Gas-Modified Pyrolysis Coke for in Situ Catalytic Cracking of Coal Tar

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ABSTRACT: Modified pyrolysis coke can be used as a catalyst for tar cracking. In this paper, pyrolysis coke was used as a carrier for modification by using gases (H$_2$O, CO$_2$, and NH$_3$), and the optimal modified gas was selected. On the basis of this, pyrolysis coke with different modified flow rates, temperatures, and times were prepared to catalyze the cracking of tar. The effect of gas-modified pyrolysis coke on tar cracking products was studied. Also, pyrolysis coke was characterized by Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller analysis, and scanning electron microscopy. The results show that the optimal gas is H$_2$O, and the optimal preparation conditions are 450 mL/min, 650 °C, and 60 min. The pyrolysis coke catalyst under the optimal conditions has the best cracking effect on tar. Also, the gas and tar yields have been further improved.

1. INTRODUCTION

Coal tar plays an important role in the chemical industry. The treated coal tar has a wide range of applications and can provide raw materials such as polycyclic aromatic hydrocarbons and high carbon.$^{1,2}$ In low-rank coal, low-temperature staged pyrolysis can be used to extract phenols, oil, and gas resources and produce clean solid fuel technology.$^{3,4}$ Low-temperature carbonized tar is one of the important sources of man-made oil. Through the development of catalytic cracking technology, the process of producing high-yield fuel oil, diesel oil, and gasoline from medium- and low-temperature coal tar has been widely used, which will gradually improve the current situation of rich coal and little oil.$^{5,6}$

At present, the research work on catalytic cracking of coal tar has been done, and some progresses have been made.$^{7,8}$ Catalytic pyrolysis is generally divided into two cases, one is the catalyst and the coal sample or biomass mixed pyrolysis, and the other is the pyrolysis of raw coal to form a gas-phase product and then catalytic cracking reaction with the catalyst.$^{9,10}$ The coal pyrolysis reaction can be roughly divided into two steps. First, the pyrolysis of the coal macromolecular structure forms a primary pyrolysis product, and then the primary pyrolysis product interaction undergoes a secondary reaction, eventually forming a product such as tar and gas.$^{11,12}$ If the secondary reaction in the coal pyrolysis process is oriented, then a higher yield of the target product can be obtained.$^{13}$ The research on catalytic cracking of coal pyrolysis gas-phase tar mainly separates the pyrolysis of coal and the catalytic cracking of gas-phase tar; that is, the coal and catalyst are placed separately, and the gas-phase tar produced by the coal pyrolysis reaction enters the catalytic section before being condensed. After the action of the catalyst, the targeted conversion of heavy tar is finally achieved.$^{14,15}$ In the study of tar catalytic modification, it is found that, using metal oxides, semi-coke, and supported metal pyrolysis catalysts, molecular sieves can improve the tar yield.$^{16-18}$ Since pyrolysis coke (PC) is a solid waste generated by coal pyrolysis, it has a large production yield, needs to occupy a large amount of space for storage, and is also harmful to the environment.$^{19-21}$ Therefore, from the perspective of waste utilization and environmental protection, pyrolysis coke catalysts are the preferred catalyst for tar catalytic cracking.$^{22}$

In recent years, many researchers began to pay attention to the catalytic reforming of pyrolysis coke produced from low-rank coal for pyrolysis gas tar.$^{23}$ It was found that pyrolysis coke showed good catalytic activity, which could eventually reduce the tar production and increase the yield of light oil and gas in the product.$^{24-26}$ Pyrolysis coke has many advantages, but to prepare a better pyrolysis coke catalyst, it must be modified to increase the functional groups and pore structure on the surface of pyrolysis coke so as to improve the catalytic cracking effect.$^{27,28}$ Generally, the methods of catalyst modification include acid–base-modified, gas-modified, and supported metal or nonmetal methods.$^{29}$

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In the process of acid-base modification, waste acid and alkali will inevitably be produced, which will cause environmental pollution and increase the cost of treatment. Therefore, the method of acid–base activation of pyrolysis coke will bring more negative effects. The supported catalytic materials have some disadvantages, such as high ignition temperature, catalyst poisoning, activity degradation, heavy metal pollution, and so on. The gas-modified pyrolysis coke can increase the functional groups and dredge the thermal defocusing aperture, thereby increasing the specific surface area, and it has the characteristics of cheap price, excellent performance, low production cost, and environmental friendliness, which is in line with the green low-carbon economy. So, gas-modified pyrolysis coke can effectively improve the activity and the impact on tar cracking.

Gas modification is the use of active gases (such as vapor, air, etc.) to perform the weak oxidation of carbon at higher temperatures, dredge the pyrolysis pore diameter, and then increase the specific surface area. Compared with chemical activation, gas modification has the characteristics of cheap price, excellent performance, low production cost, and environmental friendliness. Vapor activation is a commonly used method for the preparation of activated carbon, and it has a significant effect on the activation of carbonaceous materials. Vapor and carbon atoms are more reactive, vapor easily diffuses into the material at low temperatures, and the vapor concentration easily reaches dynamic equilibrium inside and outside the pores, creating conditions for the emergence of new pores.

Coal pyrolysis and the coal tar in situ catalytic cracking process are performed simultaneously. The heavy components in the gas-phase tar are lightened to form small molecular substances in the catalyst layer, which requires lower energy consumption and facilitates the condensation of coal tar downstream of the process separation, with good economic benefits. Pyrolysis has the advantages of a unique pore structure, large specific surface area, and good selection of catalytic performance. It can transform the fused aromatics into useful chemicals and raw materials during the pyrolysis process, which can increase its utilization value.

Therefore, this paper uses pyrolysis coke as a carrier, and gases (H_{2}O, CO_{2}, and NH_{3}) were used for modification. The pyrolysis coke catalysts with different modified flow rates, temperatures, and times were prepared to catalyze the cracking of tar. The effect of gas-modified pyrolysis coke on the cracking products of tar was studied.

2. RESULTS AND DISCUSSION

2.1. Coal Sample Analysis. 2.1.1. Proximate and Ultimate Analyses. The proximate analysis of coal refers to the general term for the determination of four analysis items including coal moisture (M_{ad}), ash (A_{ad}), volatiles (V_{ad}), and fixed carbon (F_{C,a}). The proximate analysis of coal is the main indicator for understanding the characteristics of coal yield and also the basis for evaluating coal yield. Generally, the moisture, ash, and volatiles of coal are measured directly, while fixed carbon is calculated by subtraction. The ultimate analysis of coal is the detection and analysis of the element content in the coal (generally expressed by mass percentage). The ultimate analysis is an important index for studying the degree of deterioration of coal, calculating the calorific value of coal, and estimating the carbonization products of coal and is also the basis for calorific calculation when using coal as fuel in industry.

Table 1 shows the proximate and ultimate analyses of coal samples.

| proximate analysis (%) | ultimate analysis (%) |
|------------------------|------------------------|
| M_{ad} | A_{ad} | V_{ad} | F_{C,a} | C | H | N |
| 15.23 | 16.58 | 36.56 | 32.53 | 58.9 | 4.09 | 1.13 |

2.1.2. Thermal Weight Analysis of Lignite. The weight loss curve (TG) and weight loss rate curve (DTG) of lignite under a N_{2} atmosphere at a heating rate of 15 °C/min are shown in Figure 1. The weight loss of lignite was divided into three stages: The first stage was between room temperature and 150 °C, and this stage was the drying stage, mainly the precipitation of moisture and adsorbed gas. The second stage was between 150 and 300 °C, and this stage was in the preheating stage. No obvious pyrolysis occurred. There was no obvious change in the TG and DTG curves. The third stage was between 300 and 500 °C. This stage was a pyrolysis stage of coal, a functional group was decomposed such as a phenolic carboxyl group having poor thermal stability in a molecular structure, and a bridge structure was broken between an aromatic ring and a side chain of fat in a macromolecular network. A large number of gaseous hydrocarbons and tar vapors were released. The coal lost weight quickly and had a maximum rate of weight loss. The DT curve of the coal dropped sharply after 400 °C, and the DTG curve also showed the highest peak of weight loss. The peak temperature of the pyrolysis was 450 °C, which was the temperature corresponding to the maximum weight loss temperature. The maximum weight loss temperature reflected the stability of the coal macromolecular structure. The lower the peak temperature, the more easily the network structure in coal was destroyed. The higher the reactivity of coal, the more unstable the structure during pyrolysis.

Figure 1. TG and DTG curves of lignite.
furnace. Figure 2 shows the cracking effect of PC modified by different gases on gas-phase tar.

Figure 2a shows the effect of PC modified by different gases on gas and tar yields. It can be seen that the higher the gas yield, the lower the tar yield. Compared with raw coal, the tar yield decreased by 15%, and the gas yield increased by 33.3%. The order of the cracking effect of gas-modified pyrolysis is H2O > NH3 > CO2.

Figure 2b shows the yield of H2, CO2, CH4, and CO produced by cracking tar change after adding PC modified by different gases, which shows that the effect is different. The yields of H2, CO2, CH4, and CO produced by HPC cracking tar are 202, 89, 28, and 8 mL/g, and the cracking effect is the best. Compared with PC, NPC and CPC do not improve greatly, and the cracking effect decreases. Therefore, HPC has a good effect on the production of combustible gas from tar cracking. At the same time, 3 g of vapor-modified PC is used for experiments. The pyrolysis gas produced is 0.05 L, and the content of H2, CO2, and CH4 is very small. Therefore, the effect of PC-generated gas is not considered. Compared with raw coal, the content of H2 increases by 115%. The main sources of H2 are the following five elementary reaction modes: (1) dehydrogenation of hydrogenated aromatic structures, (2) condensation of organic matter, (3) cyclization of aliphatic paraffins, (4) polycondensation of aromatic hydrocarbon reaction dehydrogenation, and (5) reaction of PC with pyrolysis water.

\[
C + H_2O \rightarrow CO + H_2 \tag{A1}
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \tag{A2}
\]

Figure 2c shows the effect of PC modified by different gases on tar composition. It can be seen that PC modified by different gases is used for tar cracking, and the change in the content of different oil products is similar: naphthalene oil < phenol oil < light oil < washing oil < anthracene oil < asphalt. In the tar grouping, the higher the content of light oil, phenol oil, naphthalene oil, and washing oil, the lower the content of asphalt and anthracene oil and the better the yield of the tar. Therefore, adding gas-modified PC to improve tar cracking improves tar yield. It can be seen that, when PC modified by different gases is added, tars with different boiling points are
cracked to cause the percentage content to change, and the tar cracking by HPC decreases the content of pitch and anthracene oil and increases the content of light oil, phenol oil, naphthalene oil, and wash oil. Therefore, from the change in tar composition, HPC has the best effect on tar cracking. Table 2 shows the changes in light components and heavy components after tar cracking by PC modified by gases. The light components are the yields of light oil, phenol oil, naphthalene oil, and wash oil, and the heavy components are the total yields of anthracene oil and asphalt. The ratio of the light group is higher and the effect is better. HPC tar cracking is obvious, and the ratio of light components increases from 26.8 to 43.77%.

Table 2. After Tar Cracking by PC Modified by Gases

| gas-modified pyrolysis | coal   | PC     | HPC   | NPC   | CPC   |
|-------------------------|--------|--------|-------|-------|-------|
| light component (g)     | 0.3551 | 0.4390 | 0.4929| 0.4972| 0.4763|
| heavy component (g)     | 0.9689 | 0.7620 | 0.6331| 0.7128| 0.7547|
| light component ratio (%)| 26.8  | 36.55  | 43.77 | 41.09 | 38.69 |

Figure 3. (a–c) Cracking effect of modified PC with different vapor flow rates on gas-phase tar.

2.2.2. Effect of Modified PC with Different Vapor Flow Rates on Tar Cracking. Put the PC catalyst prepared at 2 h and 750 °C into the tubular furnace, introduce vapor for modification, and set the modified temperature to 350 °C, the time to 30 min, and the flow rates to 150, 300, 450, and 750 mL/min; the prepared PC catalysts are named HPC-150 mL/min, HPC-300 mL/min, HPC-450 mL/min, and HPC-750 mL/min, respectively. Weigh 3 g of modified catalyst and place it in the second-stage furnace to catalyze the pyrolysis of gas tar produced in the first-stage furnace. Figure 3 shows the cracking effect of modified PC with different vapor flow rates on gas-phase tar.

Figure 3a shows the effect of modified PC with different vapor flow rates on the total gas and tar yields. It can be seen...
that, when the vapor flow rate is 150 mL/min, the gas yield is the lowest and the tar is the highest, with values of 10.2 L and 1.12 g, respectively. The gas and tar yields of HPC-450 mL/min are 13.6 L and 1.06 g, and those of HPC-750 mL/min are 13.7 L and 1.06 g, respectively. There is not much difference between the gas and tar yields. Therefore, it can be understood that, when the vapor flow rate is 450 mL/min, the modified PC has reached the saturation state, and when the vapor flow rate increases, the amount of gas and tar will not be changed. Therefore, HPC-450 mL/min has a better catalytic cracking effect. Under this condition, the effect is the best. Compared with raw coal, the tar yield decreases by 19.72%, and the gas yield increases by 37.37%.

Figure 3b shows the effect of modified PC with different vapor flow rates on gas components. It can be seen that, after the vapor flow increases, the amount of H₂, CO₂, CH₄, and CO gases produced by cracking tar shows an increase first and then a decrease, indicating that modified PC with different vapor flow rates has different effects. Among them, the combustible gases H₂, CH₄, and CO prepared by HPC-450 mL/min and HPC-750 mL/min catalytic cracking have a larger increase than raw coal, and the catalytic effect is better; the amount of flammable gas produced by the two is similar.

| Table 3. After Tar Cracking by PC Modified by Flow |
|-----------------------------------------------|
| vapor flow-modified PC | coal | PC | HPC-150 mL/min | HPC-300 mL/min | HPC-450 mL/min | HPC-750 mL/min |
| light component (g)    | 0.3551 | 0.4390 | 0.4728 | 0.4731 | 0.4570 | 0.4335 |
| heavy component (g)    | 0.9689 | 0.7620 | 0.6465 | 0.6329 | 0.6060 | 0.6273 |
| light component ratio (%) | 26.8 | 36.55 | 39.63 | 42.78 | 42.99 | 40.87 |

Figure 4. (a–c) Cracking effect of modified PC with different vapor temperatures on gas-phase tar.
But after the vapor flow rate exceeds 450 mL/min, the yield of flammable gas is very small, and the flammable gas output of HPC-750 mL/min is 1 mL/g less than HPC-450 mL/min. When the vapor flow rate is 450 mL/min, the modified PC has reached the saturation state, and when the vapor flow rate increases, the amount of gas and tar will not be changed. Therefore, the catalytic cracking effect of HPC-450 mL/min is the best.

Table 4. After Tar Cracking by PC Modified by Temperature

| vapor flow-modified PC | coal | PC | HPC-350 °C | HPC-450 °C | HPC-550 °C | HPC-650 °C | HPC-750 °C |
|------------------------|------|----|------------|------------|------------|------------|------------|
| light component (g)    | 0.3551 | 0.4390 | 0.4648 | 0.4811 | 0.4849 | 0.4537 | 0.4420 |
| heavy component (g)    | 0.9689 | 0.7620 | 0.6450 | 0.6380 | 0.6194 | 0.5512 | 0.5597 |
| light component ratio (%) | 26.8 | 36.55 | 41.88 | 42.99 | 43.91 | 45.15 | 44.12 |

Figure 5. (a–c) Cracking effect of modified PC with different vapor times on gas-phase tar.

higher the content of light oil, phenol oil, naphthalene oil, and washing oil, the lower the content of asphalt and anthracene oil and the better the yield of the tar. It can be seen that the content of light oil, phenol oil, naphthalene oil, and wash oil increases first and then decreases, and the content of anthracene oil and asphalt decreases with the increase in vapor flow rate. It can be concluded that, as the vapor flow rate increases, the tar yield gradually improves. HPC-450 mL/min has an obvious effect on tar cracking, which makes the asphalt content, naphthalene oil content, and washing oil content
decrease and the anthracene oil content, light oil content, and phenol oil content increase. Therefore, from the change in tar composition, HPC-450 mL/min has the best cracking effect on tar.

Table 3 shows the changes in light components and heavy components after tar cracking. The light components are the yields of light oil, phenol oil, naphthalene oil, and wash oil, and the heavy components are the total yield of anthracene oil and asphalt. The ratio of light group is higher and the effect is better. ZHPC-5 min tar cracking is obvious, and the ratio of light components increases from 36.65 to 55.80%.

2.2.3. Effect of Modified PC with Different Vapor Temperatures on Tar Cracking. Put the PC catalyst prepared at 2 h and 750 °C into the tubular furnace, introduce vapor for modification, and set the modified time to 30 min, the flow rate to 450 mL/min, and the temperatures to 350, 450, 550, 650, and 750 °C; the prepared PC catalysts are named HPC-350 °C, HPC-450 °C, HPC-550 °C, HPC-650 °C, and HPC-750 °C, respectively. Weigh 3 g of modified catalyst and place it in the second-stage furnace to catalyze the pyrolysis of gas tar produced in the first-stage furnace. Figure 4 shows the cracking effect of modified PC with different vapor temperatures on gas-phase tar.

Figure 4a shows the effect of modified PC with different vapor temperatures on the total gas and tar yields. It can be seen that the higher the gas yield, the lesser the tar, indicating more tar cracking. Also, the effect of vapor-modified temperature on PC is different. In the gas and tar yields of HPC-350 °C, the gas yield is the lowest and the tar yield is the highest, with values of 11.4 L and 1.11 g, respectively. In the gas and tar yields of HPC-750 °C, the tar yield increases, the gas output decreases, and the tar cracking effect decreases. In the gas and tar yields of HPC-650 °C, the gas yield is the highest and the tar yield is the lowest, with values of 13.8 L and 1.00 g, respectively; both the gas and tar yields reach the optimal value. Therefore, HPC-650 °C has a better catalytic cracking effect. Under this condition, the effect is the best. Compared with the raw coal, the tar yield decreases by 24.10%, and the gas yield increases by 39.40%.

Figure 4b shows the effect of modified PC with different vapor temperatures on gas components. It can be seen that, after the vapor flow increases, the amount of H2, CO2, CH4, and CO gases produced by cracking tar shows an increase first and then a decrease, indicating that modified PC with different vapor temperatures has different effects. Among them, under the condition of HPC-650 °C, the combustible gases H2, CH4, and CO produced by catalytic cracking have a larger increase than raw coal, and the catalytic effect is better. Compared with raw coal, H2 increases by 143.91%, CH4 increases by 48.48%, CO increases by 63.72%, and the overall combustible gas increases by 98.32%. Therefore, HPC-650 °C has the best catalytic cracking effect.

Figure 4c shows the effect of modified PC with different vapor temperatures on tar components. In the tar grouping, the higher the content of light oil, phenol oil, naphthalene oil, and washing oil, the lower the content of asphalt and anthracene oil and the better the yield of the tar. It can be seen that the tar cracking at HPC-650 °C is obvious, the total content of light oil, phenol oil, naphthalene oil, and washing oil is the highest, and the reduction of anthracene oil and asphalt is the largest. Compared with raw coal, the ratio of light oil increases by 6%, that of phenol oil increases by 5%, that of naphthalene oil increases by 3%, that of washing oil increases by 5%, that of bitumen decreases by 3%, and that of anthracene oil increases by 16%. Therefore, from the change in tar composition, HPC-650 °C has the best cracking effect on tar.

Table 4 shows the changes in light components and heavy components after tar cracking. The light components are the yields of light oil, phenol oil, naphthalene oil, and wash oil, and the heavy components are the total yields of anthracene oil and asphalt. The ratio of light group is higher and the effect is better. HPC-650 °C tar cracking is obvious, and the ratio of light components increases from 26.8 to 45.15%.

2.2.4. Effect of Modified PC with Different Vapor Times on Tar Cracking. Put the PC catalyst prepared at 2 h and 750 °C into the tubular furnace, introduce vapor for modification, and set the modified temperature to 650 °C, the flow rate to 450 mL/min, and the times to 30, 45, 60, and 90 min; the prepared PC catalysts are named HPC-30 min, HPC-45 min, HPC-60 min, and HPC-90 min, respectively. Weigh 3 g of the modified catalyst and place it in the second-stage furnace to catalyze the pyrolysis of gas tar produced in the first-stage furnace. Figure 5 shows the cracking effect of modified PC with different vapor times on gas-phase tar.

Figure 5a shows the effect of vapor-modified PC on the total gas and tar yields. It can be seen that the modified time has a certain effect on the tar cracking. The yield of gas increases first and then decreases, and the tar yield decreases first and then increases. It can also be understood that the higher the gas yield, the lower the tar yield and the more the tar cracking. In HPC-30 min, the gas yield is the lowest and the tar is the highest, with values of 10.9 L and 1.015 g, respectively; in HPC-60 min, the gas yield is the highest and the tar yield is the lowest, 13.8 L and 1.005 g, respectively. Therefore, it can be concluded that the gas and tar yields reach the best values in HPC-60 min. Under this condition, the effect is the best. Compared with raw coal, the tar yield decreases by 24.10%, and the gas yield increases by 39.40%.

Figure 5b shows the effect of modified PC with different vapor times on gas components. It can be seen that the yield of H2, CO2, CH4, and CO produced by cracking tar changes with the addition of modified PC. The results show that it has a certain effect. HPC-60 min produces the most flammable gases and has a better catalytic effect. When the modified time is exceeded, the gas yield will decrease. Therefore, HPC-60 min has the best catalytic cracking effect.

Figure 5c shows the effect of modified PC with different vapor times on tar components. As can be seen, when PC with different vapor times is added, tars with different boiling points crack and the percentage content changes. HPC-60 min tar cracking is obvious, which causes a significant reduction in asphalt content and anthracene oil content and a significant increase in light oil and phenol oil content; the naphthalene oil content and washing oil content produced by tar cracking decrease slightly. Therefore, HPC-60 min tar has the best cracking effect from the change in tar composition. It can be seen in Figure 6 that, after a series of modifications, the PC has a better cracking effect on meteorological tar, and the color of the tar is obviously lighter, which fully illustrates that the tar is catalytically cracking.

Table 5 shows the changes in light components and heavy components after tar cracking. It can be seen that HPC-60 min cracking of tar significantly reduces the asphalt content, increases the anthracene oil content, significantly increases the light oil content and phenol oil content, and slightly reduces the naphthalene oil content and wash oil content. HPC-60 min

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tar cracking is obvious, and the ratio of light components increases from 26.8 to 45.15%.

2.3. Characterization. 2.3.1. BET Analysis. 2.3.1.1. Specific Surface Area of PC Modified by Different Gases. The specific surface area of PC modified by different gases is shown in Table 6. As can be seen, the specific surface area of the gas-modified PC catalyst increases a lot. The reason is that gas modification is a process in which the gas is eluted by thermal devolatization, and some closed pores inside the PC are opened during the gas washing process, thereby increasing the specific surface area. Among them, the specific surface area of PC modified with the vapor increases the most, reaching 151.40 m²/g. The specific surface area of PC after the reaction becomes small. The main reason is that the surface of PC adsorbs some tar macromolecules, and the pores are blocked, so the specific surface area is reduced.

2.3.1.2. Optimal Vapor Pyrolysis Focal Surface Area. Table 7 is the specific surface area of the optimal vapor-modified PC. It can be seen that the specific surface area of the PC catalyst modified with the vapor is 331.15 m²/g, and it has been greatly improved. The main reason is that vapor can open the closed space during modification to form more pore structures and voids, so the specific surface area has been greatly improved. The specific surface area of the optimal HPC after the reaction has decreased to 142.23 m²/g; the main reason is that the surface of PC adsorbs some tar macromolecules, and the pores are blocked, so the specific surface area is reduced.

2.3.2. FT-IR Analysis. 2.3.2.1. FT-IR Analysis of PC Catalyst Modified by Different Gases. Figure 7 shows the infrared spectrum of the PC catalyst modified by different gases. It can be seen that there is no significant difference in the functional group before and after the reaction.

A broad and strong absorption peak appears near 3400 cm⁻¹, and the peak of hydrogen bonding and absorption of the OH group in the peak are related to HPC < HPC < NPC < CPC after the reaction. The asymmetric deformation peak of methylene ketone appears at 1415 cm⁻¹, the peaks of CPC after the reaction are larger, and the peak area before the reaction is smaller. The main reason is that PC reacts with the tar to form more pore structures and voids, so the specific surface area has been greatly increased. In the range of 1800 to 800 cm⁻¹, it is mainly formed by aromatic [−C=O], [−C=C−], [−C−O], [−CH₃], and hydrogen atoms outside the aromatic nucleus. At about 1400 cm⁻¹, the transmission peak is formed by [−CH₃] and [−CH₂] on the aromatic alkane bond structure. Some relatively broad and strong peaks appear around 600 cm⁻¹, which may be amide or phosphorus-containing groups. In the range of 1800 to 800 cm⁻¹, the peak area formed on PC after the reaction is larger, and the peak area before the reaction is smaller. The main reason is that PC reacts with the tar macromolecular substance when cracking the tar and then forms the functional group; therefore, the peak area of PC after the reaction in the range of 1800 to 800 cm⁻¹ is larger. In short, the oxygen content in PC is higher when modified in a H₂O vapor atmosphere. The reason may be that the H₂O molecule itself contains an oxygen atom, which interacts with

Table 5. After Tar Cracking by PC Modified by Time

| vapor flow-modified PC | coal (g) | PC (g) | HPC-30 min (g) | HPC-45 min (g) | HPC-60 min (g) | HPC-90 min (g) |
|------------------------|---------|-------|---------------|---------------|---------------|---------------|
| light component (g)    | 0.3551  | 0.4390| 0.4164        | 0.4282        | 0.4537        | 0.4176        |
| heavy component (g)    | 0.9689  | 0.7620| 0.5985        | 0.5787        | 0.5512        | 0.5939        |
| light component ratio (%) | 26.8 | 36.55 | 41.03         | 42.53         | 45.15         | 41.70         |

Table 6. Specific Surface Area of PC Modified by Different Gases (m²/g)

| PC catalyst | PC       | CPC      | NPC      | HPC      | HPC after reaction |
|-------------|----------|----------|----------|----------|-------------------|
| specific area (m²/g) | 68.9     | 123.03   | 136.14   | 151.40   | 73.19             |

Table 7. Specific Surface Area of PC Modified by Optimal Vapor (m²/g)

| PC catalyst | optimal HPC | optimal HPC after reaction |
|-------------|-------------|----------------------------|
| specific area (m²/g) | 331.15 | 142.23 |
lignite during pyrolysis, hinders the cleavage reaction of an oxygen-containing functional group such as a carboxyl group, an ether bond, or a ketone group, and protects the oxygen-containing functional group.

2.3.2.2. FT-IR Analysis of the HPC at Optimum Condition. The FT-IR before and after the optimal vapor reforming pyrolysis reaction is shown in Figure 8.

Figure 8 shows that there is no significant difference in the function group before and after the reaction. At about 3400 cm\(^{-1}\), it is an absorption peak formed by vibration of [\(-\text{OH}\)], such as an alcohol, phenol, or carboxyl group. The [\(-\text{OH}\)] content is the highest in the PC catalyst before and after the reaction, but the [\(-\text{OH}\)] before the reaction is higher and that after the reaction is lower. The [\(-\text{OH}\)] is mainly consumed in the reaction process, which promotes the cracking of the tar. There are several small peaks in the range of 3000 to 2800 cm\(^{-1}\), which are formed by [\(-\text{CH}_3\)] and [\(=\text{CH}_2\)], respectively. [\(-\text{CH}_3\)] and [\(=\text{CH}_2\)] before the reaction are higher, indicating that these two functional groups can promote the cracking of tar. In the range of 1800 to 800 cm\(^{-1}\), it is mainly formed by aromatic [\(=\text{C} = \text{O}\)], [\(-\text{C} = \text{C} -\)], [\(-\text{C} = \text{O}\)], [\(=\text{CH}_2\)], and hydrogen atoms outside the aromatic nucleus. At about 1400 cm\(^{-1}\), the transmission peak is formed by [\(=\text{CH}_3\)] and [\(-\text{CH}_3\)] on the aromatic alkane bond structure. Some relatively broad and strong peaks around 600 cm\(^{-1}\) may be amide or phosphorus-containing groups. In the range of 1800 to 800 cm\(^{-1}\), the peak area formed on PC after the reaction is larger, and the peak area before the reaction is smaller. The main reason is that PC reacts with the coke oil macromolecules when cracking the coke oil and then forms the functional group on PC. Therefore, the peak area of the pyrolysis coke after the reaction in the range of 1800 to 800 cm\(^{-1}\) is larger.

2.3.3. The Analysis of SEM. 2.3.3.1. SEM Analysis of PC Modified by Different Gases. The SEM images of PC modified by different gases are shown in Figure 9.

Figure 9 shows the SEM images of CPC, NPC, and HPC before and after the reaction. It can be seen that, after gas modification, the PC surface produces more particles, and the generated particles can increase the specific surface area and the adsorption performance of the PC and provide more active sites for tar cracking. Figure 9a–c shows that the surface of the CPC has less particulate matter and has larger particles. The surface of the NPC has more particulate matter and has smaller particles, while the surface of the HPC has more particulate matter and has larger particles. Therefore, the large amount of particulate matter can provide more active sites for tar cracking to gain more light oil and gas efficiently. Comparing Figure 9c and Figure 9d, it is found that the surface of the HPC after the reaction also has a lot of small particles, and there are almost no large particles. The reason is that larger particles are consumed to become smaller during the cracking process. After the modification, the surface of PC produces a lot of large particles, which provide active sites for the cracking of tar, so the HPC pyrolysis tar has the best cracking effect.

2.3.3.2. SEM Analysis of Optimal Vapor Activation PC. The SEM of the optimal vapor-modified PC is shown in Figure 10.

Figure 10 shows the SEM images of the HPC prepared at the optimal condition before and after the reaction. The structure of the HPC changes greatly. A large number of large particles are dispersed in the interior of the PC catalyst, and the cracking is remarkable, thereby increasing its specific surface area. In turn, the adsorption of the tar oil increases, and the cracking effect of the tar is promoted. After the reaction, the particles on the HPC surface become smaller, and the active sites decrease. Therefore, the active site of the HPC surface reduces after the reaction, and the catalytic cracking effect also reduces.

3. CONCLUSIONS

In this paper, pyrolysis coke prepared under optimal conditions is used as a raw material, different gases (CO\(_2\), H\(_2\)O, and NH\(_3\)) are used for modification, and the optimal modified gas is selected. Then, the optimal gas flow rate, temperature, and time are selected. The effect of the flow rate, temperature, and time of modified gas on the catalytic cracking of gas tar was studied. The results show the following:

1. Gas-modified pyrolysis coke can catalyze the cracking of gas-phase tar, and the vapor-modified pyrolysis coke has the best effect.
2. The optimal modification conditions of vapor-modified pyrolysis coke are as follows: the modified flow rate is 450 mL/min, the temperature is 650 °C, and the time is 60 min.
3. Compared with the pyrolysis of raw coal, the vapor-modified catalytic cracking tar yield increases from 9.9 to 13.8 L, and the gas production increases by 39.40%; the tar yield decreases from 1.324 to 1.0049 g, and the tar cracking rate increases by 24.10%.
4. The ratio of light components increased from 26.8 to 45.15%.

4. MATERIALS AND METHODS

4.1. Materials. The lignite used in the experiment was produced in Ordos, China. The lignite is crushed, and particles with a particle size of 3 to 5 mm are screened, dried in a 60 °C drying box, and placed in a dryer for use. The experiment used 3–5 mm lignite particles to prepare pyrolysis coke named PC.

4.2. Preparation of Gas-Modified PC.

1. The PC catalyst was placed in a tube furnace, and the gases CO\(_2\), H\(_2\)O, and NH\(_3\) were introduced for modification. The flow rate was set to 150 mL/min, the temperature was 350 °C, and the time was 30 min. The prepared PC catalysts were named CPC, HPC, and NPC.
(2) The best gas in (1) was selected as the modified gas. The temperature of the tube furnace was set at 350 °C, the modified time was 30 min, and the flow rates were 150, 300, 450, and 750 mL/min. Prepare the modified PC catalysts with different flow rates.

(3) The optimum modified gas was introduced, and the optimal flow rate in (2) was selected as the modified flow rate. The modified time of the tube furnace was set to 30 min, and the modified temperatures were 350, 450, 550, 650, and 750 °C. Prepare the modified PC catalysts with different temperatures.

(4) The optimal modified gas was introduced, the optimal modified flow rate was set, the optimum temperature in (3) was selected as the modified temperature, and the modified times of the tube furnace were set to 30, 45, 60, and 90 min. Prepare the modified PC catalysts with different times.

(5) The optimal modified gas, flow rate, temperature and time were selected as the optimal modified conditions for the PC.

4.3. Catalyst Activity Evaluation. Weigh 20 g of lignite coal sample and place it in the quartz tube of furnace 1; weigh 3 g of prepared PC catalyst and place it in the quartz tube of furnace 2. The tar catalytic cracking process is shown in Figure 11.

4.4. Detection of the Gas and Tar. 4.4.1. Gas Detection. The gas composition was analyzed by an Agilent-7820A gas chromatograph. The working conditions of the instrument are shown in Table 8.

4.4.2. Tar Detection. The detection of tar was mainly carried out by means of simulated distillation to analyze the distribution of each fraction and carried out on a simulated distillation chromatogram. The principle of this method was a nonpolar column with a certain degree of separation, testing the retention time of known mixture components under linear temperature programming conditions. Then, under the same chromatographic conditions, the samples were sequentially separated according to the boiling points of the components, and the slice integration was performed to obtain the corresponding cumulative area and the corresponding...
retention time. After temperature−time interpolation correction, a temperature corresponding to a percent yield was obtained, which was a distillation range. The cumulative area percentage was the yield. Table 9 shows boiling point range for classifying tar fractions.

### 4.5. Characterization of the Catalysts.

Thermogravimetric analysis of raw coal was carried out using a Swiss Mettler−Toledo TGA/SDTA851e thermogravimetric analyzer. During the experiment, the carrier gas was selected from high-purity N2, the gas flow rate was 60 mL/min, the temperature range was 24−500 °C, and the heating rate was 15 °C/min.

For specific surface area analysis (BET), the JW-BK122W type surface and pore size analyzer was used to measure the specific surface area of different types of pyrolysis coke catalysts.

For scanning electron microscopy (SEM), a JSM-6460LV with a working voltage of 20 kV and 5000× magnification was used.

X-ray photoelectron spectroscopy was an important technique for analyzing the surface structure and composition of an element, and it can get the composition of the test object.

For X-ray diffraction analysis, an XD-3 X-ray diffractometer was used, and the test parameters were as follows: voltage, 36 kV; current, 25 mA; target, Cu; 2θ/θ, 10° to 80°; scanning speed, 4°/min.

| coal tar fraction | light oil | phenolic oil | naphthalene oil | washing oil | anthracene oil | asphalt |
|------------------|-----------|-------------|----------------|-------------|----------------|---------|
| boiling point (°C) | <170      | 170−210     | 210−230        | 230−300     | 300−360        | >360    |
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Z.L.(F) and Z.L.(M) conceptualized the study. S.H. prepared the methodology. J.Y. provided the software needed for the study. J.Y. and S.H. validated the data. Z.L.(F) conducted the investigation. S.H. curated the data. S.H. prepared and wrote the original draft of the manuscript. S.H. reviewed and edited the manuscript.

Notes
The authors declare no competing financial interest.

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