



Investigation on the Distribution of Yimin Lignite Pyrolysis Products and the Stability of its Char

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ABSTRACT: This paper introduces the utilization of lignite in China and abroad and studies the influence of different process conditions on the pyrolysis products of lignite. The effects of pyrolysis temperature, residence time, and heating rate on the yield and stability of pyrolysis products were studied by standard lattice low-temperature distillation of coal. The results showed that the final pyrolysis temperature of lignite increases gradually, which is a key factor affecting the pyrolysis performance of lignite. At the same time, the combustible gas yield and tar yield were also significantly improved. Semichar yield and semichar volatile content showed a downward trend. From the range of pyrolysis products, the heating rate also has an important influence on the pyrolysis performance of lignite. Through the thermal stability test of lignite, it is concluded that the particle size distribution of carbon black products is not significantly different, and most of the coal particles are mainly distributed in the range of more than 6 mm.

1. INTRODUCTION

With the general trend of world economic development, the energy demand is increasing rapidly, and the impact of environmental pollution in the process of energy utilization is gradually increasing.^{1,2} Cleaning new energy, energy utilization, and reducing environmental pollution caused by energy use are priority issues for scientists around the world.^{3,4} High-quality coal is still dominant in the utilization of coal resources. With the rapid development of large industrial enterprises, the demand of coal is increasing, the consumption of high-quality coal such as bituminous coal and anthracite coal is increasing, and the supply has become increasingly challenging.⁵⁻⁷ Under this circumstance, the utilization of low rank coal such as lignite has also been studied.^{8,9} China has relatively abundant coal reserves, with oil, natural gas, and other energy sources. Low- and medium-rank coal accounts for 55% of the total coal reserves, of which lignite accounts for about 13%, mainly distributed in Inner Mongolia, Yunnan, Shanxi, and Shaanxi. Some domestic power plants have transformed lignite to achieve efficient and clean utilization of lignite, which is of great significance to alleviate energy supply problems and optimize China's energy structure.¹⁰⁻¹²

At present, coal combustion and power generation, gasification, liquefaction, pyrolysis, and so on are commonly used lignite utilization methods. The most common direct use is combustion. Therefore, the lignite produced by the lignite producing countries in the world is mainly used for the combustion power generation of pithead power stations. Only a small amount of coal is partially dried or made into briquette and transported to other places for various industrial boilers. Gasification is more acceptable for lignite upgrading than combustion. However, the disadvantage is that lignite is a kind of "three high and two low" coal. Many processes are not suitable for running large quantities of lignite as raw materials; there are still many problems and technical difficulties in the application process. The direct liquefaction of lignite is also called the deep conversion process of lignite (hydroliquefaction process). This is a utilization method with high technical requirements and high equipment requirements. In addition, the microbial treatment process of lignite will also become the main direction of future development. The

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microbial transformation of lignite is mainly the use of fungi, bacteria, and actinomycetes to achieve the dissolution of the lignite liquefaction process so that it can be transformed into soluble for water-related substances, special valuable chemicals and industrial additives, plant growth promoters, and clean fuels extracted from the water. Methane, methanol, and ethanol were produced from coal products after anaerobic microbial treatment. Oil can be replaced as clean fuel. At present, the lignite pyrolysis processes in China and abroad mainly include the fluidized-bed rapid pyrolysis process in Australia, the LR process of Germany, the multistage converter process in China, and the new, solid heat carrier distillation process. There are also the former Soviet Union semichar solid heat carrier lignite pyrolysis process and the United States series (4) fluidized-bed gas-solid heat carrier low-temperature fast pyrolysis process.^{13,14} The pyrolysis process not only changed the physical and chemical properties of lignite, fundamentally removed the moisture in coal, and effectively reduced the moisture content of lignite but also solved the problems of lignite spontaneous combustion and moisture reabsorption.15,1

The analysis, treatment, collection, and utilization of products and oil products from pyrolysis are the key to study the lignite pyrolysis technology, but pyrolysis products are affected by a series of reaction conditions (such as coal nature, reaction temperature, heating rate, reaction atmosphere, etc.).¹⁷ Yimin lignite has the characteristics of high moisture, high volatility, low calorific value, large porosity, spontaneous combustion, easy weathering and fragmentation, easy oxidation, etc. $^{18-20}$ If these properties of lignite can be comprehensively utilized, it will create a higher economic value and reduce environmental pollution.²¹ At present, the pyrolysis of coal is a key step in the classification process, widely used in coal gasification, liquefaction, combustion, and carboniza-22-24 2^{2-24} In China, how to reasonably use coal resources and tion.² economically and effectively improve coal utilization technology is particularly important.²⁵⁻²⁷ Yimin lignite is one of the typical coals suitable for pyrolysis conversion.^{28,29} During the pyrolysis process, the composition and structure of lignite changes, and the products include tar, combustible gas, and char products.^{30,31} Research in recent years has shown that char can be used as a new type of tar cracking catalyst or catalyst carrier. Its activity is affected by the specific surface area, pore volume, and alkali metal and alkaline earth metal content in semichar.^{32,33} The tar produced is formed by the condensation of many hydrocarbons and oxygen-containing compounds.³⁴ The main components are acidic phenols and polycyclic aromatic hydrocarbons with complex structures.^{35–37} In this paper, the pyrolysis mechanism, structural characteristics, and composition of lignite were analyzed by studying the pyrolysis temperature, pyrolysis atmosphere, heating rate, and residence time of final temperature of lignite.

These studies have important guiding significance for lignite combustion, gasification, liquefaction, and other conversion processes. In this paper, the effects of different final pyrolysis temperatures, residence time of final temperature, and different heating rates on the yield of pyrolysis products were discussed through the standard low-temperature distillation process and stability experiments. The industrial analysis results of semichar production, tar production, gas production and composition, pyrolysis water production, and semichar under different conditions were obtained.

2. RESULTS AND DISCUSSION

2.1. Effect of Different Final Reaction Temperatures on Pyrolysis Products. 2.1.1. Effect of Different Final



Figure 1. Effect of different temperature control ranges on combustible gases.

 Table 1. Effect of Different Temperature Control Intervals

 on Tar Yield



Figure 2. Study on the effect of different temperature control intervals on the volatile content and production of semichar.

Pyrolysis Temperatures on Pyrolysis Gas Production. In the pyrolysis system, the original lignite sample was kept at 20 g, the particle size was less than 0.2 mm, the residence time of final temperature was 15 min, and the heating rate was 5 °C/ min. Under the above conditions, on changing the temperature (450, 550, and 650 °C), the change of combustible gas in pyrolysis products was studied.

It can be observed from Figure 1 that when the pyrolysis temperature was lower, the proportion of CO production was larger, while the contents of CH_4 and H_2 were relatively low. When the pyrolysis temperature reached 550 °C, it can be seen that the three kinds of gas production had different degrees of

35

30

25

20

15

10

5

0

Total pyrolysis gas(%)



Figure 3. Study on the influence of residence time at different final temperatures on the production of combustible gas.







increase and CO still occupied a high proportion. When the pyrolysis temperature was increased to 650 °C, H₂ and CH₄ increased significantly, accounting for about 20%. Currently, the upward trend of CO was not very obvious and the proportion was not as high as that of the other two gases. The reason for this phenomenon was that when the pyrolysis temperature was low, the large proportion of CO was mainly due to the reaction between a small amount of O2 and combustible carbon in the device, and a small amount of O_2 was mainly derived from the oxygen element in lignite. However, due to the low reaction temperature of CH_4 and H_{24} lignite undergoes cracking, so the yield of CH₄ and H₂ was low. When the pyrolysis temperature was 550 °C, the main reason for the slight increase of the CO content was the decomposition of carbonyl and ether groups in the coal structure. As the final temperature of pyrolysis increases again,



total oil and water (g)	water quality (g)	tar quality (g)	semichar yield (g)
4.103	3.650	0.453	12.110
4.178	3.700	0.478	12.440
4.096	3.600	0.496	12.000
	total oil and water (g) 4.103 4.178 4.096	total oil and water (g) water quality (g) 4.103 3.650 4.178 3.700 4.096 3.600	total oil and water (g) water quality (g) tar quality (g) 4.103 3.650 0.453 4.178 3.700 0.478 4.096 3.600 0.496



Figure 6. Effects of different heating rates on semichar and semichar volatiles.

with the increase of final pyrolysis temperature, the decomposition reaction inside the coal is enhanced, and some methyl side chains, acid groups, and methylene bridge bonds are broken to form CH₄, which makes the proportion of CH₄ increase significantly at 650 °C. The source of H₂ was mainly the condensation of organic matter and the cyclization and aromatization of hydrocarbons. The sudden rise of H₂ was due to the increase of final pyrolysis temperature, which provides a certain energy basis for the condensation reaction of organic matter, the cyclization and aromatization of hydrocarbons, and other structural changes, resulting in an intensified condensation reaction and the secondary cracking of primary cracking products. Finally, it is concluded that with the gradual increase of final pyrolysis temperature, the yield of combustible gas increases significantly. Especially in the temperature range of 550-650 °C, the change of gas yield was more obvious. Therefore, it also shows that the final

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 CH_4

H,



Figure 7. Thermogravimetry (TG) with different heating rates.



Figure 8. DTA with different heating rates.

Table 4. Analysis of the Semichar Aperture under Different Final Temperatures

temperature (°C)	specific surface area (m²/g)	adsorption pore size (nm)	total pore volume for single- point adsorption (cm ³ /g)
450	50.07022	4.80563	0.05901
550	64.66517	4.08627	0.06635
650	120.51399	3.41492	0.06635

pyrolysis temperature was a crucial factor affecting the yield of combustible gas.

2.1.2. Effect of Different Final Pyrolysis Temperatures on Tar Yield. It can be seen from Table 1 that at 650 $^{\circ}$ C, the

pyrolysis tar yield of Yimin lignite (20 g) reaches the maximum and the tar output is 1.532 g. Compared with 550 $^{\circ}$ C, the tar yield directly increased from about 10% to about 30%. It can be concluded that under the condition of constant final temperature residence time and heating rate, the tar yield increases gradually with the increase of final temperature.

It also shows that with the deepening of pyrolysis, the amount of tar in coal gradually increases, and more functional groups are thermally decomposed.

According to relevant information, the temperature range of tar production is 300-600 °C, and the temperature of secondary pyrolysis of tar is about 500-600 °C. When the pyrolysis temperature reached 450 °C, the yield of tar increased greatly, and then the trend of the increase was

Та	ble	5.	Semichar	Stability	Test	Experiment	for	Lignite"	
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final temperature (°C)	accumulated gas flow (L)	tar and water production (g)	semichar yield (g)	particle size (mm)	particle size mass distribution (g)	distribution percentage (%)	volatile (%)
				>6	10.87	88.3	26.4
450	1.3	5.431	12.282	3-6	1.217	9.89	25.0
				<3	0.223	1.81	_
				total	12.31	100	_
				>6	10.903	94.86	12.6
550	1.8	5.386	11.476	3-6	0.459	3.99	_
				<3	0.132	1.15	_
				total	11.494	100	_
				>6	9.016	87.37	8.16
650	3.2	5.662	10.159	3-6	1.084	10.5	7.43
				<3	0.219	2.12	_
				total	10.319	100	_
an n	.11	1					

^a"—" in the table means that the quality is lower than the standard inspection quality.

more obvious. This phenomenon shows that the difference in tar yield between 550 °C and 650 °C may be because the gas tar component generated in the experiment does not undergo secondary cracking due to the influence of device insulation, which leads to the rapid condensation of the tar that should be pyrolyzed, resulting in a sudden increase in tar yield, or a short stay time at this temperature stage, leading to the lack of sufficient time for secondary cracking of tar, thus resulting in a sudden increase in tar yield. However, it needs to be affirmed that most of the tar collected in the experiment is only the tar components with a low molecular weight that can be vaporized and those tar components with a large molecular weight that can exist in liquid form are still left in the surface and pores of coal particles or are decomposed into small molecules by heating.

2.1.3. Effect of Different Final Pyrolysis Temperatures on the Contents of Semichar and Semichar. It can be seen from Figure 2 that the influence trends of different temperature control intervals on semichar yield (g) and semichar volatile content (%) were consistent.

With the increase of pyrolysis temperature, the semichar yield and semichar volatile content are gradually reduced. It can be observed from Figure 2 and Table 1 that the semichar yield of Yimin lignite is about 13.1 g at 450 °C and less than 12.5 g at 550 °C compared with 450 and 550 °C. The reason is that when the temperature is 450 °C, the water in coal and some functional groups with strong reactivity and poor thermal stability is mainly decomposed.

When the pyrolysis temperature increased to 550 $^{\circ}$ C, the polymerization reaction in the coal structure gradually intensified, more functional groups and various side-chain structures began to be thermally decomposed, and the yields of pyrolysis gas and tar increased. Therefore, the semichar production is greatly reduced with the increase of pyrolysis temperature. The volatile tar and gas content in raw coal samples also make the measured semichar volatile content to decrease gradually.

2.2. Effect of Residence Time of Final Temperature on Pyrolysis Products. 2.2.1. Effect of Residence Time at Different Terminal Temperatures on Gas Production. In the pyrolysis system, the original lignite sample was kept at 20 g, the particle size was less than 0.2 mm, the residence time of final temperature was 15 min, and the heating rate was 5 °C/ min. Under the above conditions, the final pyrolysis temper-

ature (450, 550, and 650 $^{\circ}$ C) was changed to study the change of combustible gas in pyrolysis products.

It can be seen from Figure 3 that when the residence time was 5 min, the proportion of CH₄ was the largest, while the content of H₂ was relatively small, and the content of CH₄ was maintained at about 11%. At 15 min, the two gases H₂ and CH₄ showed a slower upward trend, and the CO content showed a significant upward trend. The reason for this phenomenon was that with the pyrolysis final temperature of 550 °C, the extension of the residence time causes the functional groups, side chains, groups and bridges that have not been completely or uncracked in the first 5 min to continue to crack or start to break. This leads to an increase in the amount of gas produced. The CO mainly comes from the decomposition of carbonyl and ether groups, but the reactivity of carbonyl and ether groups is weak. Therefore, only when the pyrolysis temperature is high, the CO content increases. It can be seen from the figure that when the residence time was 25 min, the content of H₂ gradually increased, and the content of CH₄ and CO decreased again. Finally, H₂, CH₄, and CO were stabilized at about 6.5, 11.3, and 11.4, respectively.

The increase in the H_2 content was mainly due to the prolonged residence time, which intensifies the polycondensation reaction of organic matter and increases the tendency of hydrocarbon cyclization and aromatization. However, the effect of increasing the H_2 yield is not obvious, which may be mainly due to the excessive residence time of the coal sample at this fixed temperature stage, and the degree of H_2 overflowed completely at this constant temperature. The content of CH₄ was slightly reduced. In fact, the amount of CH₄ generated is still increasing, but because the output of other gases is greater, the proportion of CH₄ in the gas has no obvious upward trend.

The conclusion shows that the change of residence time of final temperature has little effect on the composition of lignite pyrolysis gas products. The influence of final pyrolysis temperature on the composition of lignite pyrolysis gas is greater than that of residence time on the composition of lignite pyrolysis gas.

2.2.2. Effect of Residence Time at Different Final Temperatures on Tar Yield. It is observed from Table 2 that under the condition of constant final pyrolysis temperature, with the extension of residence time, the tar yield increases to different degrees.

The reason for this situation was that with the extension of the residence time, the structure (functional groups, side chains, groups, etc.) that can be thermally decomposed under this final temperature condition was decomposed more and more completely, resulting in an increasing trend of the amount of tar obtained by condensation. Compared with the time when the residence time was 15 min, the tar output changed significantly, which was presumably due to the insufficient cracking of most of the functional groups that generated tar before 15 min. But between 15 and 25 min, the degree of lysis began to increase.

By comparing the results in Section 2.1, it can be concluded that the change of final pyrolysis temperature has the same influence trend on tar yield but the influence of changing residence time on the tar yield is relatively small. The results show that the residence time is not the key factor for the change of pyrolysis products.

2.2.3. Effect of Different Residence Times on Semichar and Semichar Volatiles. As can be seen from Figure 4the yield of char gradually decreases with the extension of residence time during pyrolysis. According to Figure 2 and Table 1, the yield of tar and the yield of pyrolysis gas gradually increase. It showed that the residence time was prolonged and the degree of pyrolysis at the final temperature was also deepened. At the same time, more functional groups were decomposed by heat or decomposed by heat more thoroughly and completely. As a result, the amount of tar precipitation increased, causing the amount of gas generated by pyrolysis to gradually increase, which is consistent with the principle of material conservation. From a practical point of view, the content of semichar volatiles at a residence time of 15 min has a reference value for industrial applications. If the volatile content of semichar is too high, it will limit the industrial application and usually coking occurs, and the material composition after combustion will be more complex. If the volatile content of char is too low, it means that the inflammable components in coal are less, which greatly reduces the calorific value and the utilization value of coal.

2.3. Effect of the Heating Rate on Pyrolysis Products. *2.3.1. Study on the Effect of Different Heating Rate on Pyrolysis Gas.* In the pyrolysis system, the pyrolysis conditions of raw lignite sample of 20 g, particle size of less than 0.2 mm, residence time of 15 min, and the effects of different heating rates (3, 5 and 7 °C/min) on combustible gases in pyrolysis products were studied.

As can be seen from Figure 5, as the heating rate increases, H_2 tends to decrease first and then increase. The trends of CO and CH₄ are declining. The reason is that the degree of pyrolysis of lignite decreases as the heating rate increases. Therefore, the time for lignite to reach high temperature is also shortened, and the final temperature residence time is 15 min. This series of reasons lead to insufficient secondary pyrolysis of lignite. With the increase of heating rate, the decreasing trend of CO is due to the deoxidation of oxygen-containing groups during coal pyrolysis. These CO are released only at the early stage of pyrolysis by a thermally unstable carboxyl group. The other oxygen-containing groups all form CO during the secondary cracking, but due to the increase of the heating rate, the time for the secondary cracking is shortened, so the CO content is gradually reduced.

2.3.2. Effect of Heating Rates on Tar Yield. It can be seen from Table 3 that the heating rate increases gradually, and the yield of tar also increases. The overall trend analysis shows that

the main reason is that the time to reach the final pyrolysis temperature is shorter and shorter with the increase of the heating rate in the pyrolysis process.

Short time effectively promoted the mass transfer and heat transfer process, thus reducing the occurrence of side reactions. At the same time, it also makes the volatile matter quickly leave the surface of the coal sample, further improving the yield of tar. In other words, the effect of heating rate on tar content of pyrolysis products mainly comes from the secondary reaction.

2.3.3. Effects of Different Heating Rates on Semichar and Semichar Volatiles. It can be seen from Figure 6 that the volatile content of semichar increases first and then decreases under the conditions of the heating rate of 3, 5, and 7 °C/min. The main reason is that the residence time of the coal sample in the dry distillation furnace is also gradually prolonged during the heating process under the condition that the heating rate is 3 °C/min, which directly leads to the deepening of the pyrolysis degree of the coal sample.

Through the analysis of the collected gas yield, more substances were obtained by volatilization. At the heating rate of 7 °C/min, the volatile content of semichar decreased compared with that of 5 °C/min, which was mainly due to the increase of the tar yield and heating rate, thereby increasing the residence time of volatile. In a high-temperature environment, secondary cracking is promoted. Therefore, compared with the heating rate of 5 °C/min, the volatile content of semichar will also decrease. However, when the heating rate continues to increase, the volatile matter decreases. Combining Figures 7 and 8 can show that the pyrolysis hysteresis is not proportional to the heating rate. When the heating rate is too fast, the effect on the volatile matter is not very significant.

2.3.4. Effect of Different Heating Rates on Coal Pyrolysis Kinetics. Considering that the thermogravimetric analysis instrument cannot separate and identify the heating rates of 3, 5, and 7 $^{\circ}C/min$, the main reason is that the step distance between the heating rates is too small. So, the experiment changed the heating rates to 5, 10, and 15 $^\circ C/min$ for thermogravimetric analysis and speculated that the mechanism is consistent with the small step distance. Figures 7 and 8 show the effects of different heating rates (5, 10, and 15 $^{\circ}$ C/min) on TG curves of coal pyrolysis. It can be seen from the figure that with the gradual increase of the heating rate in the experiment, the starting temperature and the ending temperature of the reaction both increased to varying degrees. The TG curve moves to the high-temperature side, causing thermal hysteresis. The main reason is that the pyrolysis of coal is an endothermic reaction, and at the same time due to the poor thermal conductivity of coal, the reaction takes some time to proceed and the volatiles are separated. When the heating rate increases, a part of the samples in the lignite is too late to volatilize and a part of the structure is too late to decompose. Therefore, it needs to volatilize, decompose, and react at a higher temperature, resulting in thermal hysteresis. It is observed from the figure that the experimental thermal hysteresis does not increase positively with the heating rate. When the heating rate is too fast, the increase of the starting temperature and the ending temperature of the TG curve is not obvious. At the same time, it is again confirmed that the change of the heating rate has an important influence on the pyrolysis reaction.

2.3.5. Pore Size Analysis of Semichar Products. Table 4 lists the specific surface area and pore size of the semichar under the conditions of the heating rate of 5 $^{\circ}$ C/min, residence

time of 15 min, and final temperatures of 450, 550, and 650 $^{\circ}$ C. It can be seen from Table 4 that when the final pyrolysis temperature increases, the pore size of the semichar gradually decreases, the specific surface area increases, and the pore is mainly medium. The main reason is that when the pyrolysis temperature is higher, the volatile content decreases, the pore size decreases, the specific surface area increases, and the pore size decreases, the specific surface area increases, and the pore size decreases, the specific surface area increases, and the pore size decreases, the specific surface area increases, and the pore size form a porous structure.

2.4. Research Results on Stability of Yimin Lignite Char. Using lignite particle size of 6-13 mm coal samples, in the preparation of about 5, 10, and 15% semichar volatile process conditions, each experiment used 20 g of coal samples for the pyrolysis experiment.

According to the analysis in Table 5, the selected semichar volatiles were approximately 5, 10, and 15%. The stability of Yimin lignite was tested. The particle size distribution of semichar at 450 and 650 °C was roughly the same. The semichar particles larger than 6 mm accounted for about 88% of the total semichar, the semichar particles between 3 and 6 mm accounted for about 10%, and the particles smaller than 3 mm accounted for only about 2%. Under the condition of 450 °C semichar volatile content, regardless of the particle size, the basic volatile content is about 25%. At 650 °C, the volatile content of char is about 7%. At 550 °C, the particle size distribution of char is as follows: the particle size of char larger than 6 mm is 94%, the particle size of char between 3 and 6 mm is 4%, and the particle size of char smaller than 3 mm is less than 2%. The volatile content of char larger than 6 mm is 12.6%.

3. CONCLUSIONS

- (1) When the final pyrolysis temperatures were 450, 550, and 650 °C, the residence time was 15 min, and the heating rate was 5 °C/min, yield of combustible gases increased significantly with the gradual increase of pyrolysis temperature, and the yield of tar also increased to varying degrees. The semichar yield and semichar volatiles showed a decreasing trend. This indicates that the final pyrolysis temperature is the key factor affecting the yield of pyrolysis products.
- (2) When the pyrolysis temperature was 550 °C, the heating rate was 5 °C/min, and the residence times were 5, 15, and 25 min, with the extension of residence time, the amount of flammable gas and tar increased slightly, and the corresponding semichar yield and semichar volatile content showed a weak downward trend. It is proved that changing the residence time is not an important factor affecting the pyrolysis products.
- (3) In the pyrolysis system, the tar yield increased gradually with the increase of the heating rate. The production of combustible gases varies considerably. This indicates that the change of the heating rate is also an extremely important factor affecting the yield of pyrolysis products.
- (4) In the stability test of lignite semichar, the process conditions with semichar volatiles of approximately 5, 10, and 15% were selected. When the pyrolysis temperatures were 450 and 650 °C, the particle size distribution of char yield was more than 6 mm accounting for about 88%, between 3 and 6 mm it was about 10%, and the particles less than 3 mm accounted for less than 0.5%. At 550 °C, most of the semichar particle size distribution was greater than 6 mm, and

only a small amount of distribution was between 3 and 6 mm and less than 3 mm.

4. EXPERIMENTAL PART

4.1. Materials. The raw material is lignite samples from Yimin City, Inner Mongolia, with high moisture content. To

Table 6. Gas Used in the Experiment

gas composition	concentration (%)	factory
N_2	99.999	Beijing Puxi General Instrument Co., Ltd.
Ar	99.2	Beijing Puxi General Instrument Co., Ltd.
H_2	99.999	Beijing Puxi General Instrument Co., Ltd.
Dry air		Beijing Puxi General Instrument Co., Ltd.
Standard gas	H ₂ —15.0%; CO—15.0%; CO ₂ — 20.0%; CH ₄ —10.1%; N ₂ —39.9%	Foshan Ke Di Co., Ltd.

reduce the influence of moisture in the coal on pyrolysis reaction gas, first, the coal was first dried at low temperatures. Then, the coal sample was crushed by a jaw crusher to form particles smaller than 0.2 mm in size. Finally, it was sealed and stored for future use. The experimental gas parameters are shown in Table 6.

Acetone: after collecting pyrolyzed tar, the tar is separated by rotary evaporation.

Toluene: used to the determine the moisture in the pyrolysis condensates.

4.2. Experimental Methods and Instruments. The pyrolysis experiment was carried out using the standard low-temperature dry distillation process of Gejin. The experimental device is shown in Figure 9. The experimental method, principle, and steps of this device were the the same as those used in the temperature distillation experiment of Chinese national standard coal. The corresponding pyrolysis products were obtained by changing the final pyrolysis temperature, heating rate, and final temperature residence time by analyzing the generation of combustible gases (three gases of H_2 , CO, and CH_4), the generation of tar, the generation of semichar, and the generation of pyrolysis water and semichar volatiles; the corresponding experimental parameters were obtained.

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Figure 9. Pyrolysis equipment. 1—furnace; 2—quartz tube; 3—flask; 4—cooling tank; 5—filter; 6—mass flowmeter; 7—gas collection gag; and 8—gas chromatography.

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Notes

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REFERENCES

(1) Zhang, L.; Gao, H.; Chang, X.; Zhang, L.; Wen, X.; Wang, Y. S. An application of green surfactant synergistically metal supported cordierite catalyst in denitration of selective catalytic oxidation. *J. Cleaner Prod.* **2020**, *249*, No. 119307.

(2) Lei, Z.; Yang, J.; Lei, Z.; Huibin, H.; Chao, Y.; Min, L.; Lintian, M. Preparation of soybean oil factory sludge catalyst by plasma and the kinetics of selective catalytic oxidation denitrification reaction. *J. Cleaner Prod.* **2019**, *217*, 317–323.

(3) Wang, H.; Zhao, H. Y.; Bo, G. Z. Existing forms and changes of nitrogen inside of horizontal subsurface constructed wetlands. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 771–781.

(4) Ali, A.; Zhao, C. Direct liquefaction techniques on lignite coal: A review. *Chin. J. Catal.* **2020**, *41*, 375–389.

(5) Bi, C. Y.; Wang, X.; You, Q.; Liu, B. Y.; Li, Z.; Zhang, J. B.; Hao, Q. Q.; Sun, M.; Chen, H. Y.; Ma, X. X. Catalytic upgrading of coal pyrolysis volatiles by Ga-substituted mesoporous ZSM-5. *Fuel* **2020**, 267, No. 117217.

(6) Liu, L.; Gong, Z. Q.; Wang, Z. B.; Zhang, H. T. Study on combustion and emission characteristics of chars from low-temperature and fast pyrolysis of coals with TG-MS. *Environ. Eng. Res.* 2020, 25, 522–528.

(7) Chang, S. Q.; Zhang, Z. K.; Cao, L. X.; Ma, L. Q.; You, S. M.; Li, W. L. Co-gasification of digestate and lignite in a downdraft fixed bed gasifier: Effect of temperature. *Energy Convers. Manage.* **2020**, *213*, No. 112798.

(8) Gai, H. J.; Zhang, X. W.; Chen, S.; Wang, C.; Xiao, M.; Huang, T. T.; Wang, J.; Song, H. B. An improved tar-water separation process of low-rank coal conversion wastewater for increasing the tar yield and reducing the oil content in wastewater. *Chem. Eng. J.* **2020**, *383*, No. 123229.

(9) Ren, J.; Liu, Y. L.; Zhao, X. Y.; Cao, J. P. Biomass thermochemical conversion: A review on tar elimination from biomass catalytic gasification. *J. Energy Inst.* **2020**, *93*, 1083–1098.

(10) Kanca, A. Investigation on pyrolysis and combustion characteristics of low quality lignite, cotton waste, and their blends by TGA-FTIR. *Fuel* **2020**, *263*, No. 116517.

(11) Li, X. H.; Li, H. J.; Wang, R. Q.; Feng, J.; Li, W. Y. Acid pretreatment effect on oxygen migration during lignite pyrolysis. *Fuel* **2020**, *262*, No. 116650.

(12) Liu, H. P.; Chen, T. P.; Fang, L. X. Evolution of char structure during non-isothermal low temperature pyrolysis of Zhun Dong coal by microwave heating: A comparative study with conventional heating. *J. Energy Inst.* **2020**, *93*, 1195–1206.

(13) Savuto, E.; May, J.; Di Carlo, A.; Gallucci, K.; Di Giuliano, A.; Rapagna, S. Steam Gasification of Lignite in a Bench-Scale Fluidized-Bed Gasifier Using Olivine as Bed Material. *Appl. Sci.* **2020**, *10*, No. 2931.

(14) Mochizuki, Y.; Ma, J.; Kubota, Y.; Uebo, K.; Tsubouchi, N. Production of high-strength and low-gasification reactivity coke from low-grade carbonaceous materials by vapor deposition of tar. *Fuel Process. Technol.* **2020**, *203*, No. 106384.

(15) Rybicki, M.; Marynowski, L.; Simoneit, B. R. T. Composition of organic compounds from low-temperature burning of lignite and their application as tracers in ambient air. *Chemosphere.* **2020**, *249*, No. 126087.

(16) Hao, W.; Jia, W.; G. Z. B; Shuang, R. W.; L. T. L. Degradation of pollutants in polluted river water using Ti/IrO_2 - Ta_2O_5 coating electrode and evaluation of electrode characteristics. *J. Cleaner Prod.* **2020**, 273, No. 123019.

(17) Hao, W.; Bing, X. Q.; Guo, Z. B.; Yao, Z. Z.; Lu, L.; Jian, S. Z.; Xin, Y. Z.; Chun, H. Z. Advanced oxidation treatment of dissolved organic matter from wastewater treatment plant secondary effluent using scattering electrical reactor. *J. Cleaner Prod.* **2020**, 267, No. 122258.

(18) Sadasivam, S.; Zagorscak, R.; Thomas, H. R.; Kapusta, K.; Stanczyk, K. Experimental study of methane-oriented gasification of semi-anthracite and bituminous coals using oxygen and steam in the context of underground coal gasification (UCG): Effects of pressure, temperature, gasification reactant supply rates and coal rank. *Fuel* **2020**, *267*, No. 122258.

(19) Santamaria, L.; Arregi, A.; Lopez, G.; Artetxe, M.; Amutio, M.; Bilbao, J.; Olazar, M. Effect of La_2O_3 promotion on a Ni/Al2O3 catalyst for H-2 production in the in-line biomass pyrolysis-reforming. *Fuel* **2020**, 262, No. 116593.

(20) Liu, R. T.; Liu, M.; Han, X. Q.; Yan, J. J. Drying characteristics and kinetics analyses for Yimin lignite at various temperatures *Drying Technol.* 2020, DOI: 10.1080/07373937.2020.1729174.

(21) Tahmasebi, A.; Maliutina, K.; Matamba, T.; Kim, J. H.; Jeon, C. H.; Yu, J. L. Pressurized entrained-flow pyrolysis of lignite for enhanced production of hydrogen-rich gas and chemical raw materials. *J. Anal. Appl. Pyrolysis* **2020**, *145*, No. 104741.

(22) Zhang, L.; Shu, H.; Jia, Y.; Zhang, L.; Xu, D. Study on Solid Waste Pyrolysis Coke Catalyst for Catalytic Cracking of Coal Tar. *Int. J. Hydrogen. Enery.* **2020**, *45*, 19280–19290.

(23) Zhang, L.; Jia, Y.; Shu, H.; Zhang, L.; Wen, X.; Luo, M.; Wang, Y. S.; Xu, D. Application of Surfactant-modified Cordierite-based Catalysts in Denitration Process. *Fuel* **2020**, *268*, No. 117242.

(24) Lei, Z.; Hao, S.; Lei, Z.; Yang, J. Gas modified pyrolysis coke for in-situ catalytic cracking of coal tar. *Acs. Omega.* **2020**, *5*, 14911–14923.

(25) Zhang, L.; Chen, J. H.; Lei, Z.; He, H. B.; Wang, Y. S.; Li, Y. H. Preparation of soybean oil factory sludge catalyst and its application in selective catalytic oxidation denitration process. *J. Cleaner Prod.* **2019**, 225, 220–226.

(26) Wang, H.; Wang, J.; Lu, H.; Bo, G. Z.; Zhang, X. Y.; Cao, Y. Q.; L L; Zhang, J. S.; Zhang, W. Analysis of coating electrode characteristics in the process of removing pollutants from wastewater. *Fresenius Environ. Bull.* **2020**, *29*, 715–721.

(27) Song, Q.; Zhao, H. Y.; Jin, W. J.; Zhang, F.; Wang, Z. P.; Wen, Lv.; Li, Y.; Zhang, W.; Zhang, Y.; Shu, X. Q. Characterization of the products obtained by pyrolysis of oil sludge with steel slag in a continuous pyrolysis-magnetic separation reactor. *Fuel* **2019**, *255*, No. 115711.

(28) Song, Q.; Zhao, H. Y.; Jia, L. W.; Yang, L.; Lv, W.; Bao, J. W.; Shu, X. Q.; Gu, Q. X.; Zhang, P. Pyrolysis of municipal solid waste with iron-based additives: A study on the kinetic, product distribution and catalytic mechanisms. *J. Cleaner Prod.* **2020**, *258*, No. 120682.

(29) Song, Q.; Zhao, H. Y.; Jia, L. W.; Yang, L.; Lv, W.; Gu, Q. X.; Shu, X. Q. Effects of demineralization on the surface morphology, microcrystalline and thermal transformation characteristics of coal. *J. Anal. Appl. Pyrolysis* **2020**, *145*, No. 104716.

(30) Zhao, H. Y.; Li, Y. H.; Song, Q.; Liu, S. C.; Yan, J.; Ma, Q. X.; Ma, L.; Shu, X. Q. nvestigation on the thermal behavior characteristics and products composition of four pulverized coals: Its potential applications in coal cleaning. *Int. J. Hydrogen Energy* **2019**, *44*, 23620– 23638.

(31) Zhao, H. Y.; Song, Q.; Liu, S. C.; Li, Y. H.; Wang, X. H.; Shu, X. Q. Study on catalytic co-pyrolysis of physical mixture/staged pyrolysis characteristics of lignite and straw over an catalytic beds of char and its mechanism. *Energy Convers. Manage.* **2018**, *161*, 13–26.

(32) Zhao, H. Y.; Li, Y. H.; Song, Q.; Liu, S. C.; Ma, Q. X.; Shu, X. Q.; et al. Catalytic reforming of volatiles from co-pyrolysis of lignite blended with corn straw over three different structures of iron ores. *J. Anal. Appl. Pyrolysis* **2019**, *144*, No. 104714.

(33) Zhang, J. H.; Sun, G.; Liu, J. Y.; Evrendilek, F.; Buyukada, M. Co-combustion of textile dyeing sludge with cattle manure: Assessment of thermal behavior, gaseous products, and ash characteristics. *J. Cleaner Prod.* **2020**, 253, No. 119950.

(34) Chen, J. C.; Zhang, J. H.; Liu, J. Y.; Yao, H.; Evrendilek, F.; Buyukada, M.; Xie, W. M.; Sun, S. Y. Co-pyrolytic mechanisms, kinetics, emissions and products of biomass and sewage sludge in N_2 , CO₂ and mixed atmospheres. *Chem. Eng. J.* **2020**, 397, No. 125372.

(35) Qiang, S.; Hong, Y. Z.; Sheng, Q. C.; Li, Y.; Fang, Z.; Xin, Q. S.; Peng, Z. Study on the catalytic pyrolysis of coal volatiles over hematite for the production of light tar. *J. Anal. Appl. Pyrolysis* **2020**, *151*, No. 104927.

(36) Zhuo, Y. T.; Shen, Y. S. Modelling of the pyrolysis of low-rankcoal briquettes in an industrial-scale gas heat carrier pyrolyzer. *Powder Technol.* **2020**, 361, 52–61. (37) Wang, Y.; Liu, B.; Qi, Y. A risk evaluation method with an improved scale for tunnel engineering. *Arabian J. Sci. Eng.* **2018**, 23, 2053–2067.