originated from coconut shells. Both materials reduced the content of heavy tar and increased the content of light tar with a boiling point below 360 °C. Compared with a char catalyst, activated carbon showed much better catalytic performance. Fu et al. discussed the effect of preparation temperature and the method of straw char on the upgrading of lignite pyrolysis volatiles. The results showed that char prepared by fast pyrolysis had a larger specific surface area and more active sites. Also, it had much better catalytic cracking characteristics than the char prepared by slow pyrolysis. The improvement of coal tar quality was mainly attributed to the catalytic conversion of heavy components in coal tar, especially pitch, into light tar and gas. The fraction of tar that can be soluble in n-hexane is increased by 30.31%. Kawabata et al. developed a circulating fluidized bed (CFB) reactor consisting of a pyrolysis reactor and a combustion reactor in which lighter components in tar formed by enhancing the contact time of tar and char during pyrolysis. Zeng et al. studied the role of a char catalyst in a two-stage
fluidized bed. More light components in tar were observed in the presence of a char catalyst, and the polymerization reaction was strongly compressed.

Based on the discussion above, the carbon material filled in the granular bed duster has the advantage of removal of dust in tar and catalytic upgrading of tar. This paper presents a simple and feasible novel method of preparing a carbon material by heating the blend of biochar and coal. As an environmentally friendly material with inherent alkali and alkaline earth metals (AAEMs), carbon materials are easily obtained from the pyrolysis of coal or biomass at a low cost. It is expected that the prepared carbon material can be used as the filter media in the granular bed duster to decrease the content of dust in tar and simultaneously help the catalytic upgrading of coal pyrolysis volatiles. In this study, the catalytic upgrading of prepared carbon materials on volatiles will be discussed in detail. The expected results will provide theoretical support for regulating the distribution of pyrolysis products and enhancing a scientific understanding of the development of composite dust removal technology.

2. EXPERIMENTAL SECTION

2.1. Samples. The samples used in this paper include a Naomaohu (NMH) long flame coal with high volatiles, a Malan (ML) fat coal that is rich in metaplast, a corn cob biomass (COB), and its corn cob biochar (COBC). Table 1 shows the proximate and ultimate analysis of these samples. The particle size of the NMH coal used in the experiments was 0.25–0.43 mm, and the coal sample was dried in a vacuum oven at 105 °C for 12 h before the experiments.

2.2. Preparation of the Carbon Materials. The carbon materials were prepared by coking the blend of biochar and coal, and the steps are shown in Figure 1. COBC was prepared by pyrolysis of COB in a muffle furnace with a cover from room temperature to 650 °C at 10 °C/min, and the holding time at the final temperature was 1 h. The COBC with particle size less than 0.60 mm and the ML coal with particle size less than 3 mm were mixed with various ratios of 1:9, 2:8, and 3:7 by mass at a stirring kneader for 30 min. The carbon material was prepared by heating the homogeneously mixed samples to a temperature of 950 °C in a muffle furnace with a cover at a heating rate of 3 °C/min, and the holding time at the final temperature was 1 h. Due to the fat coal’s special property (metaplast will be generated during pyrolysis), biochar and fat coal were blended and bonded into a lump carbon material after being heated at 950 °C. The lump carbon material was crushed and sieved to 3.00–4.00 mm. Then, the particles with 3.00–4.00 mm were carbonized at 950 °C for 30 min in a fixed bed reactor with a flow rate of N2 at 1600 mL/min. The carbonized carbon material (BC) samples are named as 10%BC, 20%BC, and 30%BC according to different COBC ratios. Based on the carbonization conditions, these prepared carbon materials were activated under 50% steam and 50% N2 for 70 min at 950 °C to increase the active sites and pores. Correspondingly, the activated carbon materials (BHC) are named as 10%BHC, 20%BHC, and 30%BHC, respectively.

The formation mechanism of the carbon materials is shown in Figure 2. According to Table 1, the volatile content of COB is up to 80.83 wt %, which could generate a large number of bubbles and form weak chars with large pores. Thus, the biomass samples were processed to reduce the content of volatiles before blending with coal. The processed biomass char named COBC only contains 6.06 wt % volatiles, which provides the opportunity to combine the softening coal to form carbon materials with high strength. When the COBC and the ML coal are blended, coal initiates softening to combine with the COBC to form the metaplast that expands and forms bubbles. As bubbles move, merge, and escape, the metaplast solidify to form char. At a higher temperature, carbon materials are formed along with the shrinkage of char. Previous studies have suggested that carbon components that are originated from biomass char are more preferentially activated than those from coal char. Therefore, it is expected that the corresponding pore structure for the carbon material

| sample | proximate analysis (wt %) | ultimate analysis (wt %, daf) |
|--------|-------------------------|-----------------------------|
|        | Md | Ad | Vdaf | C | H | N | S | O* |
| NMH    | 19.5 | 5.8 | 50.12 | 74.35 | 5.13 | 0.72 | 0.31 | 19.49 |
| ML     | 0.52 | 9.66 | 23.45 | 89.86 | 4.98 | 1.56 | 1.12 | 2.48 |
| COB    | 1.57 | 2.61 | 80.83 | 44.69 | 5.44 | 0.57 | 0.08 | 49.22 |
| COBC   | 2.88 | 6.20 | 6.06 | 76.12 | 1.21 | 0.31 | 0.07 | 22.29 |

*Ad, air-dried basis; d, dry basis; daf, dry and ash-free basis; *, by difference.
prepared from the blends of biochar and coal is also enhanced. The prepared carbon material is expected to meet the various requirements of different components in coal tars for catalytic upgrading.

2.3. Characterization of the Carbon Materials. N2 adsorption of the carbon materials was measured on a physical adsorption apparatus (ASAP 2460, Micromeritics, US) at \(-196^\circ\text{C}\). The samples were pretreated at 300 \(^\circ\text{C}\) for 6 h in vacuum before adsorption. The parameters of the specific surface and pore structure were analyzed by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The carbon structural features of carbon materials were determined by a Renishaw inVia micro-Raman spectrometer (RENISHAW, LTD, UK) equipped with an excitation laser at 514 nm. The laser was focused to about 2 \(\mu\text{m}\) in diameter at a power of 2 mW. The recorded Raman spectra were from 800 to 1800 cm\(^{-1}\). A scanning electron microscope (Hitachi SU8010, Japan) was operated at 3 kV, and a transmission electron microscope (Tecnai G2 F20 S-Twin, FEI, US) was operated at 200 kV for local characterization of the carbon materials.

2.4. Pyrolysis Equipment and Experimental Procedures. To investigate the effect of different carbon materials on the catalytic cracking and carbon deposition of NMH coal pyrolysis volatiles, quartz beads (QB), BC, BHC, commercial coal-based activated carbon (AC-1), and commercial coconut shell activated carbon (AC-2) with a particle size of 3.00–4.00 mm were subjected to pyrolysis experiments. Figure 3 shows the schematic diagram of the experimental apparatus in this study. The device contains a self-designed low-rank coal pyrolysis-char collection section reactor. The unit is mainly composed of a feeder (1), a reactor (2), heating systems (3 and 7), condensing systems (8, 9, 10, 11, and 12), and a gas analysis system (17). The reaction tube is made of quartz with a total height of 2450 mm. The reactor is composed of the upper pyrolysis section with a length of 1677 mm, the lower char collection section with a length of 773 mm, and the horizontal section with a length of 690 mm for studying the reaction of volatiles. All reactors’ inner diameters are 20 mm.

Oxygen will be introduced to ensure that the wall of the reactor is clean before the experiment. The prepared carbon material (60 mL) was placed in the horizontal volatile reaction section with a bed length of about 115 mm before each experiment. N2 was used as the carrier gas. The temperature of the pyrolysis section was set to 600 \(^\circ\text{C}\), and the temperature of the volatile reaction section was set to 500 \(^\circ\text{C}\), which matches the industrial temperatures. To prevent the condensation of pyrolysis volatiles, the temperature of the char collection section was set to 300 \(^\circ\text{C}\). The flow rate of N2 was 2050 mL/min. When the N2 flow was stable and the temperature of each section reached the set value, 100 g of NMH coal was continuously fed through the feeder at a feeding rate of 1.0 g/min, and the feeding time of each experiment lasted for 100 min to ensure the stable operation of the device. The total flow of pyrolysis gas was detected by a wet flow meter (14) to ensure the accuracy of the experiment. Pyrolysis gases passed through a cotton filter (13), a high molecular cellulose filter (15), and a desiccant (16) before they were analyzed by a Raman laser gas analyzer. Tar in the pyrolysis products was collected by the condensing system. After each test, all pipelines and absorption bottles were washed with THF several times to recover the tar. The reactor with carbon deposits was heated to 600 \(^\circ\text{C}\) at a heating rate of 10 \(^\circ\text{C}/\text{min}\) under a mixed gas of O2 and N2, during which CO and CO2 were produced and detected by a Raman laser gas analyzer. The quantity of CO and CO2 was calibrated by integration, and the weight of C in CO and CO2 was defined as Coke-D. The solid product char was taken out of the lower section of the reactor to calculate the product yield.

2.5. Analysis and Characterization of Pyrolysis Products. The pyrolysis gas was analyzed by a Raman laser gas analyzer (RLGA-2811, ARI, US) that could detect N2, O2, CO, CO2, H2, CH4, C2H6, and C3H8. The RLGA was calibrated with standard gases before the experiments to ensure the deviation was within 0.25%. The THF-insoluble substances in liquid products (tar) were filtered by using a 0.45 \(\mu\text{m}\) organic filtration membrane (JINTENG, CHN), and the filtered product was named Coke-S. The carbon deposit in the carbon material was named Coke-C, and it was calculated from the mass difference of the carbon material before and after each experiment. The filtered liquid was treated by anhydrous magnesium sulfate to remove water. Tar solution (2 mL) was placed in a Petri dish to calculate the content of the soluble tar after allowing the THF to completely vaporize from the Petri dish. The yields of gas, tar, water, char, and carbon deposits (coke) were calculated based on the drying base of the NMH coal. The yield of coke was the sum of the yield of Coke-D, Coke-S, and Coke-C.

A simulated distillation gas chromatograph (Agilent 7890B, US) was used to analyze the fraction of coal tar according to the boiling point. Tar was divided into light oil (<170 \(^\circ\text{C}\)), phenol oil (170–210 \(^\circ\text{C}\)), naphthalene oil (210–230 \(^\circ\text{C}\)), washing oil (230–300 \(^\circ\text{C}\)), anthracene oil (300–360 \(^\circ\text{C}\)), and pitch (>360 \(^\circ\text{C}\)). Fractions with boiling points of below 360 \(^\circ\text{C}\) were defined as light tar. The chemical compositions of tar were analyzed by GC×GC–MS that includes an Agilent 7890B gas chromatograph, a ZX-2 thermal modulator (Zoex, US) connecting two chromatography columns (DB-1 MS and BPX-50 MS), and an Agilent 5977A MSD mass spectrometer (US). The column oven temperature was set from 70 to 300

![Figure 3. Schematic diagram of the experimental apparatus.](https://example.com/figure3.png)
°C at a heating rate of 3 °C/min. In the modulator, the hot jet temperature was set from 280 to 300 °C at a heating rate of 15 °C/min, and the cool jet temperature was maintained at −80 °C. Tar was divided into aliphatic hydrocarbons, aromatic hydrocarbons, phenolic compounds, oxygen-containing compounds, and heterocyclic compounds containing N and S.

3. RESULTS AND DISCUSSION

3.1. Effects of Carbon Materials on the Distribution of Pyrolysis Products and Carbon Deposition. The long residence time could promote the reaction of volatiles, which thus intensifies the polymerization reaction of the free radicals in tar and results in a higher coke yield.

To keep consistent residence time for the volatiles in the horizontal tube, the pyrolysis experiment under the inert material quartz beads was carried out as a blank experiment. Figure 4 shows the yield of pyrolysis products under QB and different carbon materials. It can be seen that the content of biochar and the activation of the carbon material have a significant effect on the distribution of pyrolysis products. Compared with QB, the tar yields under 10%BC and 30%BC are slightly reduced. Meanwhile, the 20% BC leads to the highest tar yield but a lower gas yield. After BC is activated, 10%BHC, 20%BHC, and 30%BHC can significantly decrease the tar yield but increase the coke yield. Also, the activation effect on the distribution of pyrolysis products becomes much clearer for the carbon material with a higher biochar content.

Carbon materials could catalyze the decomposition of hydrocarbons by cracking C–C and C–H bonds. The activated carbon material increased the catalytic reactivity related to the heterogeneous cracking and repolymerization of volatiles. This could be attributed to the variation in physical and chemical structures, such as pore structure, carbon structure, AAEM distribution, and the number of active oxygen-containing functional groups of the carbon materials during activation.

The carbon structure of biochar is more disorderly and supplies more active sites to participate in the catalytic reforming reaction to crack tar molecules than coal char. With the increase in biochar in the activated carbon materials, the tar yield decreases significantly. Also, it will convert into water, gas, and coke, which indicates that the content of biochar plays an important role in the catalytic cracking performance of volatiles. Furthermore, the prepared carbon material not only improves the catalytic cracking activity of tar but also shows high strength as filter media for the granular bed duster. The strength of fat coal char prepared at 950 °C is quite high.

Figure 5 shows the distribution of different types of coke depositions under the action of QB and carbon materials. The yields of Coke-C, Coke-D, and Coke-S are all affected by the carbon materials. Compared with QB, the carbon material increases the yield of Coke-C, and a significant increase is observed when the prepared carbon material is activated. The yield of Coke-C is also related to the content of biochar, and a dramatic increase is observed for the activated carbon material containing 30% biochar. This could be related to the larger specific surface area for the activated carbon material that is conducive to adsorbing tar molecules on the active site. Therefore, more Coke-C is formed on the surface of activated carbon materials through a series of dehydrogenation, cyclization, and condensation reactions of tar molecules.

Another observation is that the yield of Coke-S seems to decrease with the increasing content of biochar in the carbon material. Coke-S is obtained by filtering THF solution dissolving coal tar using an organic filtration membrane with pores of 0.45 μm; therefore, all particles with less than 0.45 μm are included in Coke-S that may contain coal, char, dust, and coke originated from volatiles’ reaction. This shows that the dust content in tar is significantly reduced after adding filter media. Also, the activated carbon material tends to result in a lower yield of Coke-S than the inactivated ones. The effect of the activated carbon material is stronger than that of the inactivated carbon material.

3.2. Influence of Carbon Materials on the Quality of Tar. Compared with QB, the yield of light oil increases from 2.37 to 2.58, 4.75, and 3.04 wt % under 10%BC, 20%BC, and 30%BC, respectively, as shown in Figure 6. These results indicate that the BC is conducive to cracking the heavier components in tar and improving the yield of light oil with a boiling point below 170 °C. The yield of each fraction in tar is reduced by the activated carbon material, particularly, for the carbon materials with high biochar content, such as 20%BHC and 30%BHC. For these two carbon materials, the yields of light oil, phenol oil, and naphthalene oil decrease slightly, while the yields of washing oil, anthracene oil, and pitch decrease significantly. The yield of anthracene oil decreases by 0.66 and 0.77 wt %, the yield of washing oil decreases by 0.54 and 0.71

Figure 4. Distribution of pyrolysis products of NMH coal under QB and different carbon materials.

Figure 5. Distribution of different types of coke depositions under QB and different carbon materials.
wt %, and the yield of pitch decreases by 2.20 and 2.42 wt %, respectively. The yield of light tar with a boiling point below 360 °C increases by 1.14 wt %, and the yield of heavy tar pitch decreases by 0.77 wt % over 20%BC, as can be seen in Figure 7. Overall, the carbon material reduces the yield of both light tar and heavy tar, and this trend is particularly clear for the activated carbon material. In terms of tar with different boiling points, Figure 7 also indicates that heavy tar shows a larger cracking ratio than light tar. Compared with the content of pitch obtained by QB, the cracking ratio of pitch under the action of inactivated carbon materials can reach 17.6%, while it is above 50% for the activated carbon materials. However, it leads to a significant decrease in tar yield.

3.3. Influence of Carbon Materials on Compositions of Tar and Gas. There are significant differences in coal tar compositions under the action of carbon materials in Figure S1. By classification of compounds in tar, the compositions of tars are shown in Figure 8. Also, the carbon material can significantly affect the chemical compositions of tar. Compared with QB, all carbon materials increase the content of phenolic compounds but reduce the content of aromatic hydrocarbon compounds, oxygen-containing compounds, and heterocyclic compounds containing N and S. The content of oxygen-containing compounds decreases by 5.42, 4.63, 4.76, 11.07, 10.18, and 10.41% under 10%BC, 20%BC, 30%BC, 10%BHC, 20%BHC, and 30%BHC, respectively. The BHC carbon materials result in the most distinct decrease of the oxygen-containing compounds. Zhang et al.27 suggested that the activated carbon material may possess a certain amount of oxygen-containing groups after activation by steam; some acidic centers are formed on the carbon surface, and it will promote the cracking of oxygen-containing compounds. The dissociation energy of $\text{C}_n\text{H}_m\text{C}_l\text{O}$ existing in NMH coal is lower than those of other bonds in volatiles, such as $\text{C}_n\text{H}_m\text{C}_l$ and $\text{C}_n\text{H}_m\text{C}_l\text{C}_l$, so the content of oxygen-containing compounds is significantly reduced.

For both the activated and inactivated carbon materials, the content of phenolic compounds increases with the ratios of biochar. The contents of phenolic compounds under 10%BC, 20%BC, 30%BC, 10%BHC, 20%BHC, and 30%BHC increase by 17.22, 23.70, 30.01, 16.77, 28.27, and 29.51%, respectively. It indicates that the carbon materials have good selectivity for the formation of phenolic compounds. The carbon materials can increase the amount of the one ring and two rings of phenols, shown in Figure 9. However, a more significant increase is observed for the monocyclic phenolic compound. Also, it can be seen that a higher content of biochar in the carbon material promotes a higher amount of monocyclic phenols. There are abundant phenoxy groups in pyrolysis tar, which connect to the macromolecular part through the C−O bond. The C−O bond may crack during pyrolysis and form free radical molecular fragments, and then, phenolic com-

![Figure 6](https://example.com/figure6.png) Yield of fractions in tar under QB and different carbon materials.

![Figure 7](https://example.com/figure7.png) Yield of light and heavy components in tar under QB and different carbon materials.

![Figure 8](https://example.com/figure8.png) Compositions of tars under QB and different carbon materials.

![Figure 9](https://example.com/figure9.png) Different phenolic contents under QB and different carbon materials.
pounds could be generated after combining with H free radicals.

Figure 10 shows the number of aromatic rings in aromatics under QB and different carbon materials. The contents of aromatics with more than three rings decrease by 3.37, 5.62, 5.64, 3.66, 5.41, and 5.21% under 10%BC, 20%BC, 30%BC, 10%BHC, 20%BHC, and 30%BHC, respectively. The oxygen-containing functional groups on the surface of the carbon materials can form some acidic centers that combine with the π electron system of negatively charged aromatics to activate the cracking reaction of these compounds, resulting in a decrease in the content of polycyclic aromatic compounds.

Figure 11 shows the yield of pyrolysis gas under QB and different carbon materials. Carbon materials reduce the CO, CH4, and CO2 yields and increase the H2, CO, and C2 yields in the product gas. The increase in CO yield is related to the reduction of oxygen-containing compounds in tar in Figure 8, which is consistent with the result reported by Wu et al. Small molecules such as CH4 and CO2 can be converted into small free radicals, and these free radicals could combine with the tar precursor to improve the quality of tar. Therefore, the yield of CH4 and CO2 decreases, and the yield of light oil with a boiling point below 170 °C increases under the prepared carbon materials. H2 is a byproduct of polymerization and polycondensation reactions. The yields of H2 over activated carbon materials are higher than those over inactivated carbon materials. This confirms that BHC can cause tar cracking and polymerization to be converted into coke deposition, which also corresponds to the rapid increase in the yield of Coke-C. However, the CH4 yield increases under 20%BHC and 30%BHC, which could be attributed to the cracking of aliphatic chains, functional groups containing methyl groups, and aromatic side chains, especially the cracking of aromatic methyl groups.

3.4. Characterization of the Carbon Materials. Table 2 shows the N2 adsorption characterization of carbon materials. It is found that activated carbon materials contain both micropores and mesopores compared with inactivated carbon materials. The activated carbon materials have more abundant pores than those before activation (shown in Figure 12); especially, 20%BHC and 30%BHC have mesopores around 10 nm. These results indicate the existence of porous structures in the activated carbon materials. Thus, the yield and distribution of tar obtained under inactivated and activated carbon materials differ significantly. The large surface area for the existing micropores in carbon materials can significantly improve their adsorption capacity. Also, the abundant pores can extend the residence time of volatiles, which provides the opportunity for volatiles to be cracked. So, the tar yield decreases significantly over activated carbon materials, which results in an increase in the yield of Coke-C in Figure 5. Combining with the decrease of S BET and S mic for the activated carbon materials after experiments, it shows that Coke-C may block some micropores and reduce the specific surface area. This indicates that the micropore structure increases the transformation of tar into coke. Both Hosokai et al. and Nestler et al. also clearly reported that micropores were active sites for carbon deposition.

To clarify this, experiments were conducted in the horizontal tube filled with AC-1 and AC-2, which have abundant micropores and high specific surface areas of 1221.24 and 953.34 m2/g, respectively. The yield of Coke-C under the carbon materials is lower than that under AC-1 and AC-2, as can be seen in Table 3. Therefore, it can be proven that the carbon materials with rich microporous structure are not suitable as the filter media of the granular bed duster. Also, Figure 5 shows that the yields of Coke-C under inactivated carbon materials are much lower than those under activated carbon materials, which are consistent with the result reported by Ravenni et al. that appropriate pore size distribution is beneficial to the diffusion of macromolecular compounds in volatiles. Also, it inhibits the polycondensation and polymerization reactions.

It can be seen from Table 2 that there is no significant difference in the specific surface areas for 10%BHC, 20%BHC, and 30%BHC. However, the distribution of pyrolysis products and the composition of tar show that these carbon materials have a significantly different catalytic cracking activity. Carbon structure may play a major role in catalysis. To further clarify the effect of biochar content and steam activation on the structure of carbon materials, the Raman spectral curves with a Raman shift between 800 and 1800 cm−1 were fitted into 10 Gaussian peaks according to the method reported in the references. The Raman spectrum of carbon materials before and after experiments is shown in Figure S2. An example of the peak-fitting curve of 20%BHC is shown in Figure S3, and the assignments of the Raman peaks could be obtained from previous literature.
attributed to the aromatic ring system with regular structure, and the D band is attributed to a defective structure composed of a large aromatic ring system with not less than six aromatic rings. Therefore, the peak area ratio of these main spectral bands can reflect the degree of condensation of aromatic rings, defects in graphite carbon structure, and the ratio between large and small aromatic ring systems.38 A/D/A represents the ratio of the defective structure and the relatively ordered carbon structure.

Figure 13 shows the A/D/A of the prepared carbon materials. The A/D/A ratios for the activated carbon materials are larger than those of the inactivated carbon materials, indicating that activated carbon materials have more carbon structure defects than the inactivated carbon materials. The activated carbon materials have a larger carbon structure defect to promote the cracking of pitch in tar. This is consistent with the decrease of pitch yield under activated carbon materials in Figure 6. As the content of biomass char in activated carbon materials increases, the ratio of the defect carbon structure also increases. It will offer more active sites to crack pitch, so the cracking ratio increases gradually on the role of activated carbon materials as shown in Figure 7. The ratios of A/D/A of all spent carbon materials are lower than those of fresh carbon materials. This may be because the volatiles react on the active sites in carbon materials to form new heavy aromatics, and the defect structure is reduced.

Figure 13. A/D/A of the prepared carbon materials.

Table 2. Nitrogen Adsorption Characterization of the Carbon Materials

| sample | S_{BET} (m²/g) | S_{mic} (m²/g) | S_{ext} (m²/g) | V_{tot} (cm³/g) | V_{mic} (cm³/g) | V_{mes} (cm³/g) | D_{ave} (nm) | a (nm) |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|--------|
| 10%BC  | 1.71           | 1.44           | 0.27           | 0.00           | 0.00           | 0.00           | 5.58        | 228.90 |
| 20%BC  | 5.59           | 4.86           | 0.73           | 0.01           | 0.00           | 0.00           | 4.38        | 47.80  |
| 30%BC  | 1.42           | 0.81           | 0.61           | 0.00           | 0.00           | 0.00           | 8.65        | 31.10  |
| 10%BHC | 102.19         | 58.10          | 44.09          | 0.05           | 0.02           | 0.03           | 2.57        | 1.20   |
| 20%BHC | 98.53          | 49.64          | 48.90          | 0.06           | 0.02           | 0.04           | 2.61        | 47.20  |
| 30%BHC | 129.06         | 83.48          | 45.59          | 0.07           | 0.03           | 0.04           | 3.14        | 47.20  |
| 10%-S  | 2.26           | 1.55           | 0.71           | 0.01           | 0.00           | 0.00           | 6.41        | 228.80 |
| 20%-S  | 7.49           | 4.35           | 2.10           | 0.01           | 0.00           | 0.01           | 8.86        | 116.60 |
| 30%-S  | 6.46           | 4.35           | 2.10           | 0.01           | 0.00           | 0.01           | 8.86        | 116.60 |

Table 3. Yield of Coke-C under Different Carbon Materials

| sample | AC-1 | AC-2 | 10%BC | 20%BC | 30%BC | 10%BHC | 20%BHC | 30%BHC |
|--------|------|------|-------|-------|-------|--------|--------|--------|
| Coke-C | 3.59 | 2.03 | 0.07  | 0.15  | 0.20  | 0.53   | 1.30   | 1.46   |

4. CONCLUSION

The cracking performance of the prepared carbon materials on the coal pyrolysis volatiles is evaluated. The content of biochar affects the carbon structure of the carbon material and also...
changes the catalytic performance to pyrolysis volatiles. The composition and distribution of tar have obvious differences over the prepared carbon materials. The inactivated carbon material is beneficial to improve the yield of light oil with the boiling point below 170 °C. The steam-activated carbon material has more defects in carbon structure than the inactivated carbon material, which is more conducive to cracking the pitch in tar. However, it is also easy to form more coke deposits (Coke-C). The yields of Coke-C on the surface of AC-1 and AC-2 are higher than those of carbon materials. This can be attributed to the abundant micropores that intensify the conversion from tar into Coke-C. More components rich in hydrogen are cracked to generate radicals that could combine with the phenols’ precursor over carbon materials. Also, the content of phenols in tar would be increased. In terms of improving the quality of tar, 20%BC has significant advantages for being applied as filter media in the granular bed duster during coal pyrolysis.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05467.
(Figure S1) 3D distribution of coal tar produced at carbon materials from GC×GC−MS, (Figure S2) Raman spectrum of carbon materials before and after experiments, and (Figure S3) diagram of Raman’s fitting curve of 20%BHC (PDF)

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Notes
The authors declare no competing financial interest.

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