

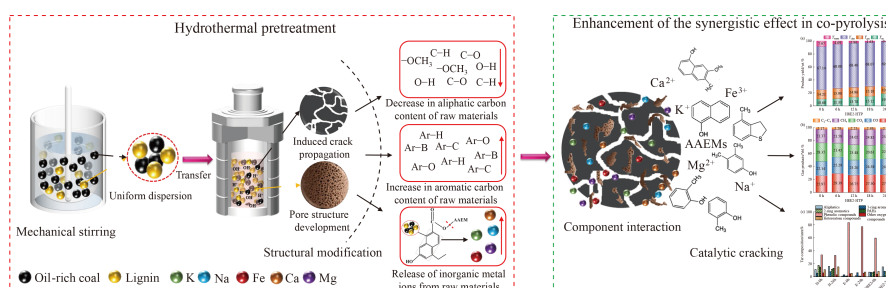
Study on the mechanism of enhanced synergistic effect in co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin by hydrothermal pretreatment

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Abstract: Co-pyrolysis of oil-rich coal and biomass is an effective approach to maximize the oil and gas production from oil-rich coal. To address the challenge of unclear mechanisms for the enhancement of



synergistic effects during the co-pyrolysis of oil-rich coal and biomass, a Huangling coal (H) and an enzymatic hydrolysis lignin (E) were used as the research samples and the structural evolution of raw materials and those by hydrothermal pretreatment (HTP) was systematically investigated using a suite of techniques such as proximate analysis, ultimate analysis, scanning electron microscopy (SEM), inductively coupled plasma optical emission spectrometry (ICP-OES) and nuclear magnetic resonance (¹³C-NMR). Combined with fixed-bed pyrolysis experiments, the mechanism by which hydrothermal pretreatment strengthens the co-pyrolysis synergistic effect of the Huangling coal and enzymatic hydrolysis lignin blend was explored. The results indicate that after hydrothermal pretreatment, the oxygen content of the raw materials decreases, the pore structure becomes more developed, and the concentrations of inorganic metal ions (e.g., calcium, potassium, and iron) in the aqueous phase increase. The structure of Huangling coal and enzymatically hydrolyzed lignin undergoes significant modification, with the contents of aliphatic carbon, aromatic carbon and carbonyl/carboxyl carbon in enzymatically hydrolyzed lignin approaching those in Huangling coal, and with the bridge carbon ratio increasing, resulting in improved thermal stability for the enzymatically hydrolyzed lignin and a pyrolysis temperature approaching that of Huangling coal. By the hydrothermal pretreatment, the co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin generally exhibit an increase in tar yields. When the H/E ratio is 8:2 and hydrothermal pretreatment is conducted for 24 h, the co-pyrolysis tar yield increases by 80.52%, with significant increases in the contents of aliphatic compounds and monocyclic aromatic hydrocarbons in the tar. Meanwhile, the yields of H₂, CO and CH₄ in the gas increase by 5.47%, 10.98% and 9.27%, respectively, the generation of CO₂ and pyrolysis water is inhibited, and the pore structure of semi-coke is enriched. This is primarily attributed to the multiple mechanisms of “component interaction-structural modification-catalytic cracking” during hydrothermal pretreatment, which enhance the co-pyrolysis synergistic effect of the H/E blend. The findings provide theoretical support for developing the technologies to enhance the co-pyrolysis synergistic effect between oil-rich coal and biomass, and expand new avenues for the low-carbon, high-quality utilization of oil-rich coal.

Key words: co-pyrolysis; synergistic effects; hydrothermal pretreatment; multiple mechanisms; high-quality

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The direct pyrolysis conversion of oil-rich coal faces the problems such as poor tar quality, low yield, and low economic benefits^[1–2]. Therefore, in the context of the “dual-carbon” era, the high-value utilization of oil-rich coal is of great significance for achieving the sustainable development of resources and the environment. Coal and biomass co-pyrolysis is an effective approach to realize the low-carbon and efficient conversion of coal. Owing to its “hydrogen-rich” characteristic, biomass can serve as a high-quality hydrogen source during co-pyrolysis with coal, which is conducive to the hydro-upgrading of coal pyrolysis tar and the degradation of heavy components. Meanwhile, biomass has low nitrogen and sulfur contents, so it also helps reduce the emission of pollutant gases^[3–4]. Biomass is mainly composed of cellulose, hemicellulose and lignin^[5], among which lignin is a unique source of renewable aryl compounds in nature. Lignin not only has a wide range of sources and huge output, and the global pulp and paper industry alone produces 150–180 million tons of waste lignin annually. Furthermore, lignin also possesses unique chemical properties such as a high H/C ratio, and its aromatic structure is similar to that of coal. This lays a structural foundation for the synergistic transformation of coal and lignin^[6–8].

Enzymatic hydrolysis lignin is a byproduct generated during the production of fuel ethanol via biomass refining^[9–10]. In recent years, with the growing attention to the replacement of traditional fossil fuels with biomass-based fuel ethanol, the yield of enzymatic hydrolysis lignin has been increasing annually. Additionally, compared with lignosulfonates, alkaline lignin, and other types of lignin, enzymatic hydrolysis lignin retains a large number of active groups such as phenolic hydroxyl groups and alcoholic hydroxyl groups due to its mild preparation conditions^[11], which endows it with greater advantages in the synergistic transformation with coal. For instance, Fan et al.^[12] found that during the co-pyrolysis of lignin and coal, lignin promoted the tar formation and inhibited the pyrolysis gas generation. Meanwhile, it led to a more complex surface morphology of the co-pyrolysis char, and the fractal dimension of the char from individual pyrolysis was smaller than that from co-pyrolysis. Byambajav et al.^[13], in their study on the co-pyrolysis of enzymatic hydrolysis lignin and coal, observed that in the co-pyrolysis, the yields of pyrolysis gas and char were lower than the predicted values, while the tar yield increased slightly. Moreover, various compounds such as fatty alcohols, aldehydes and ketones were detected in the tar components, which were not found in the tar from the individual pyrolysis of coal. However, some researchers have also found that the co-pyrolysis process of coal and biomass is highly complex, influenced by multiple factors, and may have no or insufficient significant synergistic effect^[14]. This is mainly due to the significant differences in their overall structures, mismatched pyrolysis temperature ranges, and insufficient interfacial contact^[15–16]. Therefore, there is an urgent need to explore a method and a mechanism for enhancing the

synergistic effect of coal-biomass co-pyrolysis, so as to realize the low-carbon and high-value utilization of oil-rich coal.

As an efficient pretreatment method^[17], hydrothermal pretreatment holds significant potential for enhancing the synergistic effect of coal-biomass co-pyrolysis. The core mechanism of hydrothermal treatment lies in the fact that in a high-temperature and high-pressure aqueous environment, hydrothermal action can promote the cleavage of some chemical bonds in coal and biomass, generating more active sites and small molecular fragments, thus reducing the activation energy of the pyrolysis reaction. Meanwhile, it improves the internal pore structure of samples and increases the specific surface area through the swelling effect, creating a favorable condition for heat transfer and the diffusion of reactants and products. Furthermore, it can also remove some impurities and moisture, reducing their adverse effects on the pyrolysis process^[18]. Specifically, hydrothermal pretreatment can optimize the composition and structure of coal and make the pores more developed^[19]. For lignin, hydrothermal pretreatment can not only increase the pore structure, but also destroy its complex three-dimensional network structure, reduce the degree of macromolecular polymerization, fully expose the originally encapsulated active functional groups, and greatly enhance the chemical activity of lignin^[20–22]. Therefore, hydrothermal pretreatment is expected to become an effective method for enhancing the synergistic effect of coal-biomass co-pyrolysis.

Thus, a Huangling coal and an enzymatic hydrolysis lignin were taken as the research objects, addressing the problems of low synergistic efficiency and unclear understanding of the action mechanism in coal-biomass co-pyrolysis. By adopting the hydrothermal pretreatment method, the co-pyrolysis characteristics of oil-rich coal and lignin were examined, and the effects of hydrothermal pretreatment on the structure and composition of oil-rich coal and lignin were systematically investigated. Meanwhile, combined with the fixed-bed pyrolysis experiments, the enhancement mechanism of hydrothermal pretreatment on the co-pyrolysis synergistic effect of Huangling coal-enzymatic hydrolysis lignin blends was explored, aiming to provide a solid theoretical basis and practical guidance for the efficient synergistic conversion and utilization of oil-rich coal and biomass.

1 Experimental

1.1 Raw materials

A Huangling coal sample was collected from the No. 2 Coal Seam of Ruinen Coal Mine, Huangling Coal Industry Group Co., Ltd., and is abbreviated as H in this paper. A raw enzymatic hydrolysis lignin was purchased from the Shandong Longli Biomass Technology Co., Ltd. Since raw enzymatic hydrolysis lignin exhibits weak acidity, the

research sample was repeatedly washed with deionized water until neutrality for subsequent use, and is abbreviated as E in this paper. Before the experiment, all raw materials were crushed, ground, and sieved to a particle size of less than 0.074 mm, then dried at 105 °C and stored in a desiccator for subsequent use.

1.2 Hydrothermal pretreatment experiments

1.2.1 Preparation of as-prepared blends, boiling pretreatment, and acid-washing pretreatment

Preparation of as-prepared blends: An appropriate amount of Huangling coal (H) and enzymatic hydrolysis lignin (E) was weighed according to different mass ratios. The materials were then placed in a mortar, ground and stirred until the color was uniform, and the mixed sample was subsequently sieved to a particle size of less than 0.074 mm. Finally, the sample was dried in an oven at 105 °C to obtain a blend sample denoted as H_xE_y (where *x* and *y* denote the mass ratios of H to E; for example, H8E2 indicates an 8:2 mass ratio of H to E). These blend samples were stored in a desiccator for subsequent use, and they are the same samples prepared by mechanical stirring in subsequent sections.

Boiling pretreatment: 10 g of the research samples were weighed, including Huangling coal, enzymatic hydrolysis lignin, and H8E2 blend samples. The samples were then placed in a beaker, 50 mL of deionized water was added, and subsequent boiling pretreatment was conducted at 110 °C for 24 h. Finally, the samples were dried, ground, and sieved to a particle size of less than 0.074 mm, then stored in a desiccator for subsequent use. This pretreatment method is named BLP-24 h.

Acid-washing pretreatment (PT): An appropriate amount of H8E2 blend sample was weighed and placed in a beaker. A mixed solution of hydrofluoric acid and hydrochloric acid with a volume ratio of 1:3 (liquid-to-solid ratio of 5:1) was added, and the sample was stirred and soaked at 80 °C (2000 r/min, 6 h). After soaking, the sample was washed repeatedly with deionized water until the pH value of the filtrate was neutral. Finally, the sample was dried, ground, and sieved to a particle size of less than 0.074 mm, then stored in a desiccator for subsequent use. This pretreatment method is named PT.

1.2.2 Hydrothermal pretreatment

Samples for the hydrothermal pretreatment include Huangling coal, enzymatic hydrolysis lignin, original blend samples H_xE_y, and the H8E2 blend samples by acid washing pretreatment. 10 g of each sample was weighed and placed in a beaker. 50 mL of deionized water was added, and after sufficient dispersion with mechanical stirring (2000 r/min, 1 h), the mixture was transferred to a

reaction kettle and subjected to the hydrothermal pretreatment at 180 °C for 6, 12, 18, or 24 h. After the completion of hydrothermal pretreatment, the mixed solution was transferred to a beaker and dried in an oven at 105 °C. Finally, the solid sample was crushed, ground, and sieved to a particle size of less than 0.074 mm, and then stored in a desiccator for subsequent use. Preliminary pre-experiments showed that the solid products of Huangling coal, enzymatic hydrolysis lignin, and their blends exhibited the maximum mass loss after 24 h of hydrothermal pretreatment. Under this condition, the yields of solid products for Huangling coal and enzymatic hydrolysis lignin were 98.97% and 83.33%, respectively, while the yields of solid products for blends H8E2, H5E5 and H2E8 were 94.71%, 89.23% and 85.49%, respectively.

1.2.3 Pyrolysis experiments

Pyrolysis experiments of different samples were conducted using the experimental apparatus shown in Figure 1. For each experiment, 10 g of the sample to be pyrolyzed was taken, including the samples by the hydrothermal pretreatment and the original samples without hydrothermal pretreatment. The fixed-bed aluminum alloy reaction tube used in the experiment has an inner diameter of 15 mm and a length of 550 mm. In the pyrolysis experiment, a programmed temperature rise method was adopted, with a heating rate of 10 °C/min and a final pyrolysis temperature of 650 °C; after the temperature reached 650 °C, the reaction was maintained for 1 h. Before the temperature rise, the air inside the reaction device was first purged with carrier gas N₂ for 5 min, and then the airtightness of the device was checked. The experimental device was started only after the carrier gas flow rate was stabilized at 100 mL/min. During the temperature rise process, the gas generated by pyrolysis began to be collected when the temperature of the reaction tube reached 200 °C. During pyrolysis, the resulting tar enters a collection tank inside the cooling pump along with the carrier gas and condenses into an oil-water mixture. Tar dehydration was carried out in accordance with the standard GB/T 480—2010 to obtain the mass of pyrolysis tar and the mass of water. The mass of the solid product (semi-coke) was measured directly by weighing the residue in the reaction tube, while the mass of the gaseous product was calculated using the difference method, i.e., mass of gas = total mass of raw material – mass of solid product – mass of liquid product (tar and pyrolysis water). In addition, the calculation formulas for the yields of the four pyrolysis products (semi-coke, tar, pyrolysis water, and pyrolysis gas) are specifically shown below.

Semi-coke yield:

$$Y_{\text{char}} = \frac{m_{\text{char}} - m_{\text{Ad}}}{m(1 - M_{\text{ad}} - A_{\text{ad}})} \times 100\% \quad (1)$$

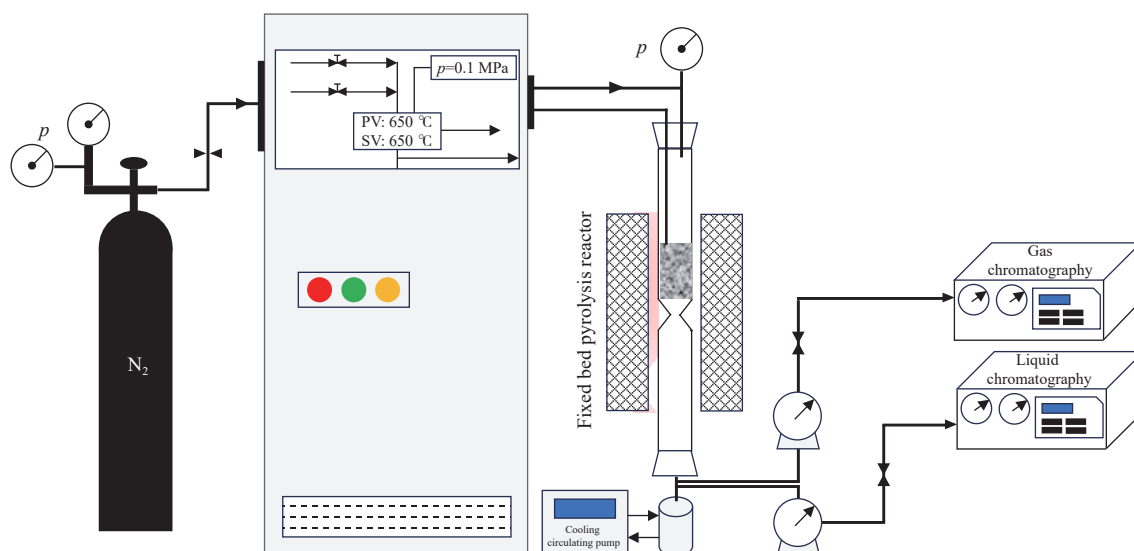


Fig. 1 Schematic diagram of the pyrolysis experimental setup

Pyrolysis water yield:

$$Y_{\text{water}} = \frac{m_{\text{water}} - m_{\text{Mad}}}{m(1 - M_{\text{ad}} - A_{\text{ad}})} \times 100\% \quad (2)$$

Tar yield:

$$Y_{\text{tar}} = \frac{m_{\text{liquid}} - m_{\text{water}}}{m(1 - M_{\text{ad}} - A_{\text{ad}})} \times 100\% \quad (3)$$

Gas yield:

$$Y_{\text{gas}} = 1 - Y_{\text{char}} - Y_{\text{water}} - Y_{\text{tar}} \quad (4)$$

where m , m_{char} , m_{liquid} and m_{water} represent the mass of the sample used (air-dried basis), semi-coke, liquid products (tar and pyrolysis water), and pyrolysis water, respectively; A_{ad} and M_{ad} denote the ash content and moisture content in the sample, respectively. To ensure the reliability and accuracy of the experimental data, each group of pyrolysis experiments was replicated 3 times, and the experimental errors were calculated using the standard deviation. The results showed that the yield errors of pyrolysis water, semi-coke, tar and pyrolysis gas did not exceed $\pm 0.35\%$, $\pm 0.28\%$, $\pm 0.42\%$ and $\pm 0.31\%$, respectively.

1.3 Analytical and characterization methods

1.3.1 SEM analysis

The microstructure of the materials was characterized using a scanning electron microscope (Zeiss Sigma 300, Germany). An appropriate amount of sample was adhered to the surface of a conductive tape, then placed on a sample holder, and the adhered particles on the conductive tape were blown off using a rubber bulb.

1.3.2 ICP-OES analysis

Inductively coupled plasma optical emission

spectrometry (ICP-OES, Model 715-ES, USA) was used for the quantitative analysis of metal ion concentrations in the materials. After the solution obtained from the hydrothermal pretreatment of the sample was diluted 100-fold with ultrapure water, it was filtered through a $0.45 \mu\text{m}$ filter membrane, and 25 mL of the filtrate was taken. A calibration curve was established using standard solutions with a concentration gradient of 0.1–10 mg/L. Under the conditions of a plasma power of 1500 W and a nebulizer gas flow rate of 0.7 L/min, the emission intensities at characteristic wavelengths were determined, and the ion concentrations were calculated.

1.3.3 ^{13}C -NMR analysis

The structural information of carbon atoms in coal was detected using a solid-state nuclear magnetic resonance spectrometer (AVANCE NEO 600M, Bruker Corporation, Germany) equipped with a MAS DVT probe. The resonance frequency was 150 MHz, and the rotation frequency was 14 kHz. Using Cross-Polarization Magic Angle Spinning (CP/MAS) and Total Sideband Suppression (TOSS) techniques, with a contact time of 2 ms for cross-polarization (CP) and a recycle delay time of 3 s, the ^{13}C -NMR spectra were acquired.

1.3.4 TG-DSC analysis

Thermogravimetric analysis (TGA) of the samples was performed using a METZSCH STA 449 F3 thermogravimetric analyzer. For each test, approximately 15 mg of sample was placed in an alumina ceramic crucible and heated under a constant nitrogen flow (30 mL/min). The temperature was gradually increased from 25 to 1000 °C at a heating rate of 10 °C/min to ensure the experimental stability and data accuracy.

1.3.5 GC-MS analysis

The composition of tar samples was analyzed using an Agilent 8890-5977C instrument. The carrier gas flow rate was 1.0 mL/min, and the split ratio was 10:1. The column oven temperature programming was set as follows: The initial temperature was 40 °C and held for 4 min; then, the temperature was increased to 70 °C at a rate of 4 °C/min and held for 2 min, followed by an increase to 200 °C at a rate of 10 °C/min and held for 3 min; finally, the temperature was raised to 300 °C at a rate of 4 °C/min and held for 5 min. The injection port temperature and ion source temperature were set to 300 and 230 °C, respectively. The mass spectrometer was set to an electron ionization mode with an energy of 70 eV, with a mass-to-charge ratio (m/z) range of 50 to 500. Compounds were identified via the probability matching method based on the data from the NIST20 and NIST20s spectral libraries. The relative content of each compound was calculated using the peak area normalization method.

2 Results and discussion

2.1 Effects of hydrothermal pretreatment on the composition and structure of Huangling coal and enzymatic hydrolysis lignin

2.1.1 Effects of hydrothermal pretreatment on the composition of Huangling coal and enzymatic hydrolysis lignin

The results of proximate and ultimate analyses of Huangling coal and enzymatic hydrolysis lignin before and after hydrothermal pretreatment are presented in Table 1

and Table 2. There are significant differences in proximate and ultimate analysis results between the two raw materials without hydrothermal pretreatment (HTP-0h) and after 24 h of hydrothermal pretreatment (HTP-24h). After 24 h of hydrothermal pretreatment, the volatile matter contents of Huangling coal and enzymatic hydrolysis lignin decrease, while their fixed carbon contents increase significantly. This is mainly attributed to the decomposition, dissolution, swelling, and plasma effects induced by the high-temperature and high-pressure environment during hydrothermal pretreatment, which promote the decomposition, removal, and gasification reactions of unstable organic matter in the samples. For example, the cleavage of aliphatic side chains generates small-molecule hydrocarbon volatiles, and oxygen-containing functional groups such as carboxyl groups and hydroxyl groups release the gases like CO₂ and H₂O through dehydration and decarboxylation reactions, thereby reducing the volatile matter content^[23–24], increasing the fixed carbon, and decreasing the O/C atomic ratio^[25].

2.1.2 Effects of hydrothermal pretreatment on the morphological structure of Huangling coal and enzymatic hydrolysis lignin

An investigation into the effect of hydrothermal pretreatment on the morphological structures of Huangling coal and enzymatic hydrolysis lignin was conducted using SEM analysis, with the results shown in Figure 2. As indicated in Figures 2(a) and 2(b), the original Huangling coal has a relatively smooth surface with a small number of natural fractures, while the original enzymatic hydrolysis lignin shows an irregular blocky accumulation structure on its surface.

Table 1 Proximate analysis of Huangling coal and enzymatic lignin with and without hydrothermal pretreatment

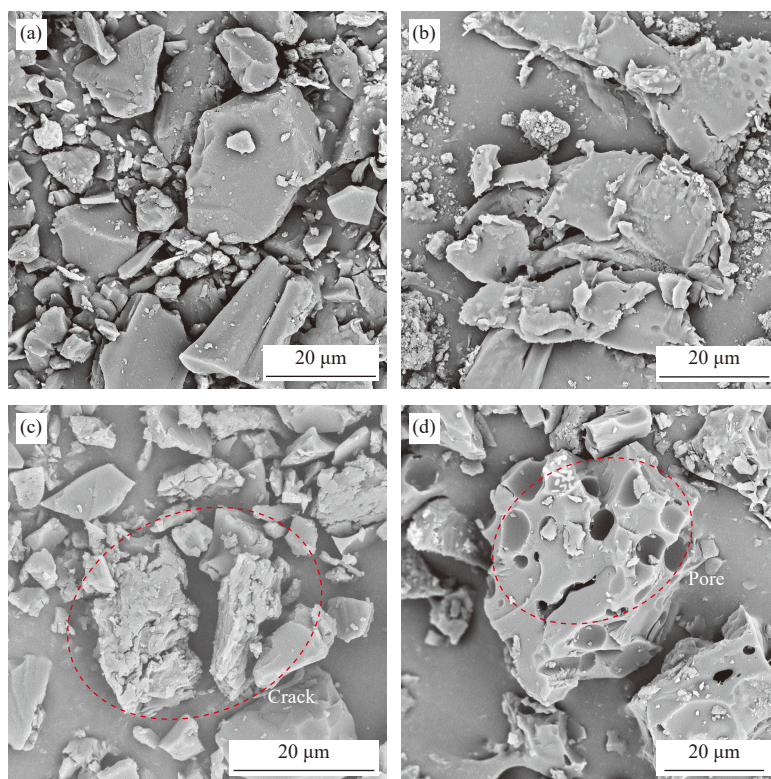
Pretreatment condition	Sample	w/%			
		M_{ad}	A_{ad}	V_{ad}	FC^*_{ad}
HTP-0h ^a	H	2.31	7.23	36.10	54.36
	E	1.92	0.43	68.11	29.54
HTP-24h ^b	H	1.78	7.17	29.70	61.35
	E	1.31	0.37	59.98	38.34

*: Calculated by difference; ^a: Raw sample without hydrothermal pretreatment; ^b: Sample after 24 h of hydrothermal pretreatment.

Table 2 Ultimate analysis of Huangling coal and enzymatic lignin with and without hydrothermal pretreatment

Pretreatment condition	Sample	w/%					Atomic ratio	
		C_{ad}	H_{ad}	O*	N_{ad}	S_t	H/C	O/C
HTP-0h	H	74.60±0.03	4.50±0.02	18.58±0.02	1.93±0.03	0.39±0.06	0.72	0.19
	E	60.16±0.02	4.71±0.02	32.26±0.01	1.79±0.04	1.08±0.04	0.94	0.40
HTP-24h	H	75.44±0.02	4.76±0.02	17.42±0.03	2.07±0.02	0.31±0.05	0.76	0.17
	E	66.54±0.01	5.30±0.03	26.37±0.02	1.65±0.05	0.14±0.02	0.95	0.30

S_t : Total sulfur.



(a), (b): H and E samples without hydrothermal pretreatment; (c), (d): H and E samples with hydrothermal pretreatment.

Fig. 2 SEM images of Huangling coal and enzymatic lignin

After hydrothermal pretreatment (as shown in Figures 2(c) and 2(d)), the overall morphology of Huangling coal becomes relatively loose, with an increase in surface fracture structures^[26], which indicates that hydrothermal pretreatment exerts a certain impact on the morphological structure of coal. In contrast, the surface of enzymatic hydrolysis lignin undergoes more significant modification, forming a large number of unevenly distributed pore structures, which is attributed to that the enzymatic hydrolysis lignin with a three-dimensional network structure consists of aromatic units connected by aliphatic bridge bonds; it has a relatively low degree of aromatic condensation and is rich in reactive functional groups such as hydroxyl groups and methoxy groups. In a high-temperature and high-pressure hydrothermal environment, it is prone to the bridge bond cleavage, functional group decomposition, and small molecule escape, which leads to more drastic changes in its structure and composition^[21,27]. Therefore, hydrothermal pretreatment not only helps improve the specific surface area and reaction activity of the original samples themselves but also contributes to enhancing the mass transfer and interaction between components in the mixed system^[28].

2.1.3 Effects of hydrothermal pretreatment on the concentration of water-soluble metal ions in Huangling coal and enzymatic hydrolysis lignin

A comparative study between hydrothermal pretreatment

and boiling pretreatment was conducted to clarify the effect of hydrothermal treatment on the dissolution of metal ions in the two pretreated samples. Since most inorganic metal elements in coal and lignin exist in the form of minerals, hydrothermal pretreatment can activate some inert minerals in the samples, such as pyrite (FeS_2) and calcite (CaCO_3), allowing the inorganic metals inside them to dissolve^[29]. As shown in Table 3, after boiling pretreatment at 110 °C for 24 h, the filtrate of Huangling coal is dominated by calcium ions, while the filtrate of enzymatic hydrolysis lignin is mainly composed of potassium and sodium ions. After hydrothermal pretreatment for 24 h, the concentrations of metal ions in the filtrates of both Huangling coal and enzymatic hydrolysis lignin increase to a large extent, while the concentrations of potassium, sodium, iron, calcium and magnesium ions in the enzymatic hydrolysis lignin filtrate increase more significantly. In addition, after hydrothermal pretreatment, the two samples undergo drying treatment by evaporating water, by which the dissolved metal ions mentioned above undergo ion exchange with oxygen-containing functional groups such as carboxyl groups ($-\text{COOH}$) and phenolic hydroxyl groups ($-\text{OH}$) on the surfaces of coal and lignin^[3,30], and are uniformly complexed and deposited on the sample surfaces. During the subsequent pyrolysis process, these metal ions can act as the catalytic active centers to promote the cleavage and recombination of chemical bonds, thereby enhancing the selectivity of pyrolysis reactions^[30].

Table 3 The concentrations of inorganic metal ions in the filtrate from boiling pretreatment and hydrothermal pretreatment of Huangling coal and enzymatic lignin

Sample	BLP-24h/(mg·L ⁻¹)					HTP-24h/(mg·L ⁻¹)				
	K	Na	Fe	Ca	Mg	K	Na	Fe	Ca	Mg
H	0.92	0.87	—	18.15	—	12.24	16.89	0.74	40.97	0.87
E	0.62	1.34	—	—	—	9.86	11.11	0.88	0.52	0.12

2.1.4 Effects of hydrothermal pretreatment on the structure of Huangling coal and enzymatic hydrolysis lignin

An exploration of the effect of hydrothermal pretreatment on the carbon skeleton structures of the two samples was conducted using ¹³C-NMR, with the results presented in Table 4 and Table 5. It is found that hydrothermal pretreatment induces significant changes in the carbon skeleton structures of Huangling coal and enzymatic hydrolysis lignin, and these changes exert a positive impact on enhancing the co-pyrolysis synergistic effect between the two samples. From the perspective of bridge carbon ratio ($X_{BP} = \frac{f_a^B}{f_a^P + f_a^H + f_a^S}$) and the changes in functional groups, after hydrothermal pretreatment, the bridge carbon ratio of Huangling coal increases slightly, while that of enzymatic hydrolysis lignin increases significantly. Meanwhile, the

decrease in the content of aliphatic carbon (f_{al}) with low pyrolysis stability in enzymatic hydrolysis lignin is greater than that in Huangling coal, whereas the increases in the contents of carbon structures with high stability including total aromatic carbon (f_a), non-protonated aromatic carbon (f_a^N), aromatic bridging carbon (f_a^B), and phenolic hydroxyl or ether oxygen bond carbon (f_a^P) in enzymatic hydrolysis lignin are all greater than those in Huangling coal. Further comparison of the calculated results of ¹³C-NMR structural parameters reveals that hydrothermal pretreatment narrows the gap in carbon skeleton structures between Huangling coal and enzymatic hydrolysis lignin. The difference in the total mass fraction of aliphatic carbon (f_{al}) with low pyrolysis stability between the two samples decreases from 9.44% before pretreatment to 3.66% after pretreatment. Also, the differences in the parameters of carbon structures with high stability, such as total aromatic carbon (f_a), non-protonated aromatic carbon (f_a^N), and aromatic bridging carbon (f_a^B), decrease simultaneously.

Table 4 ¹³C-NMR chemical shift attribution

Type	Chemical shifts δ	Structure attribution	Relative area/%			
			H-0h	H-24h	E-0h	E-24h
Aliphatic carbon	0–22	methyl (–CH ₃)	5.16	8.44	3.37	4.25
	22–35	methylene (–CH ₂)	12.59	16.52	6.95	7.92
	35–40	methine (–CH)	3.8	1.49	3.59	3.01
	40–50	quaternary carbon (C–Q)	5.74	6.02	5.21	7.22
	50–60	methoxy group (–OCH ₃)	3.02	1.51	17.22	10.42
	60–90	alcohol, ether (R–O)	5.16	0.44	8.57	5.26
Aromatic carbon	90–129	protonated aromatic carbon (Ar–H)	28.20	32.09	25.88	26.83
	129–137	aromatic bridgehead carbon (Ar–B)	8.63	10.56	7.07	10.54
	137–150	aliphatic substituted aromatic carbon (Ar–C)	11.46	12.52	11.16	13.06
	150–165	oxy-aromatic carbon (Ar–O)	4.42	4.78	3.33	5.59
Carbonyl, carboxyl carbon	165–190	carboxyl group (–COOH)	3.05	1.02	2.26	2.12
	190–240	carbonyl group (C=O)	8.77	4.61	5.39	3.78

Table 5 Calculation results of ¹³C-NMR structural parameters (%)

Sample	f_a	f_c^C	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^C	f_{al}^O	X_{BP}
H-0h	64.53	11.82	52.71	28.20	24.51	4.42	11.46	8.63	35.47	22.13	5.16	8.18	0.20
H-24h	65.58	5.63	59.95	32.09	27.86	4.78	12.52	10.56	34.42	24.03	8.44	1.95	0.21
E-0h	55.09	7.65	47.44	25.88	21.56	3.33	11.16	7.07	44.91	15.75	3.37	25.79	0.18
E-24h	61.92	5.90	56.02	26.83	29.19	5.59	13.06	10.54	38.08	18.15	4.25	15.68	0.23

Note: f_a : Mass fraction of total aromatic carbon; f_c^C : Mass fraction of carbonyl carbon; f_a^C : Mass fraction of aromatic carbon; f_a^H : Mass fraction of protonated aromatic carbon; f_a^N : Mass fraction of non-protonated aromatic carbon; f_a^P : Mass fraction of phenolic hydroxyl or ether oxygen-bonded carbon; f_a^S : Mass fraction of alkyl-substituted aromatic carbon; f_a^B : Mass fraction of aromatic bridging carbon; f_{al} : Mass fraction of total aliphatic carbon; f_{al}^H : Mass fraction of quaternary carbon, methylene carbon, and methine carbon; f_{al}^C : Mass fraction of aliphatic/aromatic methyl carbon; f_{al}^O : Mass fraction of aliphatic oxygen-bonded carbon; X_{BP} : Bridge carbon ratio.

These parameter changes indicate that hydrothermal pretreatment brings the two raw materials closer in core structural characteristics of the carbon skeleton, such as aliphatic/aromatic ratio and aromatic condensation degree, thereby providing a solid structural foundation for the co-pyrolysis synergistic effect.

After hydrothermal pretreatment, the increased bridge carbon ratio of enzymatic hydrolysis lignin indicates a more complex aromatic ring structure and a higher initial pyrolysis temperature. In addition, the aliphatic carbon content decreases significantly, while the content of carbon structures with higher stability increases significantly, which can contribute to a notable improvement in the thermal stability of enzymatic hydrolysis lignin and shift the pyrolysis to the high-temperature region. These changes promote the proximity of the pyrolysis temperature range of enzymatic hydrolysis lignin to that of Huangling coal, enhancing the compatibility of the two raw materials during pyrolysis^[31]. The narrowed gap in carbon skeleton structure mentioned above also implies a narrowed gap in pyrolysis characteristics, which helps strengthen the interaction between free radicals during co-pyrolysis of the two samples and facilitates the enhancement of the co-pyrolysis synergistic effect^[32]. Thus it can be seen that the hydrothermal pretreatment exerts the influences to different extents on the carbon skeleton structures of Huangling coal and enzymatic hydrolysis lignin, with the influence on the structure of enzymatic hydrolysis lignin being the most significant. Hydrothermal treatment improves the thermal stability of enzymatic hydrolysis lignin and helps its pyrolysis temperature range approach that of Huangling coal, which is also consistent with the subsequent thermogravimetric analysis results.

2.1.5 Thermogravimetric analysis of Huangling coal and enzymatic hydrolysis lignin with and without hydrothermal treatment

An investigation into the effect of hydrothermal pretreatment on the thermal decomposition characteristics of samples was conducted using TGA, with the results

shown in Figure 3. As indicated in Figure 3(a), the initial pyrolysis temperature of Huangling coal is significantly higher than that of enzymatic hydrolysis lignin. This is because enzymatic hydrolysis lignin contains a large number of functional groups such as hydroxyl groups ($-\text{OH}$), $\beta\text{-O-4}$ ether bonds, and methoxy groups ($-\text{OCH}_3$)^[33], which results in poor thermal stability and a low initial decomposition temperature. Hydrothermal pretreatment has little effect on the initial pyrolysis temperature of Huangling coal, but significantly increases that of enzymatic hydrolysis lignin. As shown in Figure 3(b), after hydrothermal pretreatment, there is no obvious change in the main thermal decomposition temperature range of Huangling coal. However, the main thermal decomposition temperature range of enzymatic hydrolysis lignin changes from 151–502 °C before hydrothermal pretreatment to 239–502 °C after hydrothermal pretreatment, with the initial temperature increasing by 88 °C. Combined with the ^{13}C -NMR analysis in Table 5, it is determined that there is a relation to the increase in bridge carbon ratio and the improvement in the thermal stability of enzymatic hydrolysis lignin after hydrothermal pretreatment. In addition, according to the previous experimental results of the research group on the pyrolysis of oil-rich coal, the pyrolysis tar yield of samples is relatively high at 650 °C^[34]. Therefore, based on the above thermogravimetric analysis results, the temperature for the pyrolysis or co-pyrolysis of samples in subsequent studies is set to 650 °C.

2.2 Effects of hydrothermal pretreatment on the pyrolysis characteristics of Huangling coal, enzymatic hydrolysis lignin, and their blends

2.2.1 Effects of hydrothermal pretreatment on the distribution of pyrolysis products

The distribution of products from the individual pyrolysis and co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin with and without hydrothermal pretreatment is shown in Figure 4.

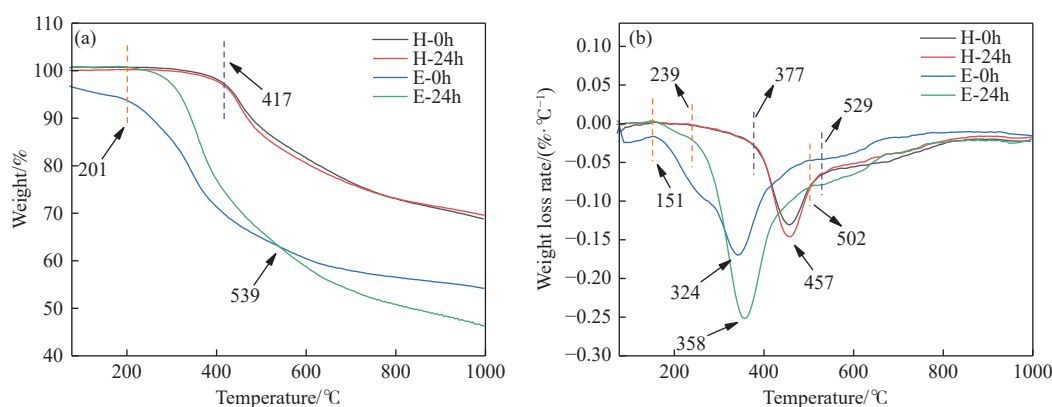
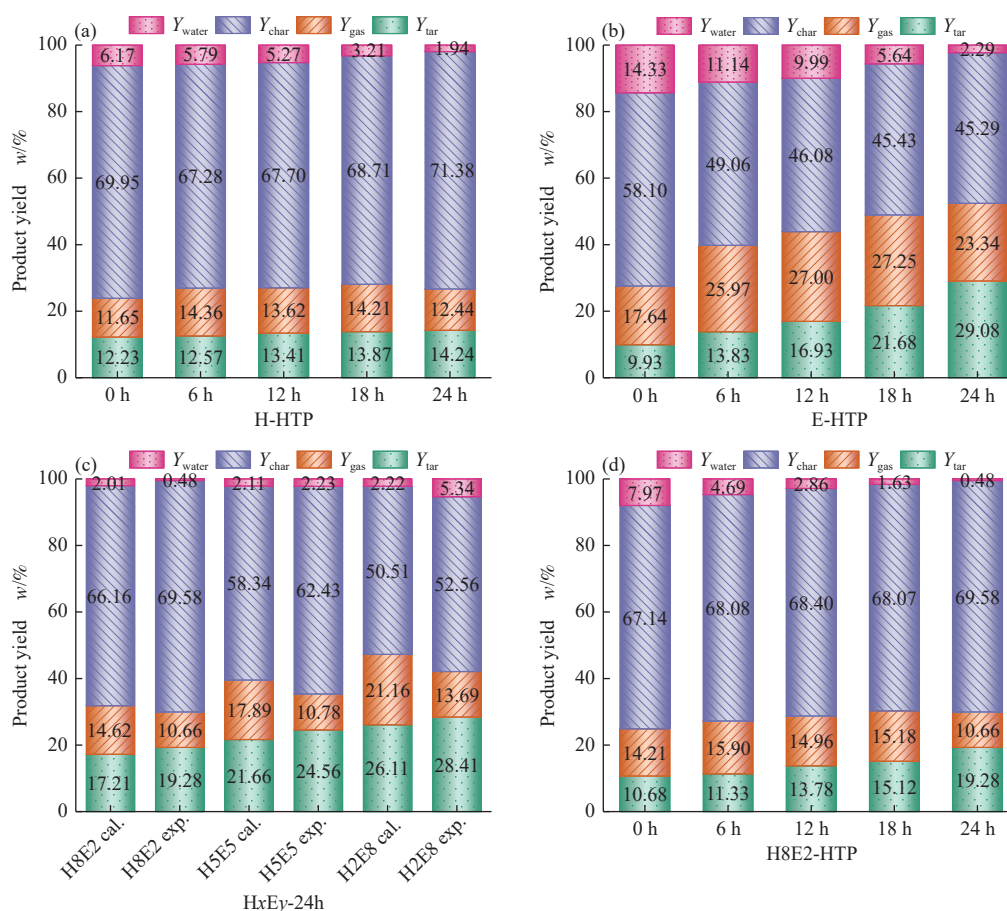


Fig. 3 TG (a) and DTG (b) curves of Huangling coal and enzymatic lignin with and without hydrothermal pretreatment



(a), (b), (d): Effects of hydrothermal pretreatment time; (c): Effects of different mixing ratios.
Fig. 4 The influence of hydrothermal pretreatment on the distribution of pyrolysis products of Huangling coal and enzymatically hydrolyzed lignin and their blends

Figures 4(a) and 4(b) indicate the effect of hydrothermal pretreatment time on the distribution of individual pyrolysis products of Huangling coal and enzymatic hydrolysis lignin. The result shows that when the hydrothermal pretreatment time is extended from 6 to 24 h, compared with untreated samples, the yields of pyrolysis tar, pyrolysis gas, and semi-coke from Huangling coal increase by 16.43%, 6.78% and 2.04%, respectively, while the yield of pyrolysis water decreases by 68.56%. For the enzymatic hydrolysis lignin, the yields of pyrolysis tar and pyrolysis gas increase by 192.85% and 32.31%, respectively, while the yields of pyrolysis water and semi-coke decrease by 84.02% and 22.05%, respectively. This result stems from the multiple effects of hydrothermal pretreatment. On the one hand, hydrothermal pretreatment promotes the loosening of raw material structures and the breaking of functional groups, which not only provides more volatiles for tar generation but also facilitates the conversion of small molecules to the gas phase^[21]. On the other hand, hydroxyl rearrangement reduces the source of pyrolysis water generation^[35], while the enriched metal ions can not only catalyze the breaking of chemical bonds to facilitate the generation of tar and gas but also inhibit the macromolecular polymerization^[30]. Overall, the yields of tar and pyrolysis gas increase, while the yield of pyrolysis

water decreases.

Based on the above research results, the hydrothermal pretreatment time is set to 24 h, and the effect of different mixing ratios of Huangling coal and enzymatic hydrolysis lignin on the distribution of their co-pyrolysis products is investigated, as shown in Figure 4(c). Herein, the theoretical predicted values of co-pyrolysis product yields refer to the weighted sum of the actual yields of individual pyrolysis products of Huangling coal and enzymatic hydrolysis lignin (under the same hydrothermal pretreatment conditions) according to their blending mass proportions. For example, the theoretical predicted tar yield of H8E2 = actual tar yield of pretreated coal $\times$ 0.8 + actual tar yield of pretreated lignin $\times$ 0.2. These values represent the expected results without synergistic effects. By comparing the theoretical predicted values and the experimental values of pyrolysis product yields of each blend (including H8E2, H5E5 and H2E8), it is found that the experimental values of pyrolysis tar and semi-coke yields for all blends are higher than the theoretical predicted values, increasing by 12.03%, 13.39%, 8.81% and 5.17%, 7.01%, 4.06% respectively. However, the pyrolysis gas yields are lower than the theoretical predicted values, with a decrease by 27.09%, 39.74% and 35.3%, respectively, with H8E2 showing the smallest decrease. The changes in pyrolysis water yields vary among

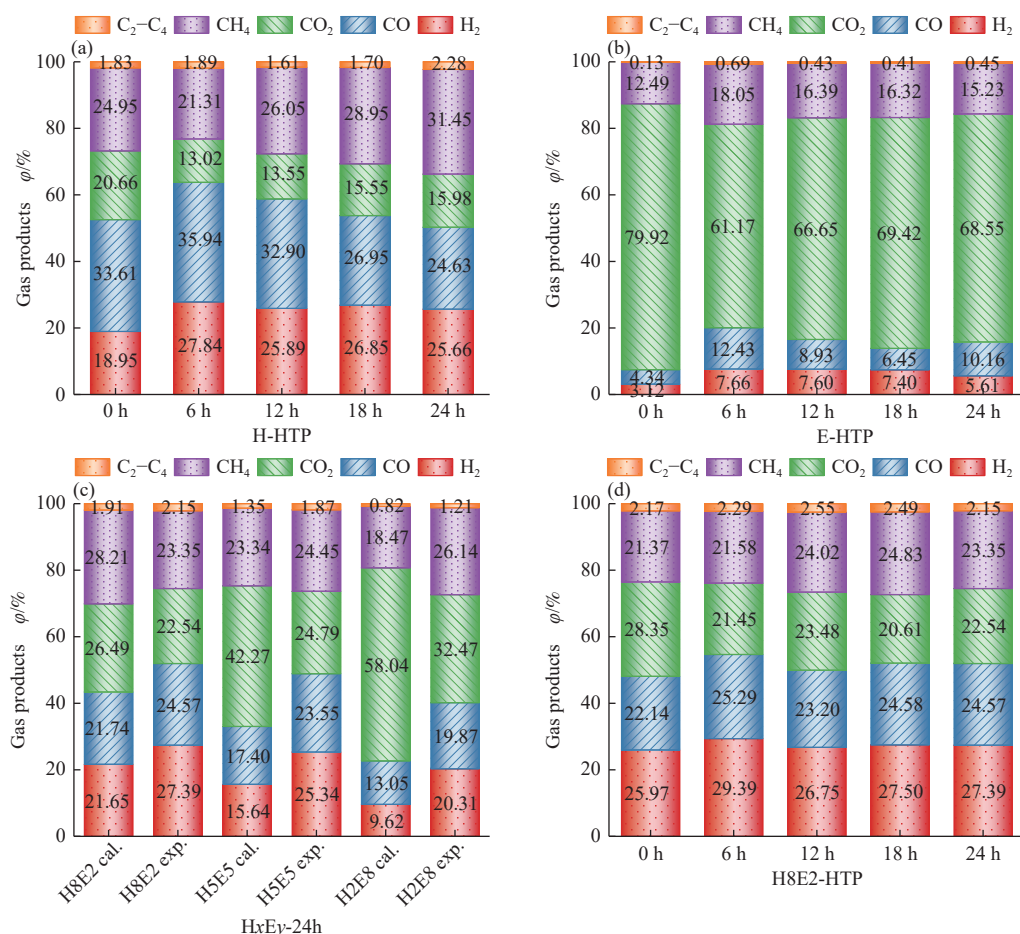
the blends, but only the experimental value of H8E2 is lower than its theoretical predicted value; thus, the H8E2 is identified as the optimal blending ratio. Further investigation into the effect of hydrothermal pretreatment time on the co-pyrolysis product distribution of H8E2 shows that, as indicated in Figure 4(d), when the hydrothermal pretreatment time is extended from 6 to 24 h, the yield of co-pyrolysis tar shows an upward trend, while the yield of pyrolysis water shows a downward trend. Meanwhile, compared with the pyrolysis products of H8E2 without hydrothermal pretreatment, the yields of pyrolysis tar and semi-coke of H8E2-24h increase by 80.52% and 3.63%, respectively, while the yields of pyrolysis gas and pyrolysis water decrease by 24.98% and 93.98%, respectively. Therefore, when the hydrothermal pretreatment time is 24 h, the efficient conversion of H8E2 can be significantly promoted.

2.2.2 Effects of hydrothermal pretreatment on the composition of gaseous pyrolysis products

By combining the results of the effect of hydrothermal pretreatment on pyrolysis product distribution, the regulatory effect of hydrothermal pretreatment on the composition of gaseous products from the individual pyrolysis of Huangling coal and enzymatic hydrolysis lignin as well as their co-pyrolysis is discussed, as shown in Figure 5. Figures 5(a) and 5(b) respectively show the effect of hydrothermal pretreatment time on the gaseous products from the individual pyrolysis of the two samples. It can be seen that as the hydrothermal pretreatment time is extended from 6 to 24 h, the H_2 yields in the pyrolysis gas of both samples increase significantly, with an increase of 35.41% and 79.81%, respectively compared with the samples without hydrothermal pretreatment. The CH_4 yields increase by 26.05% and 21.94%, respectively, while the CO_2 yields decrease by 37.12% and 23.46%, respectively. The main difference in the pyrolysis gaseous products lies in the CO yield. With the hydrothermal pretreatment, the CO yield in Huangling coal pyrolysis gas decreases by 26.72%, while that in enzymatic hydrolysis lignin pyrolysis gas increases by 134.1%. However, the CO yield of enzymatic hydrolysis lignin is always lower than that of Huangling coal, which is related to the functional group distribution and initial yield base of the two samples. From the perspective of functional group characteristics, Huangling coal originally contains more aliphatic oxygen-containing functional groups that are prone to CO generation, among which the proportion of alcohol/ether carbon is 5.16% and that of methoxy carbon is 3.02%. After hydrothermal pretreatment, a large number of such functional groups decompose, with the alcohol/ether carbon and methoxy carbon proportions decreasing to 0.44% and 1.51%, respectively, leading to an insufficient precursor for CO generation and a subsequent decrease in CO yield. For the enzymatic hydrolysis lignin, it is different, after hydrothermal pretreatment, the proportion of phenolic hydroxyl/ether oxygen bond carbon that is prone

to CO generation increases from 3.33% to 5.59%. Such aromatic carbon atoms bonded to oxygen are more likely to break and generate CO during pyrolysis^[35], thus resulting in a significant increase in CO yield. However, the CO yield of the enzymatic hydrolysis lignin without pretreatment is only 4.34%, much lower than 33.61% of Huangling coal. Therefore, even with a substantial increase in CO yield, the CO yield of the enzymatic hydrolysis lignin with the pretreatment of 24 h remains lower than that of Huangling coal. The increase in H_2 yield in the pyrolysis gas of Huangling coal and enzymatic hydrolysis lignin with the hydrothermal pretreatment mainly stems from the fact that hydrothermal pretreatment promotes the leaching of inorganic metal ions in the samples and their conversion into catalytic active sites^[30]. Secondly, the action of high temperature and high pressure causes the cracking of macromolecular structures of Huangling coal and enzymatic hydrolysis lignin, releasing more short-chain hydrocarbons and oxygen-containing functional groups such as hydroxyl groups and ether bonds, which improves the reaction activity^[31] and thus accelerates the gasification reactions such as the water-gas reaction. The decrease in CO_2 yield in the pyrolysis gas of the Huangling coal and enzymatic hydrolysis lignin with the hydrothermal pretreatment is due to that the groups prone to CO_2 generation, such as carboxyl groups and methoxy groups, are removed in advance during the hydrothermal pretreatment stage^[24]. The increase in CH_4 yield in the pyrolysis gas of Huangling coal and enzymatic hydrolysis lignin is related to the increased content of methyl and methylene groups in the Huangling coal and enzymatic hydrolysis lignin with the hydrothermal pretreatment. Such aliphatic C–H bonds are prone to breakage to generate alkyl free radicals, thereby promoting the release of small-molecule hydrocarbons^[36].

When the hydrothermal pretreatment time is 24 h, the composition of co-pyrolysis gaseous products of samples with different mixing ratios is shown in Figure 5(c). By comparing the experimental values with the theoretical predicted values, it can be observed that hydrothermal pretreatment significantly increases the yields of H_2 and CO in the pyrolysis gas of the blend, while inhibiting the generation of CO_2 , exhibiting an obvious co-pyrolysis synergistic effect. However, with the increase in the addition ratio of enzymatic hydrolysis lignin in the blend, the yields of H_2 and CO show a downward trend, while the yield of CO_2 increases. Thus, the H8E2 blend exhibits the optimal quality of co-pyrolysis gaseous products. From Figure 5(d), it can also be seen that the H8E2 blend achieves the optimal quality of pyrolysis gaseous products when subjected to 24 h of hydrothermal pretreatment. Among the gaseous products, the yields of H_2 , CO and CH_4 are increased by 5.47%, 10.98% and 9.27%, respectively compared with those in the pyrolysis gaseous products of the blend without hydrothermal pretreatment. Therefore, based on the above experimental results, 24 h is finally determined as the optimal hydrothermal pretreatment time, and H8E2 is selected as the optimal mixing ratio.



(a), (b), (d): Effects of hydrothermal pretreatment time; (c): Effects of different mixing ratios.

Fig. 5 The influence of hydrothermal pretreatment on the composition of pyrolysis gas products of Huangling coal and enzymatically hydrolyzed lignin and their blends

2.2.3 Effects of hydrothermal pretreatment on the composition of pyrolysis tar

Based on the above research results, a further exploration is conducted on the effect of hydrothermal pretreatment on the composition of pyrolysis tar from Huangling coal, enzymatic hydrolysis lignin, and their blend. As shown in Figure 6, with the hydrothermal pretreatment, the contents of aliphatic compounds, monocyclic aromatic hydrocarbons, and heteroatomic compounds in the Huangling coal pyrolysis tar increase by 4.77%, 2.53% and 4.29%, respectively, while the contents of bicyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, phenolic compounds, and other oxygen-containing compounds decrease by 6.03%, 1.58%, 0.96% and 3.02%, respectively. In the pyrolysis tar of the enzymatic hydrolysis lignin pretreated, the contents of five components including aliphatic compounds and monocyclic aromatic hydrocarbons increase by 0.48%–3.23%, respectively, while the contents of phenolic compounds and polycyclic aromatic hydrocarbons decrease by 6.34% and 0.44%, respectively. For the co-pyrolysis tar of the H8E2 pretreated, the contents of five components including

aliphatic compounds increase by 1.7%–8.01%, respectively, while the contents of polycyclic aromatic hydrocarbons and phenolic compounds decrease by 2.27% and 13.48%, respectively.

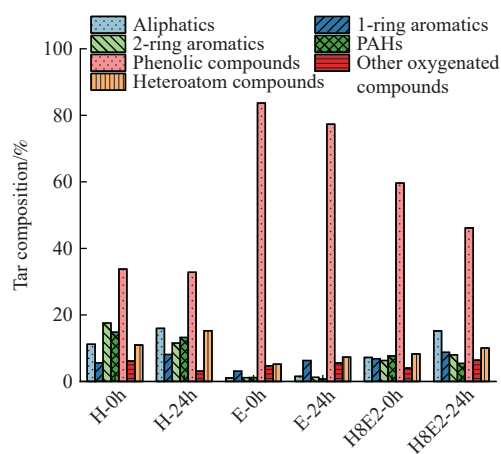


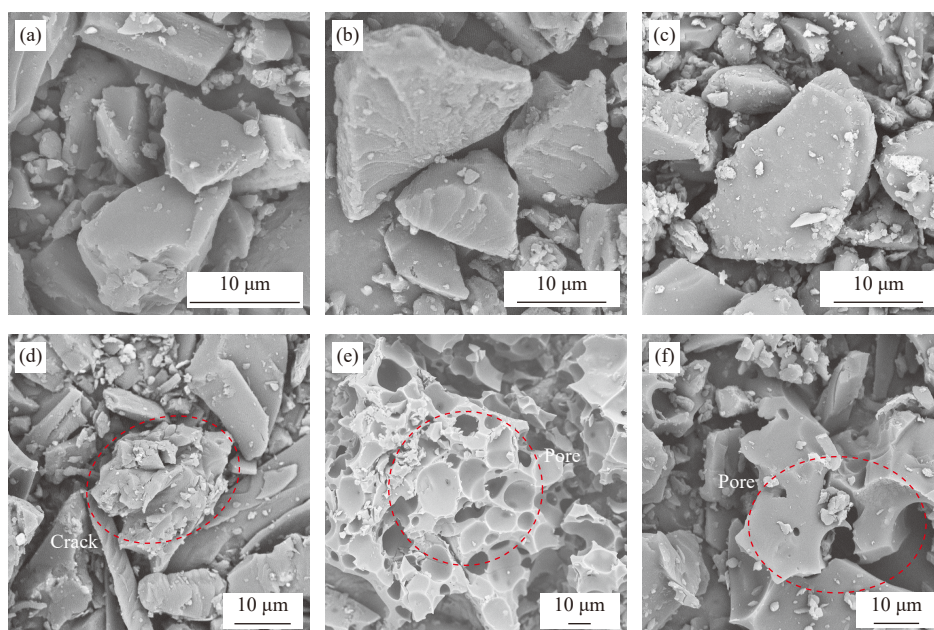
Fig. 6 The influence of hydrothermal pretreatment on the component distribution of pyrolysis tar of Huangling coal and enzymatically hydrolyzed lignin and their blends

It can be concluded that hydrothermal pretreatment not only has a significant effect on the increase in the contents of aliphatic compounds and monocyclic aromatic hydrocarbons and the reducing of the content of phenolic compounds in the pyrolysis tar of Huangling coal and enzymatic hydrolysis lignin, but also improves the quality of the co-pyrolysis tar of the H8E2 blend, which stems from the synergistic effect of multiple mechanisms. Hydrothermal pretreatment removes part of the phenolic hydroxyl groups ($-OH$) and methoxy groups ($-OCH_3$) from the raw materials in advance through reactions such as hydrolysis and decarboxylation^[24], directly reducing the generation of phenolic compounds during pyrolysis. Meanwhile, some long-chain aliphatic structures break during pretreatment, providing more precursors for the generation of aliphatic compounds during pyrolysis^[17]. At the same time, inorganic metal ions such as K, Ca, Fe and Mg enriched in the blend after hydrothermal pretreatment play a synergistic catalytic role. K and Ca provide active sites to adsorb and activate aliphatic chain fragments and aromatic precursors in the pyrolysis system, promoting the generation of short-chain aliphatic hydrocarbons and the aromatization of monocyclic aromatic hydrocarbons^[30]. Mg binds to the oxygen-containing functional groups such as phenolic hydroxyl groups and carboxyl groups, inhibiting the cross-linking reactions during pyrolysis and reducing the generation of phenolic compounds^[37]. As a transition metal, Fe can catalyze the cleavage of C–O bonds and the ring opening of aromatic rings in tar, which not only accelerates the degradation of phenols into short-chain intermediates but also inhibits the polymerization of polycyclic aromatic hydrocarbons^[38]. Furthermore, hydrothermal pretreatment narrows the difference in carbon skeleton structure between coal and lignin, enhancing the

interaction of pyrolysis free radicals from the two raw materials^[31], such as the interaction between alkyl free radicals in coal and hydroxyl free radicals in lignin, thereby reducing the generation of phenolic compounds. At the same time, the recombination of aliphatic compounds and aromatic structures is also promoted, further optimizing the composition of tar products. Therefore, hydrothermal pretreatment can effectively enhance the co-pyrolysis synergistic effect between Huangling coal and enzymatic hydrolysis lignin, and improve the quality of pyrolysis tar products.

2.2.4 Effects of hydrothermal pretreatment on the morphology of pyrolysis char

By comparing the changes in the morphology of samples with and without hydrothermal pretreatment, an in-depth insight is gained into the effect of hydrothermal pretreatment on the semi-coke structures obtained from the individual pyrolysis of Huangling coal and enzymatic hydrolysis lignin as well as their co-pyrolysis, as shown in Figure 7. From Figures 7(a)–7(c), it can be seen that without hydrothermal pretreatment, the semi-cokes from the pyrolysis of the three samples have fewer pore structures and are relatively regular in overall appearance^[39–40]. By the hydrothermal pretreatment (Figures 7(d)–7(f)), the morphology of the semi-cokes changes significantly, obvious cracks and pore structures appear on the surface of Huangling coal pyrolysis semi-coke, the surface of enzymatic hydrolysis lignin pyrolysis semi-coke mainly forms a dense and large-sized pore network, and the H8E2 co-pyrolysis semi-coke exhibits significant deformation and uneven pore distribution.



(a)–(c): Pyrolysis semi-coke of H, E and H8E2 without hydrothermal pretreatment;
(d)–(f): H, E and H8E2 pyrolysis semi-coke with hydrothermal pretreatment.

Fig. 7 SEM images of pyrolysis semi-coke of Huangling coal and enzymatic lignin and their blends

These morphological changes further confirm that hydrothermal pretreatment can effectively destroy the original dense structure of the samples, promote pore development, provide a foundation for mass and energy transfer during the co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin, and strengthen the interaction between components.

2.3 Influence mechanism of hydrothermal pretreatment on the co-pyrolysis characteristics of Huangling coal and enzymatic hydrolysis lignin

2.3.1 Effects of hydrothermal pretreatment on the structure of blends of Huangling coal and enzymatic hydrolysis lignin

An investigation into the effect of hydrothermal pretreatment on the carbon skeleton structure of H8E2 yields was conducted, and the results are shown in Table 6. By comparing with Table 5, it is found that when Huangling coal and enzymatic hydrolysis lignin undergo hydrothermal pretreatment individually, their carbon skeleton structures tend to be more stable and complex. However, the scenario differs when Huangling coal and enzymatic hydrolysis lignin undergo co-hydrothermal pretreatment. By the hydrothermal pretreatment, the bridge carbon ratio of H8E2 does not increase, while the mass fractions of carbonyl carbon (f_a^c) with high reactivity and aliphatic/aromatic methyl carbon (f_a^m) in the carbon skeleton structure increase. In contrast, the mass fractions of alkyl-substituted aromatic carbon (f_a^s) and aromatic bridging carbon (f_a^b), which have higher stability, decrease^[41]. In addition, after hydrothermal pretreatment, the total mass fraction of aliphatic carbon (f_{al}) in H8E2 and the mass fractions of aliphatic oxygen-linked

carbon (f_{al}^o) as well as quaternary, methylene and methine carbons (f_{al}^H) decrease. This is because during pretreatment, high temperatures promote reactions of the aliphatic structures, such as cyclization to form more alicyclic compounds, leading to the conversion of aliphatic carbon structures to other structures. This reduces the premature cleavage of long-chain aliphatic structures to generate small-molecule gases, prompting more intermediate products to convert into tar and semi-coke. Moreover, since aliphatic carbon structures generate the by-products such as H_2O and CO_2 during pyrolysis, the decrease in their mass fractions implies a reduction in the generation of these by-products during pyrolysis^[42–43], and this phenomenon is consistent with the analysis results of co-pyrolysis products in Figure 4(d). Therefore, hydrothermal pretreatment is beneficial for improving the reactivity of H8E2, strengthening the co-pyrolysis synergistic effect between Huangling coal and enzymatic hydrolysis lignin, and promoting the efficient conversion of H8E2.

2.3.2 Thermogravimetric analysis of blends of Huangling coal and enzymatic hydrolysis lignin with and without hydrothermal treatment

For clarifying the effect of hydrothermal pretreatment on the thermal decomposition characteristics of the Huangling coal-enzymatic hydrolysis lignin blend, a comparative thermogravimetric study on the H8E2 with and without hydrothermal pretreatment was conducted, with the results presented in Figure 8(a) and 8(b). As indicated in Figure 8(a), for the H8E2 without hydrothermal pretreatment, its thermal decomposition curve lies below that of the H8E2 with hydrothermal pretreatment when the temperature is lower than 487 °C.

Table 6 Calculation results of ^{13}C -NMR structural parameters (%)

Sample	f_a	f_a^c	f_a^m	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^m	f_{al}^O	X_{BP}
H8E2-0h	66.60	12.53	54.07	28.58	25.49	3.22	10.39	11.87	33.40	19.77	6.33	7.30	0.28
H8E2-24h	68.04	16.99	51.05	27.43	23.62	3.83	8.55	11.24	31.96	18.26	6.76	6.94	0.28

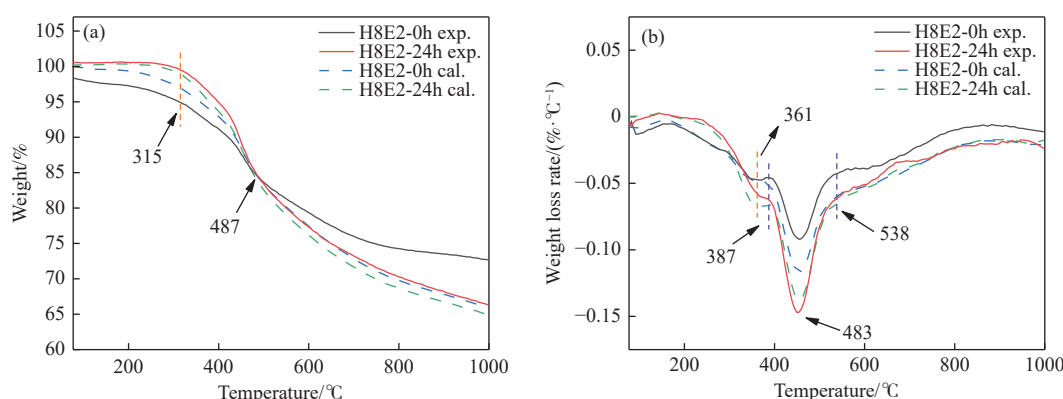


Fig. 8 TG (a) and DTG (b) curves of Huangling coal and enzymatic lignin blends with and without hydrothermal pretreatment

When the temperature exceeds 487 °C, the thermal decomposition curve of the H8E2 without hydrothermal pretreatment becomes significantly higher than that of pretreated H8E2, and its weight loss rate is notably lower than that of the H8E2 with hydrothermal pretreatment. This is primarily due to that the enzymatic hydrolysis lignin without hydrothermal pretreatment has poor thermal stability and a low initial thermal decomposition temperature; it undergoes decomposition first before 487 °C and releases a large quantity of volatile substances. When the temperature is above 487 °C, a large amount of volatile substances released by the untreated enzymatic hydrolysis lignin in the early stage inhibits the deep pyrolysis of Huangling coal, promotes the secondary polycondensation of tar or the stabilization of the semi-coke structure, and thus results in a lower weight loss rate of H8E2^[44]. Meanwhile, for the H8E2 without hydrothermal pretreatment, there is an obvious discrepancy between its experimental thermal decomposition curve and the theoretically predicted curve around 487 °C. In contrast, for the H8E2 with hydrothermal pretreatment, the experimental thermal decomposition curve and the theoretically predicted curve show a high degree of consistency in the variation trends, with no significant stage-specific differences in weight loss observed. As shown in Figure 8(b), the maximum weight loss rate of the H8E2 without hydrothermal pretreatment is significantly lower than that of pretreated H8E2, and the experimental value of the maximum weight loss rate is also notably lower than the theoretical prediction. However, the experimental value of the maximum weight loss rate of the H8E2 with hydrothermal pretreatment is higher than the theoretical prediction. In addition, the H8E2 without hydrothermal pretreatment exhibits a distinct weight loss phenomenon at 361 °C, which corresponds to the early thermal decomposition temperature of the enzymatic hydrolysis lignin in the blend. Therefore, based on the above experimental results, hydrothermal pretreatment significantly enhances the thermal decomposition activity of H8E2 and strengthens the co-pyrolysis synergistic effect between Huangling coal and enzymatic hydrolysis lignin, which is consistent with the analysis results of ¹³C-NMR structural parameters in Table 6.

2.3.3 Effects of hydrothermal pretreatment on the concentration of water-soluble metal ions in blends of Huangling coal and enzymatic hydrolysis lignin

Focusing on the effect of hydrothermal pretreatment on the dissolution of inorganic metal ions in H8E2, a

comparative experiment for the hydrothermal pretreatment and boiling pretreatment was also conducted. As shown in Table 7, by the hydrothermal pretreatment for H8E2, the concentration of calcium ions in the filtrate is nearly 4 times that by the boiling pretreatment, while the concentrations of potassium and sodium ions are slightly lower than those by the boiling pretreatment. This phenomenon is related to the fact that some potassium and sodium ions participate in the formation of insoluble compounds (such as aluminosilicate precipitates) under hydrothermal conditions, which inhibit the migration^[29,45]. By comparing the total concentrations of inorganic metal ions in the filtrate from different pretreatments of a blend, it can be concluded that hydrothermal pretreatment is more conducive to the decomposition of minerals and promotes the dissolution and activation of inorganic metal ions. It not only significantly increases the concentrations of metal ions such as iron and calcium in the filtrate^[46], but also enables these metal ions to uniformly complex and deposit in the samples. This provides favorable catalytic active sites for the co-pyrolysis, thereby enhancing the synergistic effect of co-pyrolysis and increasing the yield of target products^[47].

2.3.4 Influence mechanism of hydrothermal pretreatment on the co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin

Exploring the mechanism of hydrothermal pretreatment on the co-pyrolysis of Huangling coal and enzymatic hydrolysis lignin is of crucial significance for enhancing the synergistic efficiency of co-pyrolysis between oil-rich coal and biomass. Based on the above research results, its synergistic enhancement mechanism is embodied in the progressive synergistic effect of component interaction, structural modification, and catalytic cracking. First, component interaction lays the foundation for the synergistic reaction. Hydrothermal pretreatment significantly improves the contact conditions between Huangling coal and enzymatic hydrolysis lignin. Huangling coal forms a large number of crisscrossed irregular cracks on its surface through swelling and dissolution, while enzymatic hydrolysis lignin develops abundant pores due to functional group decomposition, small molecule escape, and hydrolysis (Figure 2). This significantly enhances the looseness and permeability of the two raw materials, provides a larger interface for direct contact between the two raw materials during co-pyrolysis, and strengthens the mass transfer and interaction between components. On this basis, structural modification further optimizes the conditions for the synergistic reaction.

Table 7 The concentrations of inorganic metal ions in the filtrate from the boiling pretreatment and hydrothermal pretreatment of the mixture of Huangling coal and enzymatic lignin

Sample	BLP-24h/(mg·L ⁻¹)					HTP-24h/(mg·L ⁻¹)				
	K	Na	Fe	Ca	Mg	K	Na	Fe	Ca	Mg
H8E2	1.75	14.28	0.26	13.62	0.72	1.70	12.96	0.57	51.70	1.23

Through adjusting the relative contents of aliphatic carbon, aromatic carbon, and carbonyl/carboxyl carbon in Huangling coal and enzymatic hydrolysis lignin, hydrothermal pretreatment narrows the gap in the carbon skeleton structure between the two materials, and increases the bridge carbon ratio at the same time (Table 5). The structural change of enzymatic hydrolysis lignin is more significant, its aromatic ring structure becomes more complex, its thermal stability is significantly enhanced, and its pyrolysis temperature range approaches that of Huangling coal (Figure 3). This improves the matching degree of the two raw materials during pyrolysis, increases the probability of free radical interaction, and provides structural support for the synergistic effect. Finally, catalytic cracking strengthens the effect of the synergistic reaction. The high-temperature and high-pressure environment of hydrothermal pretreatment promotes the dissolution of inorganic metal ions such as iron and calcium in the blend of Huangling coal and enzymatic hydrolysis lignin, and the promotion effect on the calcium ion dissolution is particularly significant (Table 3 and Table 7). During the subsequent drying process, these metal ions, with the evaporation of the aqueous solution, are uniformly complexed and deposited in the samples through ion exchange, forming a distribution state dominated by surface enrichment that acts as catalytic active sites to effectively promote the cleavage and recombination of chemical bonds

during co-pyrolysis. It is through the synergistic effects of component interaction, structural modification, and catalytic cracking that hydrothermal pretreatment significantly improves the tar yield and quality of H8E2 co-pyrolysis, increases the proportions of H_2 , CO and CH_4 in the pyrolysis gas, inhibits the generation of CO_2 and pyrolysis water, and enriches the pore structure of semi-coke. Based on the results and analysis, an enhancement mechanism of hydrothermal pretreatment on the co-pyrolysis synergistic effect between oil-rich coal and lignin, namely “component interaction-structural modification-catalytic cracking”, was proposed as shown in Figure 9.

For the further verification of the multi-effect mechanism of “component interaction-structural modification-catalytic cracking”, the effects of four pretreatment methods including mechanical stirring (MS), BLP-24 h, acid washing combined with 24 h hydrothermal pretreatment (PT+(HTP-24 h)) and HTP-24 h on the co-pyrolysis performance of H8E2 were systematically compared, with the results shown in Figure 10. It is found that mechanical stirring only achieves simple mixing of the materials and exerts a relatively limited impact on the synergistic effect of the co-pyrolysis process. BLP-24 h pretreatment can promote the dissolution of some inorganic metal ions from H8E2, leading to increased yields of tar and pyrolysis water, as well as a decrease in the yields of pyrolysis gas and semi-coke.

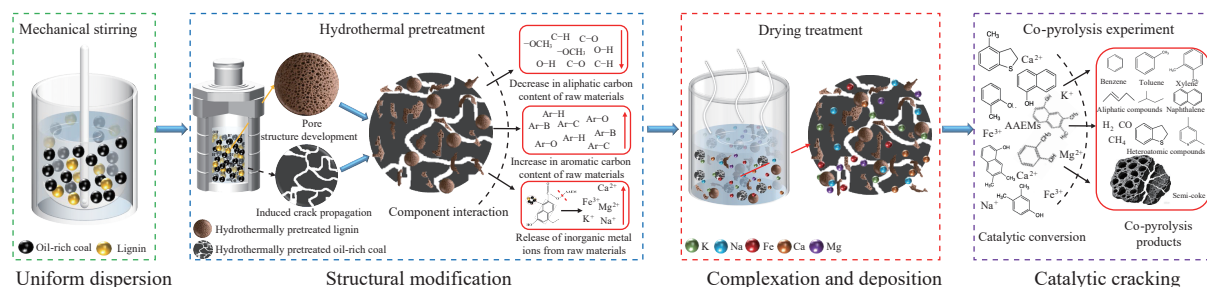


Fig. 9 Mechanism of the influence of hydrothermal pretreatment on the enhancement of synergistic effect in co-pyrolysis of oil-rich coal and lignin

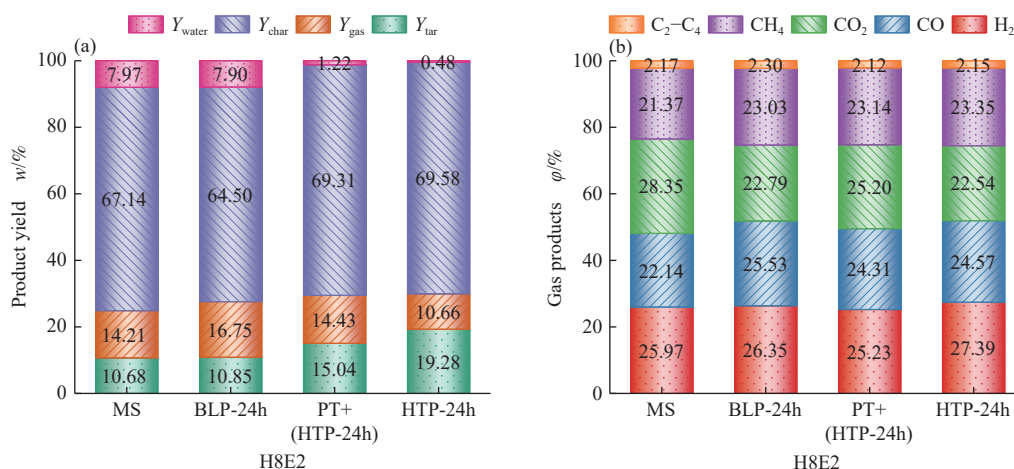


Fig. 10 The influence of different pretreatment methods on the pyrolysis products of the mixture of Huangling coal and enzymatic lignin

Compared with the co-pyrolysis products of H8E2 treated by sole hydrothermal pretreatment (HTP-24h), when using the PT+(HTP-24h) pretreatment which removes most minerals from H8E2 via acid washing^[48–49], the co-pyrolysis products of H8E2 change significantly, with the tar yield decrease by 21.99%, and the pyrolysis gas yield increase by 35.37% (in which the H₂ yield decreases by 7.89% and the CO₂ yield increases by 11.80%). This significant difference confirms that hydrothermal pretreatment can activate inert minerals in the samples and promote the dissolution of internal inorganic metals and their enrichment on the sample surface, which provides more metals with catalysis for the co-pyrolysis process. Among the four pretreatment methods, HTP-24 h shows the most prominent effect. By reshaping the structure of the two raw materials, enhancing the interaction between their components, and enabling the enrichment of inorganic metal ions, hydrothermal pretreatment not only significantly improves the yields of tar and semi-coke in the H8E2 co-pyrolysis system but also greatly reduces the generation of pyrolysis water and pyrolysis gas. In terms of regulating the composition of pyrolysis gas, compared with the other three pretreatment methods, HTP-24h can increase the yields of syngas (H₂+CO) and CH₄ more efficiently but reduce the CO₂ generation. A series of comparative experimental results fully verify the rationality of the “component interaction-structural modification-catalytic cracking” mechanism.

3 Conclusions

The effects of hydrothermal pretreatment on the pyrolysis characteristics of Huangling coal, enzymatic hydrolysis lignin, and their blends were focused on, a comprehensive and in-depth investigation was conducted, and the intrinsic mechanism by which hydrothermal pretreatment enhances the co-pyrolysis synergistic effect between Huangling coal and enzymatic hydrolysis lignin was explored. The specific conclusions are as follows:

Hydrothermal pretreatment exerts different degrees of influence on the composition and structure of Huangling coal and enzymatic hydrolysis lignin. After 24 h of hydrothermal pretreatment, both samples show a trend of decreased volatile matter, increased fixed carbon, and reduced O/C ratio. Structurally, Huangling coal develops more surface cracks, while enzymatic hydrolysis lignin exhibits a more abundant pore structure. Meanwhile, the difference in carbon skeleton structure between the two samples narrows. Additionally, the thermal stability of enzymatic hydrolysis lignin is significantly improved, and its pyrolysis temperature range approaches that of Huangling coal, creating a favorable condition for the synergistic co-pyrolysis.

Hydrothermal pretreatment improves the co-pyrolysis performance of Huangling coal and enzymatic hydrolysis lignin. For the blend by 24 h of hydrothermal pretreatment, the co-pyrolysis tar yield increases by 80.52% compared

with that for the untreated blend, and the contents of aliphatic compounds, monocyclic aromatic hydrocarbons, and other components in the tar rise significantly. The yields of H₂, CO and CH₄ in the coal gas increase by 5.47%, 10.98% and 9.27%, respectively, while the generation of CO₂ is inhibited. Meanwhile, the yield of pyrolysis water decreases by 93.98%, and the pore structure of semi-coke becomes more abundant.

Hydrothermal pretreatment enhances the co-pyrolysis synergistic effect between oil-rich coal and lignin through a multi-fold enhancement mechanism of “component interaction-structural modification-catalytic cracking”, achieving the improvement of co-pyrolysis tar yield and quality, the optimization of coal gas components, and the enhancement of semi-coke structure. In the future, a further in-depth exploration can be carried out on the microscopic reaction kinetics of hydrothermal pretreatment. By constructing a molecular interaction model of oil-rich coal and lignin, the regulation laws of hydrothermal pretreatment on the mechanisms such as electron transfer and free radical transfer can be analyzed, and the intrinsic logic of microscopic interfacial reactions driving the macroscopic synergistic effects can be clarified. This will provide theoretical support for establishing a universal mechanism framework and realizing the directional regulation of co-pyrolysis products.

Declaration of Competing Interest

The authors declare no conflict of interest.

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水热预处理对黄陵煤与酶解木质素共热解协同效应机制的研究

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摘 要: 富油煤与生物质共热解是实现富油煤油气属性最大化的有效途径。实验聚焦于富油煤与生物质共热解过程中协同效应强化作用机制不清晰的难题, 以黄陵煤(H)和酶解木质素(E)为研究样品, 采用工业分析、元素分析、扫描电镜(SEM)、电感耦合等离子体发射光谱仪(ICP-OES)和核磁共振(¹³C-NMR)等技术, 解析了水热预处理(HTP)前后原料的结构演变规律, 并结合固定床热解实验探究了水热预处理对黄陵煤和酶解木质素共混物共热解协同效应的增强机制。结果表明, 水热预处理后, 原料的氧含量减少, 孔隙结构更为发达, 水相中钙、钾、铁等无机金属离子浓度上升。黄陵煤和酶解木质素的结构发生明显改变, 两者在脂肪碳、芳香碳和羰基/羧基碳相对含量的差距缩小, 桥碳比增加, 使酶解木质素的热稳定性提高, 热解温度区间向黄陵煤趋近。黄陵煤和酶解木质素共混物, 经水热预处理后, 共热解焦油产率普遍增加, 当H/E比为8:2、水热预处理24 h时, 共热解焦油产率提高了80.52%, 且焦油中脂肪族化合物和单环芳烃等含量明显增加。同时, 煤气中H₂、CO和CH₄的产率分别提高了5.47%、10.98%和9.27%, 抑制了CO₂和热解水的生成, 丰富了半焦的孔隙结构。这主要归因于水热预处理过程“组分交互-结构改造-催化裂化”的多重机制, 增强了H/E共混物共热解的协同效应。研究结果为富油煤与生物质共热解协同效应强化技术发展提供了理论支撑, 拓展了富油煤低碳高质化利用新途径。

关键词: 共热解; 协同效应; 水热预处理; 多重机制; 高质化

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