Effect of Water Vapor on Pore Structure, Surface Functional Groups, and Combustion Performance of Pyrolytic Semicoke

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ABSTRACT: The coal tends to be affected by the water vapor from quenching coke process in the pyrolysis process during the coal carbonization process and in turn causes the variation of physicochemical properties of semicoke. The preparation of semicoke based on different pyrolysis temperatures and water vapor content was carried out in order to investigate the influence of water vapor on physicochemical properties of the pyrolytic semicoke, combined with specific surface area analysis and thermal analysis to study the pore structure and combustion properties of semicoke. The morphology of the semicoke and the alteration rule of carbon-containing functional groups were analyzed by scanning electron microscopy and X-ray photoelectron spectroscopy. The result indicates that adding an appropriate amount of water vapor (40%) instead of excess (60%) in the pyrolysis process (800 °C) is beneficial to the increase of the proportion of fixed carbon and the removal of volatile and ash. The specific surface area and the combustion performance of the semicoke is significantly improved when the appropriate amount of water vapor was added. The water vapor content has a slight effect on surface functional groups when the temperature ranges from 500 to 700 °C, whereas the higher water vapor content inhibits the improvement of physicochemical properties of the semicoke when the pyrolysis temperature is higher (800 °C). Therefore, the entry of excess water vapor (60%) into the high-temperature pyrolysis section should be avoided in the process of quenching coke or it would have an adverse impact on the performance of semicoke.

1. INTRODUCTION

With the proposal of efficient and clean application of semicoke, improving combustion performance of semicoke plays a more and more important role in blast furnaces. Pyrolysis is the main method for preparing semicoke.¹,² Pyrolysis conditions are important factors affecting the combustion performance of semicoke, and comparing the combustion performance of pyrolysis semicoke and raw coal to identify the main factors affecting the combustion performance of semicoke is vitally important. Semicoke prepared by pyrolysis by quenching, whose commonly used method in quenching coke process is wet quenching coke, can not only quickly cool down but also reduce coke quenching time.³ However, the water vapor generated during the quenching process will rise to the pyrolysis stage (as shown Figure 1).⁴ With the pyrolysis temperature increasing, the volatile matter in the coal is quickly ruled out during the pyrolysis process with more pores being opened and the adsorption capacity of the coal char increased,⁵ and the water vapor generated during quenching coke affects the change of pore structure. The coal semicoke carbon skeleton melts and collapses when the temperature is too high and part of the micropores are transformed into mesoporous pore and mesopores, which reduces the adsorption capacity and thereby affecting the combustion performance of semicoke.⁶

Zhou et al.⁷ studied the effect of different quenching methods on the coke pore structure and found that the wet quenching coke has the largest total pore area, and the micropores increase in the quenching coke process. The pyrolysis conditions in the pyrolysis section lead to the transition of the coke structure. Wang et al.⁸ pointed out that pyrolysis conditions had an important influence on the specific surface area and pore structure characteristics of coal char. The pore structure of coal char was affected by heating rate and final pyrolysis temperature. The higher the heating rate was, the larger the specific surface area of coal char was. Liu et al.⁹ pointed out that the specific surface area and pore volume of coke would decrease due to the pyrocondensation polymerization with the increase of pyrolysis time, and pyrolysis temperature and the atmosphere would have an impact on parameters such as pore diameter, porosity, and pore specific surface area.¹⁰ Xiang et al.¹¹ studied the alteration rule relevance of the specific surface area and pore volume with...
coal char. It is found that the specific surface area of coal semicoke is similar to that of micropore in the early stage of reaction under CO₂ and H₂O atmosphere, whereas more total specific surface area was produced in the CO₂ atmosphere as the reaction progressed. Scanning electron microscopy (SEM) is widely used.⁴ Scanning electron microscopy imaging provides a unique advantage for quantitative analysis of pore semicokeacteries in porous media,⁵ and using X-ray photoelectron spectroscopy (XPS) to study the change of carbon functional groups on the surface of char can also reflect the influencing factors of semicoke combustion performance. Xiang et al.⁶ used X-ray photoelectron spectroscopy (XPS) system to study the existence form and evolution mechanism of carbon on the surface of coal semicoke during the combustion process. The results show that aromatic hydrocarbons are formed on the surface during the pyrolysis process, and the content of single bonds carbon and double bond carbon is low during the combustion process. Zhang et al.⁷ investigated the forms of carbon in Datong bituminous coal and its coke by XPS. The results showed that the carbon mainly existed in aromatic carbon and aliphatic carbon.

At present, the influence of water vapor and temperature on semicoke performance during quenching coke is not clear. In this paper, the coal samples were pyrolyzed under different pyrolysis temperatures (500 °C, 600 °C, 700 °C, and 800 °C) and different water vapor contents (H₂O—0%, H₂O-20%, H₂O-40%, and H₂O-60%) with water vapor. The changes of pore structure, surface functional groups, and combustion performance of pyrolysis solid products under different pyrolysis conditions were compared to reveal the influence of water vapor on the physicochemical properties of semicoke in the quenching coke process.

2. RESULTS AND DISCUSSION

2.1. Effect of Final Pyrolysis Temperature and Water Vapor Content on Semicoke Combustion Characteristics. In order to explore the effects of pyrolysis temperature and water vapor content on the combustion performance of raw coal and its solid products after pyrolysis, thermogravimetry (STA449F3, Netzsch Instrument Inc., Germany) was used to conduct combustion reaction experiments on raw coal and its pyrolysis products, and the experimental results are shown in Table 1.

Table 1. Combustion Reactivity of Samples under Different Pyrolysis Conditions

| number | temperature (°C) | T_i (°C) | T_f (°C) |
|--------|-----------------|----------|----------|
| raw coal | 352 | 660 |
| 1 | 500 | 441 | 518 |
| 2 | 600 | 461 | 538 |
| 3 | 700 | 489 | 559 |
| 4 | 800 | 518 | 588 |
| 5 | 500-H₂O-20% | 443 | 516 |
| 6 | 600-H₂O-20% | 450 | 533 |
| 7 | 700-H₂O-20% | 471 | 569 |
| 8 | 800-H₂O-20% | 491 | 572 |
| 9 | 500-H₂O-40% | 441 | 525 |
| 10 | 600-H₂O-40% | 446 | 526 |
| 11 | 700-H₂O-40% | 472 | 564 |
| 12 | 800-H₂O-40% | 473 | 580 |
| 13 | 500-H₂O-60% | 440 | 514 |
| 14 | 600-H₂O-60% | 464 | 540 |
| 15 | 700-H₂O-60% | 491 | 570 |
| 16 | 800-H₂O-60% | 521 | 590 |

The ignition temperature (T_i) and burnout temperature (T_f) of the samples were obtained of the TG-DTG curve of the pyrolysis solid phase products, as shown in Table 1. These two indexes are used to further verify the effect of water vapor on the semicoke. The ignition temperature range of all samples is between 352 and 521 °C, and the burnout temperature range is between 514 and 660 °C. Compared with the raw coal, the ignition temperature of the pyrolysis products at different final temperatures (samples 1–4 in Table 1) are all higher, the burnout temperature is lower than the burnout temperature of the raw coal, and the combustion performance of the semicoke is lower than that of raw coal. With the pyrolysis temperature increase, the ignition temperature and burnout temperature of pyrolysis products show an increasing trend, related to the increase of fixed carbon content with the increase of pyrolysis temperature in Table 5. It can be seen that the increase of the pyrolysis temperature makes the semicoke is difficult to ignite, which greatly limits the use of semicoke as a fuel.

As shown in Figure 2a when the amounts of water vapor are 0%, 20%, 40% and 60%, with the increase of the pyrolysis temperature the pyrolysis product has the highest ignition temperature at 800 °C, and the sample prepared at 500 °C has the lowest ignition temperature. Under the same pyrolysis final temperature conditions, the ignition temperature of samples with 20% and 40% water vapor addition is significantly lower than that of the samples without water vapor. As shown in Figure 2b, the burnout temperatures of the pyrolysis products at different final temperatures are all lower than that without water vapor pyrolysis products. Under the same pyrolysis temperature condition, the sample with 40% water vapor has the lowest burnout temperature and the ignition temperature and burnout temperature of the pyrolysis product are higher than those of the pyrolysis product without water vapor when adding 60% water vapor. It can be seen that the appropriate
amount of water vapor addition would lead to the reduction of the ignition temperature and burnout temperature of the pyrolysis products, especially when the water vapor content is 40%. It indicated that the addition of water vapor makes the pyrolysis product (semicoke) easier to ignite, and its combustion performance has been improved. However, when a large amount of water vapor (60%) is introduced, the ignition temperature and burnout temperature increase and the combustion performance was further reduced.

Figure 3 shows the TG-DTG curves of the combustion reaction of semicoke and raw coal. They were pyrolyzed at different pyrolysis temperatures, and the atmosphere is air. Figure 3a is the TG-DTG curve of semicoke and raw coal. It can be seen that the semicoke has begun to lose weight at 380 °C under N₂ atmosphere, which indicates that the volatiles in the sample have begun to decompose. With the increase of the pyrolysis temperature, the weight loss of the semicoke increases obviously, caused by the rapid combustion of fixed carbon in the sample. In comparison of TG-DTG curves between semicoke and raw coal, the peak temperature and weight loss rate are higher with the increase of temperature indicating that the change of pyrolysis temperature affects the progress of the reaction.

In order to further clarify the effect of water vapor on the combustion performance of semicoke, TG-DTG curves of semicoke prepared at the same pyrolysis temperature and different water vapor content were plotted, as shown in Figure 4.

Combustion curves of semicoke prepared under different conditions are shown in Figure 4; the combustion TG curve of the pyrolysis products through adding water vapor in the pyrolysis process completed the reaction earlier than that of the samples under 0% water vapor condition. It can be seen from Figure 4a that the semicoke was obtained by pyrolysis under the condition that the water vapor content varies from 20% to 60% when the final temperature of pyrolysis is 500 °C. The DTG curve of the semicoke has a smooth U-shaped distribution, indicating that the volatile components of the prepared semicoke and the semicoke burn at the same time and the semicoke prepared by passing water vapor has a higher weight loss ratio. As shown in Figure 4b,c, the peak position of the DTG curve does not change much with water vapor content when the final pyrolysis temperature is 600 and 700 °C, respectively, indicating that the combustion reaction of semicoke has little effect on the water vapor content added in the preparation process. However, when the final pyrolysis temperature at 800 °C, as shown in Figure 4d, the peak position and size of TG-DTG curve change with water vapor content during semicoke preparation. It shows that the change of water vapor content has a great influence on the combustion performance of pyrolysis products under high-temperature conditions. When the water vapor content reaches 60%, the reaction reaches equilibrium last. To sum up, adding an appropriate amount of water vapor (20%, 40%) into the pyrolysis atmosphere can advance the combustion reaction of semicoke when the pyrolysis temper-
ature is low. The combustion reaction was more intense at the peak position of the DTG curve and ended earlier. However, a large amount of water vapor (such as 800 °C, 60%) will significantly delay the combustion of semicoke as the pyrolysis temperature increases, and the weight loss ratio would decrease dramatically, which may be related to the preparation fixed carbon lower of semicoke under this condition. Moreover, pore structure and surface functional groups also affect the combustion performance of semicoke.

2.2. Effect of Pyrolysis Final Temperature and Water Vapor Content on the Pore Structure of Semicoke. Relevant studies\(^\text{17}\) have shown that the changes in the combustion properties of pyrolysis products are related to pore structure.

2.2.1. Surface Area Analysis. The average pore diameter and specific surface area of the semicoke prepared under different water vapor and pyrolysis temperatures are shown in Table 2 and Figure 5.

As shown in Table 2 and Figure 5, the specific surface area and pore volume show similar variation. When the pyrolysis temperature is 500 °C, the amount of water vapor added in the pyrolysis process has little effect on the specific surface area and pore volume of the product. When the pyrolysis temperature is higher than 600 °C, the addition of water vapor has a significant effect on the specific surface area and
pore volume of the product. The addition of water vapor significantly reduces the specific surface area and pore volume when the pyrolysis temperature is 600 °C, whereas the addition of water vapor makes the specific surface area and pore volume of the pyrolysis product significantly larger when the pyrolysis temperature is higher than 600 °C. When the pyrolysis temperature increases, at 700 and 800 °C the specific surface and pore volume are positively correlated with the amount of water vapor added. However, when the water vapor content increases to 60% at 800 °C, the specific surface area and pore volume decrease, which may be one of the reason why the combustion performance of the pyrolysis products decreases obviously under this condition. When the pyrolysis temperature is low (such as 500 °C) in the active thermal decomposition stage of coal, the reactions are dominated by depolymerization and decomposition reactions at this stage. The volume change of coal in depolymerization and decomposition, instead of catalytic action of water vapor, mainly influences the specific surface area and pore volume during this period. As the pyrolysis temperature rises to 600 °C, the water vapor promotes the decomposition reaction to generate more gas phase (the analysis of the volatile is shown in Table 5), which should increase the specific surface area and pore volume, but the addition of water vapor at this time makes the production of liquid phase (tar) increase. However, the tar produced cannot be separate out in time and some pores are blocked, resulting in a decrease in specific surface area and pore volume after adding water vapor. When the temperature is higher than 700 °C, the pyrolysis of coal is mainly based on thermal polycondensation reaction, and the amount of tar precipitated is very slight with less volume of pyrolysis products and specific surface area. At this time, the effect of water vapor on hole-enlarging is fully reflected, and specific surface area and pore volume are proportional to the amount of water vapor. This is because that H₂O can diffuse into the internal pores of the semicoke, which enlarges the pore size. While when the temperature was at 800 °C, H₂O can react with the water gas on the carbon surface (C + H₂O → CO + H₂) to erode the carbon structure. If the added amount of water vapor is low, the specific surface area can be significantly increased. The specific surface area is instead reduced if a large amount of water vapor is added, (for example, when the amount of water vapor added is 60% at 800 °C) causing the collapse of pore wall and blocking the original pores.

2.2.2. SEM Analysis. The change rule of the pore structure of the pyrolysis semicoke was further explored by SEM, as shown in Figure 6.

It can be seen from Figure 6a,d that when the coal sample was pyrolyzed at 500 °C, the morphologies of the pore structure prepared by adding 60% water vapor and 0% water vapor were not obviously changed. When the pyrolysis temperature is 700 °C, fractures can be seen in Figure 6b with 60% water vapor and Figure 6e without water vapor, and as shown Figure 6b the fractures continue to develop. Large pore volume increases, pore walls break, and coal begins to harden. It can be seen from the morphology that the outside of the pores has collapsed. The reason for the change of pore development is the increase of pyrolysis temperature and the release of volatiles, and the collapse of surface pores is caused by the addition of water vapor. In order to further verify the effect of water vapor on the pyrolysis solid products under high-temperature conditions, the samples prepared by different water vapor additions (H₂O-0%, H₂O-60%) at 900 °C were subjected to SEM analysis. As shown in Figure 6f, the pyrolysis solid phase product prepared without adding water vapor is observed by SEM. There are many surface cracks and no obvious pores, which is because the thermal polycondensation resulted in a relatively smooth and dense surface structure on the surface of the sample when the pyrolysis temperature reached 900 °C. From Figure 6c, it can be seen that the pore structure on the surface of the coal

Table 2. Average Pore Size Total Pore Volume and BET Surface Area of Semicoke

| sample | specific surface area | total pore volume | average pore size |
|--------|-----------------------|-------------------|------------------|
|        | (m²/g)                | (cm³/g)           | (nm)             |
| 500 °C | 0.556                 | 0.005             | 9.574            |
| H₂O-0% | 0.604                 | 0.004             | 7.803            |
| H₂O-20%| 0.931                 | 0.005             | 8.397            |
| H₂O-40%| 0.525                 | 0.004             | 8.331            |
| H₂O-60%| 67.913                | 0.052             | 3.042            |
| 600 °C | 32.545                | 0.028             | 3.404            |
| H₂O-40%| 35.639                | 0.029             | 3.210            |
| H₂O-60%| 26.519                | 0.027             | 4.001            |
| 700 °C | 16.089                | 0.027             | 6.054            |
| H₂O-0% | 12.996                | 0.020             | 4.382            |
| H₂O-20%| 27.910                | 0.022             | 4.435            |
| H₂O-40%| 69.362                | 0.049             | 3.467            |
| H₂O-60%| 29.152                | 0.03              | 4.157            |
| 800 °C | 215.437               | 0.136             | 2.524            |
| H₂O-0% | 213.245               | 0.139             | 2.598            |
| H₂O-20%| 167.892               | 0.114             | 2.719            |
| H₂O-40%|                       |                   |                  |
| H₂O-60%|                       |                   |                  |

Figure 5. Relationship between water vapor content and specific surface area and pore volume at different temperatures
sample after the introduction of water vapor is significantly
different from that in Figure 6f. The organic and inorganic
substances on the surface of the sample are in a molten state,
and the pore diameter increases dramatically in the molten
state. This is the result of the combined action of the pyrolysis
polycondensation reaction and the water gas erosion reaction.
Thermal polycondensation causes the volume of the pyrolysis
product to shrink under high-temperature conditions, the
pores are reduced, and cracks are generated. The water gas
erosion causes the surface of the pyrolysis product to appear
molten, and excessive water vapor would lead to the erosion of
part of the pore walls. The increase of the pore size and the
collapse of part of the pore walls are therefore blocking the
original hole. Combined with the detection results of specific
surface area and pore volume, it can be seen that the increase
of water vapor can obviously make the pore structure of the
pyrolysis semicoke more developed under the condition of
medium- and low-temperature pyrolysis, which can promote
the pyrolysis process. However, a large amount of water vapor
is introduced at high temperatures, and it will erode the pore
wall, reduce the fixed carbon content of the product, and even
collapse the pore wall, making the physicochemical properties
of the pyrolysis product worse.

2.3. Effect of Pyrolysis Final Temperature and Water
Vapor Content on Carbon-Containing Functional
Groups on the Surface of Semicoke. The physicochemical
properties of coal pyrolysis products are affected by water
vapor, and the functional group changes are further analyzed
by X-ray photoelectron spectroscopy (XPS). The main
element in the molecular structure of coal is carbon. The
results of XPS shows that the changes of carbon-containing
functional groups in the samples were prepared under different
conditions. By fitting the tested carbon peaks (Figure 7), the
contents of C=C or C−H, C=O or C═O and O═C−O
carbon-containing groups are revealed. Table 3 shows the
change of these carbon-containing groups of 16 semicoke.

The surface occurrence state of carbon in pyrolysis products
is characterized by XPS. It can be seen from Table 3 that the
C=C content is positively correlated with pyrolysis temper-

ure. When the pyrolysis temperature is 800 °C, the C=C
content increases greatly; this is because coal undergoes
thermal polycondensing and side chain cyclizing as
pyrolysis temperature rises, resulting in an increase in

aromaticity. C−H content decreased with the increase of
pyrolysis temperature; this indicates that the volatile H2O,
CO2, CH4, H2, and CO comes from C−H groups.22 Under
the same temperature conditions, pyrolysis temperature has little
effect on others carbon-containing functional groups, and C=C
increases with the water vapor content increasing. This is
because during the low-rank coal combustion, reduction of
strong hydrophobic groups such as alkyl carbon resulted. With
the increase of water vapor content, C=O, C═O, and O═C−
O have an decreasing trend, and the decreasing of C═O or
O═C−O may be caused by hydrogen reacting with C═O.

When the temperature is below 800 °C, carbon content of
semicoke is not obviously affected by water vapor content.
With the increase of water vapor content, the temperature is
800 °C, and the carbon content of semicoke shows a
decreasing trend. This is because the surface and internal
H2O content of coal char increases, making it react with
carbon by water gas on the surface of the coal sample and
resulting in a significant decrease in carbon content; this

corresponds to the results of surface analysis. In summary,
adding excess water vapor at higher temperature will adversely
affect semicoke physical and chemical properties.

Figure 6. Scanning electron microscopy of sample at 500 °C, 700 °C, and 900 °C: (a−c) water vapor content 60%; (d−f) water vapor content 0%.

Figure 7. XPS C spectra of no. 1 coal sample.
3. CONCLUSIONS

(1) Low-pyrolysis temperature has little effect on volatiles and fixed carbon, while higher pyrolysis temperature and water vapor content have significant effects on volatiles and fixed carbon. An appropriate amount of water vapor (40%) at 800 °C promotes the removal of volatiles and the increase of fixed carbon. Excessive water vapor (60%) is not conducive to the removal of volatiles and fixed carbon, which would reduce the fixed carbon content and increase the proportion of ash.

(2) Pyrolysis temperature has a restraint effect on combustion performance of semicoke. Compared with the ignition temperature and burnout temperature of raw coal, the ignition temperature and burnout temperature of semicoke are higher with the increase of pyrolysis temperature, indicating that the combustion performance of semicoke decreases. An appropriate amount of water vapor (40%) can reduce the ignition temperature of semicoke, improve the semicoke combustion characteristics, and make it easier to ignite. Excess water vapor (60%) delays semicoke combustion, weight loss ratio decreased, and the combustion performance was affected.

(3) Water vapor has little effect on specific surface area and pore volume water vapor during low temperature. Water vapor has significant effects on pore structure when the pyrolysis temperature is at 600 °C and 700 °C. When the temperature is 600 °C, the addition of water vapor reduces the specific surface area and pore volume of semicoke. When the water vapor content is 40%, the specific surface area and pore volume of the semicoke reach the maximum value. When the temperature is 700 °C, the addition of water vapor makes the specific surface area and pore volume of the semicoke show an overall increasing trend. At higher temperatures (800 °C), physical and chemical properties of semicoke reduced with increasing water vapor content.

(4) High temperature and excess water vapor have significant effects on the surface structure and surface functional groups of the samples. Excessive water vapor (60%) at 900 °C causes water gas erosion on the sample surface to molten state. When the temperature is at 800 °C, surface carbon content of semicoke decreased significantly due to excess water vapor (60%). Therefore, the introduction of excess water vapor at a high temperature will adversely affect the physicochemical properties of semicoke.

In conclusion, excess water vapor should be avoided to enter the high temperature pyrolysis section during the process of quenching coke or it would have a detrimental impact on the semicoke performance.

4. EXPERIMENTS

4.1. Sample Selection and Preparation. Shaanxi shenmu bituminous coal were used in this study. The proximate analysis and sulfur contents are given in Table 4. Its volatilizing fraction is 39.28%, belonging to low rank coal. Pyrolysis apparatus is tube furnace TL1200 (Figure 8). When the pyrolysis temperature reaches 200 °C, water vapor is added and mixed with nitrogen, and the content of water vapor is 0%, 20%, 40%, and 60%. The final temperatures of the experiments are 500 °C, 600 °C, 700 °C, and 800 °C, respectively. The flow rate of N₂ is 500 mL/min with a heating rate of 10 °C/min in mixed atmosphere. The temperature was kept at a different final temperature for 30 min. The product cools to room temperature and the sample is removed to weigh it, pack with the label, and record. According to different preparation conditions, the products are recorded as 500 °C, 500 °C-20%...
Figure 8. Pyrolytic plant diagram.

H₂O, 500 °C-40%H₂O, 500 °C-60%H₂O, 600 °C, 600 °C-20% H₂O, 600 °C-40%H₂O, 600 °C-60%H₂O, 700 °C, 700 °C-20% H₂O, 700 °C-40%H₂O, 700 °C-60%H₂O, 800 °C, 800 °C-20% H₂O, 800 °C-40%H₂O, 800 °C-60%H₂O. Industrial analysis of all pyrolysis solid products is shown in Table 5.

Table 5. Proximate Analysis of Samples (wt %)

| number | samples | M_d | V_d | FC_d | A_d |
|--------|---------|-----|-----|------|----|
| 1      | 500 °C-0%H₂O | 1.31 | 11.84 | 75.68 | 11.17 |
| 2      | 500 °C-20%H₂O | 1.20 | 12.54 | 78.86 | 7.40 |
| 3      | 500 °C-40%H₂O | 1.09 | 11.89 | 77.33 | 9.69 |
| 4      | 500 °C-60%H₂O | 1.18 | 12.54 | 78.64 | 7.64 |
| 5      | 600 °C-0%H₂O | 0.89 | 5.84 | 85.02 | 9.50 |
| 6      | 600 °C-20%H₂O | 1.25 | 5.79 | 88.02 | 5.40 |
| 7      | 600 °C-40%H₂O | 0.94 | 5.71 | 89.02 | 4.69 |
| 8      | 600 °C-60%H₂O | 0.87 | 5.80 | 84.77 | 9.23 |
| 9      | 700 °C-0%H₂O | 1.65 | 3.43 | 86.27 | 8.56 |
| 10     | 700 °C-20%H₂O | 1.54 | 4.58 | 85.54 | 8.34 |
| 11     | 700 °C-40%H₂O | 1.73 | 3.79 | 82.93 | 11.55 |
| 12     | 700 °C-60%H₂O | 1.56 | 3.77 | 81.60 | 13.07 |
| 13     | 800 °C-0%H₂O | 1.43 | 2.68 | 89.92 | 6.26 |
| 14     | 800 °C-20%H₂O | 1.63 | 3.44 | 84.75 | 10.78 |
| 15     | 800 °C-40%H₂O | 1.15 | 5.29 | 76.43 | 18.36 |
| 16     | 800 °C-60%H₂O | 0.95 | 10.12 | 69.07 | 22.41 |

It can be seen from the industrial analysis results in Table 5 that with the increase of pyrolysis temperature, the volatile content of pyrolysis solid phase products decreases, and the content of fixed carbon increases. This is due to the increase of pyrolysis temperature, which leads to side chain bridges bonds, and functional groups in coal structures with thermally unstable structures fall off from the core structure and precipitate in the form of small molecule volatiles. The pyrolysis temperature reaches 500 °C, 600 °C, and 700 °C, the effect of water vapor content on volatiles and pyrolysis process is not obvious. When the pyrolysis temperature is higher (800 °C), the addition of a small amount of water vapor is beneficial to the volatile matter and ash deprivation and fixed carbon content increases. However, the high water vapor content is a disadvantage to the removal of volatile and ash. For the temperature at 800 °C and the water vapor content reaching 60%, the volatile matter and ash content of the solid phase product of pyrolysis increased significantly. It can be seen that the appropriate addition of water vapor during the pyrolysis process can promote the removal of volatile matter and increase the proportion of fixed carbon, but excessively high water vapor content will reduce the content of fixed carbon, thereby increasing the proportion of volatile matter and ash.

4.2. Experimental Instruments and Methods. A tube furnace (Figure 8) was used to prepare the samples. The speed of the reaction is related to the particle size. Therefore, the semicoke was ground to 200 mesh. The semifocal pore structure was measured for the relationship between pore volume and specific surface (specific surface and pore size analyzer (JW-BK222)). Thermogravimetry (STA449F3, Netzsch Instrument Inc., Germany) was used to analyze the combustion properties of the semicoke (8 mg ± 0.5 mg). The final temperature is 1000 °C, a heating rate of 10 °C/min in air atmosphere. Scanning electron microscopy (SEM) was used to analyze the surface morphology of the semicoke, and the effects of different pyrolysis temperatures and water vapor content on the pore structure of the semicoke were analyzed. The carbon-containing functional groups on the semifocal surface were analyzed by X-ray photoelectron spectroscopy (XPS). The detection conditions are hv = 1486.6 eV, the tube voltage is 15 kV, the tube current is 12 mA, and the step size is 0.05. Split peak and fit for the XPS spectrum of the C 1s orbital uses the XPS peak. By consulting the literature, the peaks of C 1s at (284.4 eV ± 0.5) eV, (285 ± 0.5) eV, (286.3 ± 0.5) eV, (287.61 ± 0.5) eV, and (289 ± 0.5) eV were assigned to In C=C, CH, C−O, C==O, and O==CO.

4.3. Data Analysis. The combustion performance of semicoke was analyzed by introducing T_i and T_f, and T_0, T_i, T_f are the ignition temperature and burn-out temperature of semicoke, determined through (TG−DTG) method.

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