

Study on the structure-activity mechanism of slurry prepared by co-blending corn stalk biochar and coal

KOU Junqiu¹, WANG Chunyu², MAO Ligong¹, DING Lu^{1,*}, YU Guangsu^{1,*}

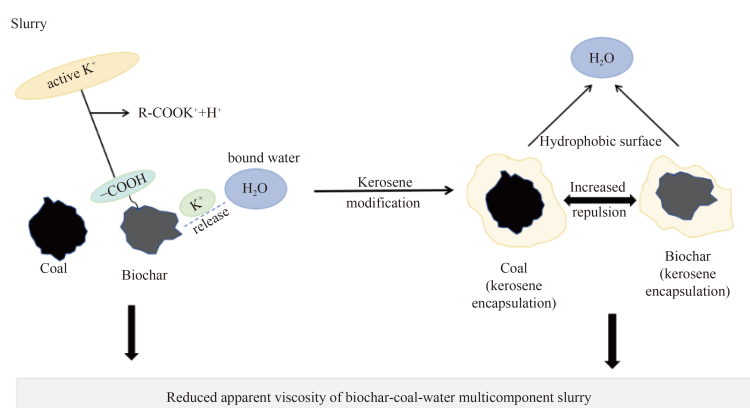
¹ Institute of Clean Coal Technology, State Key Laboratory of Coal Liquefaction, Gasification and Efficient Low-Carbon Utilization, East China University of Science and Technology, Shanghai 200237, China;

² Yancheng Institute of Technology, Yancheng 224051, China

Abstract: In this study, corn straw was used as the raw material and subjected to low-temperature pyrolysis in a tubular furnace within the range of 400–500 °C to investigate the effects of pyrolysis temperature on the physicochemical properties of biochar and the migration behavior of alkali metal potassium (K). Elemental analysis, FT-IR, SEM and BET techniques were employed to examine the effects of temperature on the properties of biochar. The results showed that with increasing pyrolysis temperature, the fixed

carbon content increased, while the volatile matter and oxygen-containing functional groups decreased. The pore structure gradually developed, with the specific surface area and pore volume reaching their maximum values at 475 °C. The total K content decreased with increasing temperature, and its occurrence transformed from water-soluble to organic-bound and residue-bound forms. When the biochar was blended with coal to prepare biochar-coal-water slurry, it was found that within 400–475 °C, potassium ions reacted with carboxyl groups to form potassium carboxylates, reducing hydrophilic groups and enhancing particle hydrophobicity, consequently, the fluidity of the multicomponent slurry is improved and its viscosity is reduced. At 500 °C, mineral deposition led to pore blockage and increased its viscosity. Furthermore, surface modification of biochar particles with kerosene significantly improved the performance of the multicomponent slurry, increasing the maximum slurry concentration by about 2.6%. The study elucidates the structure-activity mechanisms governing the performance of co-slurrying corn-stalk pyrolysis char with coal, providing a theoretical basis for the efficient utilization of biochar in coal-water slurry systems and broader energy applications.

Key words: biomass pyrolysis; alkali metal migration; multi-component slurry; slurryability; particle surface modification



Energy is the core driving force of social development and economic growth and serves as a fundamental basis for human survival and progress^[1]. However, the extensive use of fossil fuels has caused significant negative environmental impacts. Consequently, many countries around the world have adopted various measures to increase the utilization of renewable and clean energy sources in order to mitigate the environmental problems associated with conventional

fossil fuels^[2]. Biomass is the only renewable resource that can be converted into gaseous, liquid, and solid forms of energy^[3], and it can be categorized into several types, including agricultural and forestry residues, wastewater and sewage, energy crops, livestock manure, municipal solid waste and aquatic algae. In China, more than one billion tons of agricultural waste are generated every year^[4]. Due to its wide availability and high energy storage potential, it has

Received: 2025-11-10; Revised: 2025-12-02

Foundation items: Supported by National Key Research and Development Program of China (2023YFB4203803).

* Corresponding author. Tel: 13262903193, 13661801335, E-mail: dinglu@ecust.edu.cn, gsyu@ecust.edu.cn.

DOI: 10.1016/S1872-5813(26)60718-9 CSTR: 32157.14.2097-213X.2026.JFCT.0078 Associated Data DOI: 10.57760/sciencedb.j00124.00365

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

attracted considerable attention, particularly lignocellulosic biomass^[5–6]. Crop straw is an important renewable biomass resource within agricultural ecosystems. The efficient utilization of crop straw resources is of great significance for increasing agricultural productivity and farmers' income, promoting the sustainable development of the agricultural economy and improving environmental quality^[7].

Biomass pyrolysis is a complex thermochemical decomposition process in which biomass is heated under oxygen-limited conditions and decomposes into carbon-rich solids and volatile products^[8]. The process generally includes three stages: pre-pyrolysis, volatile release, and biochar polycondensation, involving the removal of free and bound water, the decomposition of major structural components, and the formation of char^[9]. Pyrolysis technology enables the high-value utilization of biomass, and the resulting products can be used for the production of high value-added chemicals as well as soil amendments, fertilizers, and activated carbon^[10]. The physicochemical properties of biochar vary with pyrolysis conditions. Rapid pyrolysis promotes the extensive release of volatiles from biomass, alters the carbon structure, and results in biochar with larger pore structures and higher reactivity. Moreover, the redistribution of surface functional groups and alkali metal elements during biomass decomposition directly influences the carbon structure of biochar and its subsequent utilization^[11–12].

Coal water slurry (CWS) mainly consists of pulverized coal, water as the dispersion medium, and dispersants. Its performance is determined by several factors, including the intrinsic properties of coal, the type of dispersant, and the particle size distribution^[13–14]. At present, CWS gasification technology is considered a clean and efficient gasification route^[15–17]. However, in practical industrial applications, CWS often exhibits unsatisfactory properties, such as relatively low slurry concentration or poor fluidity. To address these issues, industrial processes commonly employ particle size gradation to optimize particle size distribution, which can effectively improve the performance of CWS. In recent years, researchers have attempted to introduce biomass, sludge, and petrochemical wastes into CWS systems. This approach not only enhances the environmental sustainability of CWS but also enables the co-disposal of solid wastes during the gasification process^[18]. Jiang et al.^[19] prepared CWS by mixing modified municipal sludge with coal and found that higher cation valence facilitates the adsorption of dispersants onto the surfaces of coal or sludge particles, thereby improving dispersion of the slurry. Gu et al.^[20] prepared CWS using coal gasification wastewater and reported that its slurry concentration increased by 0.8 percentage points while exhibiting lower pseudoplasticity. Wang et al.^[21] investigated the co-gasification process of CWS prepared by blending waste activated carbon with coal, and the results indicated that the addition of waste activated carbon significantly

increased the CO content in the produced syngas. Mao et al.^[22–23] introduced 1,4-butanediol (BDO) tar during the preparation of CWS to explore its effects on the combustion and gasification performance of the slurry, and found that the addition of tar significantly enhanced the gasification performance of CWS.

In recent years, the incorporation of biomass into CWS preparation has emerged as a new research direction in this field. Compared with coal, biomass generally contains higher concentrations of alkali metal elements, which may lead to operational problems during industrial applications, such as ash deposition, slagging, blockage, and equipment corrosion^[24]. Existing studies have mainly focused on the influence of pyrolysis conditions on the migration behavior of alkali metals, and some studies have explored their synergistic effects in subsequent gasification processes. However, studies investigating the influence on the performance of biochar-coal-water slurry remains relatively limited. It is worth noting that the migration behavior and speciation changes of alkali metals in biomass during pyrolysis can significantly affect the physicochemical properties of the resulting char, thereby playing an important role in its performance of the multicomponent slurry. According to the Kirkendall effect in solid-state diffusion theory, the migration of alkali metal cations on the surface of carbonaceous particles can induce a pore-expansion effect^[25]. The development of pore structures directly affects the distribution characteristics of water within the slurry system, which in turn has a significant influence on the rheological properties and overall performance of CWS. Therefore, systematically investigating the influence of alkali metals on the performance of multicomponent slurries prepared from biochar and coal is of great scientific significance and engineering value for revealing the synergistic mechanism of biochar and coal in preparing biochar-coal water slurry.

In this study, corn straw was used as the raw material to prepare biochar through low-temperature pyrolysis in a horizontal furnace. A microwave digestion system combined with chemical fractionation methods was employed to investigate the content of alkali metals in different forms within the biochar and to analyze their migration and transformation behavior. In addition, various characterization techniques were applied to examine the surface functional groups, particle morphology, particle size distribution, and pore structure characteristics of the biochar. Subsequently, the biochar was mixed with Shenhua coal at a mass ratio of 1:9 to prepare multicomponent slurries, and the relationship between alkali metal migration and performance of multicomponent slurries was systematically investigated. Meanwhile, kerosene was selected as a secondary liquid to modify the surface of biochar particles in order to optimize the performance of the multicomponent slurry system.

1 Experimental

1.1 Materials

The corn straw (CS) used in this study was collected from the suburban area of Lianyungang, Jiangsu Province, China. The straw was first dried in an oven at 105 °C for 24 h, then crushed using a grinder, and sieved through a 60 mesh sieve to obtain corn straw powder. The obtained powder was further dried in an oven at 105 °C for another 24 h prior to use. The Shenhua coal (SH) used in this work was provided by Shanghai Huayi Group. The coal lumps were dried at 105 °C for 24 h and subsequently pulverized using a rod mill. The resulting coal powder was dried again for 24 h, and sieved using 40 mesh and 200 mesh sieves with a vibrating sieve shaker to obtain coal particles of different size fractions for subsequent experiments. The proximate and ultimate analysis results of the raw materials are presented in Table 1. The oxygen content was calculated by difference.

1.2 Sample preparation and analysis

1.2.1 Pyrolysis of corn straw

The pyrolysis experiments were carried out in a horizontal tubular furnace reactor, as shown in Figure 1. The reactor system mainly consisted of gas supply, reaction, condensation and drying units. The pyrolysis reactions were conducted in a quartz tube with a length of 1000 mm and an inner diameter of 50 mm, and the effective reaction zone was 150 mm. A quartz boat with a length of 150 mm and a radius of 22.5 mm was used to hold the feedstock. In a

typical experiment, 10 g of corn straw previously dried in an oven at 105 °C for 12 h was evenly spread in the quartz boat, which was then inserted into the tubular furnace and positioned in the reaction zone. High-purity nitrogen (99.99%) was introduced into the reactor at a flow rate of 0.5 L/min, and the system was purged for 5 min to remove residual oxygen and establish an inert atmosphere. Subsequently, the furnace was heated at a rate of 5 °C/min to the target temperature and maintained for 60 min. After the holding period, the reactor was allowed to cool naturally to room temperature, and the solid pyrolysis products were collected. The pyrolysis temperatures were set at 400, 425, 450, 475 and 500 °C, and the obtained char samples were denoted as PC-400, PC-425, PC-450, PC-475 and PC-500 according to the reaction temperature.

According to the GB/T 28731—2012 standard, the moisture, volatile matter, ash, and fixed carbon contents of corn straw biochar were determined using a rapid infrared coal analyzer (5E-MAG6700, China). The elemental composition (C, H, O, N and S) of the char samples was measured using an elemental analyzer (Elementar Vario MACRO Cube, Germany) in accordance with the GB/T 31391—2015 standard. The surface morphology of the corn straw after pyrolysis was observed using scanning electron microscopy (SEM, HITACHI SU1510, Japan). Changes in the surface functional groups of the biochar at different pyrolysis temperatures were analyzed using Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific Nicolet iS50, USA). In addition, the pore structure parameters of corn straw and its pyrolysis products were determined using an automatic surface area and porosity analyzer (BET, TriStar II 2460, USA) to further characterize their pore structures.

Table 1 Proximate and ultimate analysis of CS and SH

Sample	Proximate analysis w%			Ultimate analysis w%				
	A_d	V_d	FC_d	C	H	O*	N	S
CS	16.32	63.93	19.75	33.79	4.85	43.59	1.23	0.22
SH	3.98	19.81	76.21	80.42	4.85	9.21	0.93	0.61

d: dry basis; *: by difference.

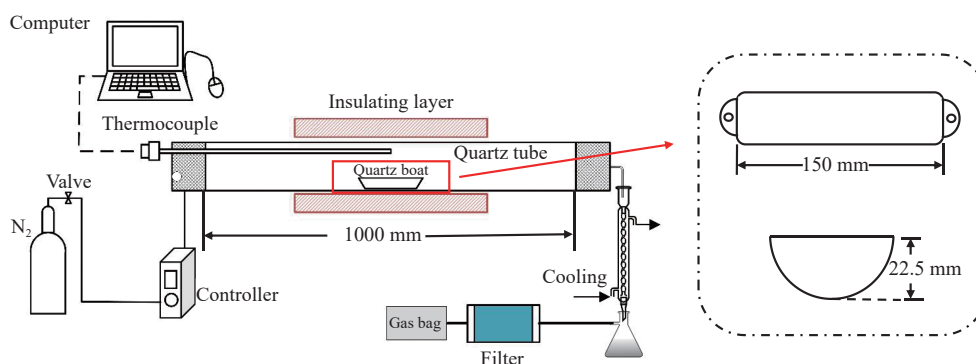


Fig. 1 Horizontal tube furnace reaction setup

1.2.2 Preparation of multicomponent slurry

Preparation of the multicomponent biochar-coal-water slurry (CCWS): A 50 g mixture consisting of biochar and SH was weighed for each sample, where the char content was maintained at 10% of the total dry solids. The SH was prepared using a 1:1 mass ratio of coarse-to-fine particles. Weighing precision was strictly controlled within ± 0.003 g for solids and ± 0.005 g for liquids. Sodium naphthalene formaldehyde sulfonate (MF) was employed as the dispersant at a dosage of 1% based on the dry solids. The solid-dispersant mixture was initially pre-mixed using an electronic stirrer at 700 r/min for 10 min. Subsequently, ultrapure water was added to achieve a target slurry concentration of 60%. The mixture was then subjected to mechanical stirring at 1000 r/min for an additional 15 min to ensure the formation of a homogeneous biochar-coal-water slurry.

Preparation of surface-modified multi-component slurry:

Initially, 5 g of biochar was weighed, and kerosene was introduced as a secondary liquid phase for surface modification. The char-kerosene mixture was mechanically stirred using an electronic stirrer at 700 r/min for 10 min to ensure effective surface treatment. Subsequently, SH particles (with the specified coarse-to-fine ratio) and MF were added to the mixture, followed by an additional 10 min of stirring at 700 r/min to achieve a high degree of homogenization. Finally, a calculated amount of ultrapure water was incorporated to adjust the total solid content to 63%. The resulting suspension was stirred at 1000 r/min for 15 min to yield the final surface-modified multi-component slurry.

In this study, the apparent viscosity of the multicomponent slurry was measured using a rheometer. The fluidity and stability of the slurry were evaluated using visual observation and the rod insertion method. Based on previous studies^[26–28], these properties were classified into four levels, and the specific criteria are shown in Table 2.

Table 2 Grading criteria for the fluidity and stability of multi-component slurries

Level	Fluidity	Stability
A	Dilute fluid with continuous and smooth flow	No stratification or sedimentation
B	Viscous fluid with relatively continuous flow; the surface is not smooth	Slight stratification or sedimentation, easily redispersed
C	Flows properly only with the assistance of external force	Noticeable stratification or sedimentation, requires stirring
D	Mud-like and non-slurry; cannot flow	Severe stratification or sedimentation, hard to redisperse

1.3 Determination and speciation of potassium in biochar

1.3.1 Determination of potassium content

The extraction of target elements from solid to liquid phase was performed using a microwave digestion system (TANK-40, Shanghai Sineo). Specifically, a 0.100 (± 0.005) g sample was weighed into a digestion vessel, followed by the addition of 8 mL HNO₃ (GR grade, 65%–68%) in a fume hood. The mixture underwent pre-digestion at 120 °C for 30 min. Subsequently, 1 mL of HNO₃ and 1 mL of HF (Ultrapure, $\geq 40\%$) were added. The vessel was then sealed and subjected to a programmed microwave digestion (as detailed in Table 3). After cooling, the solution was transferred to an acid-evaporator at 120 °C for 1 h to remove excess HF. The clarified solution was diluted to 100 mL in a volumetric flask. The potassium (K) concentration was determined *via* flame atomic absorption spectroscopy (FAAS, Analytikjena novAA350). All volumetric flasks were pre-soaked in a 10% HNO₃ solution for at least 24 h and rinsed thoroughly with ultrapure water (18.2 M Ω ·cm).

1.3.2 Determination of potassium speciation

The occurrence forms of K in corn stalk and its derived

biochar were analyzed using chemical fraction analysis (CFA). Water-soluble, ion-exchangeable and acid-soluble K were sequentially extracted using ultrapure water, 1.0 mol/L ammonium acetate (CH₃COONH₄) and 1.0 mol/L hydrochloric acid (HCl), respectively. As illustrated in Figure 2, 0.1 g of the dried sample was placed in a PTFE beaker and stirred with 30 mL of ultrapure water at 25 °C for 24 h. The suspension was then centrifuged for 10 min and filtered to collect the supernatant. The solid residue was rinsed three times, and the combined filtrate was diluted to 100 mL. The ion-exchangeable and acid-soluble fractions were extracted from the remaining solids following similar procedures.

A series of K standard solutions with appropriate concentration gradients were prepared to establish a calibration curve with a correlation coefficient (R^2) ≥ 0.995 . The K content in each fraction was then quantified using FAAS, while the residual fraction was determined by subtracting the sum of the extracted fractions from the total K content (calculated by difference).

Table 3 Setting procedures for microwave digestion apparatus

Step	Temperature/°C	Insulation time/min
1	130	5
2	160	5
3	190	30

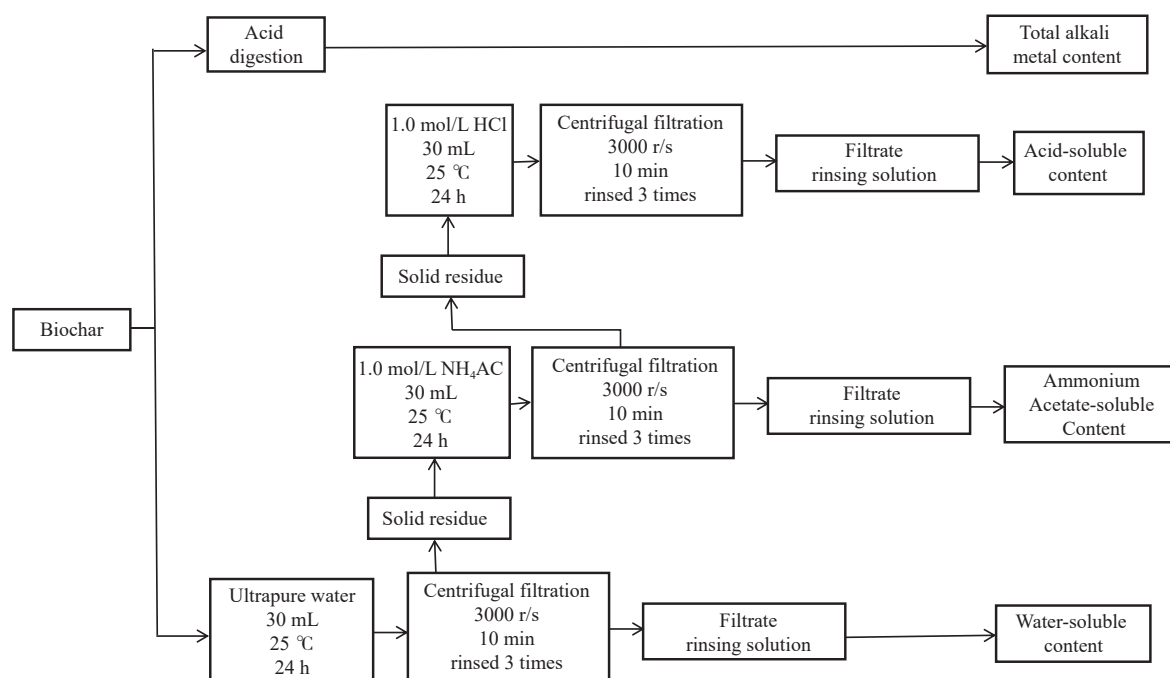


Fig. 2 Experimental flowchart of chemical fractionation analysis

2 Results and discussion

2.1 Effect of pyrolysis temperature on the physicochemical properties of biochar

The pyrolysis of corn stalk was conducted in a horizontal fixed-bed reactor to investigate the effect of temperature on the fundamental properties of the resulting biochar (Table 4). The raw corn stalk exhibited low fixed carbon (19.75%) and ash content (16.32%), while the volatile matter was relatively high at 63.93%. As the pyrolysis temperature increased, the volatile matter content in the biochar decreased, accompanied by a progressive enrichment of fixed carbon and ash. At 500 °C, the composition shifted significantly to 53.53% fixed carbon, 10.88% volatile matter, and 35.59% ash, respectively. Notably, the variations in these components became less pronounced within the 400–500 °C range. This plateau is primarily attributed to the structural characteristics of biomass components: hemicellulose, characterized by a loose structure, undergoes rapid decomposition

(dehydration, decarboxylation, and decarbonylation) at relatively low temperatures and is largely depleted by 400 °C. Similarly, cellulose decomposes intensely between 200–350 °C and approaches complete degradation as the temperature nears 500 °C. In contrast, lignin, with its more complex and robust structure, undergoes a steady and gradual decomposition without a specific high-intensity temperature interval.

Ultimate analysis revealed that the raw corn stalk was rich in carbon (33.79%) and oxygen (43.59%), with lower concentrations of nitrogen (1.23%), hydrogen (4.85%) and sulfur (0.22%). Pyrolysis promoted carbon enrichment and oxygen depletion; the oxygen was primarily liberated in gaseous forms such as CO₂ due to the decomposition and decarboxylation of cellulose and hemicellulose. Consequently, the O/C atomic ratio dropped significantly from 1.29 to 0.25. Additionally, the decomposition of hydrogen-containing compounds led to a decrease in H content, with hydrogen being released as H₂ or CH₄. The nitrogen content remained relatively stable, suggesting that no significant de-nitrification occurred during the pyrolysis process.

Table 4 Proximate and ultimate analysis of corn straw and pyrolytic carbon

Sample	Proximate analysis w _d /%			Ultimate analysis w%				
	A	V	FC	C	H	O*	N	S
CS	16.32	63.93	19.75	33.79	4.85	43.59	1.23	0.22
PC-400	33.99	18.86	47.15	45.45	3.01	16.33	1.17	0.05
PC-425	35.97	18.64	45.39	45.41	2.87	14.44	1.27	0.04
PC-450	34.13	14.36	51.51	47.24	2.68	14.69	1.23	0.04
PC-475	34.71	12.91	52.38	47.77	2.48	13.69	1.31	0.04
PC-500	35.59	10.88	53.53	48.65	2.34	12.08	1.30	0.04

d: dry basis; *: by difference.

2.2 Effect of pyrolysis temperature on potassium migration and speciation in biochar

The total K content in the biochar at different temperatures is presented in Figure 3. A clear downward trend in K concentration was observed as temperature increased. This loss is likely associated with the reaction of K with H₂O and CO₂ during pyrolysis, forming volatile hydroxides or bicarbonates that migrate into the gas phase^[29].

Figure 4 illustrates the transformation of K species within the biochar. The proportion of water-soluble K decreased from 72.36% to 67.52% as the temperature rose, with the rate of decline slowing down as hemicellulose and cellulose decomposition approached completion near 500 °C. Within the 400–475 °C range, the increase in the organic-bound K fraction suggests a phase transformation from water-soluble K to organically-associated K. However, as the temperature reached 500 °C, the organic K fraction decreased while the residual K fraction increased. This indicates that a portion of the organic K was converted into more stable mineral forms, which remained sequestered within the internal matrix or on the surface of the biochar. The acid-soluble K remained stable and represented only a minor fraction of the total K content throughout the pyrolysis process.

2.3 Effect of pyrolysis temperature on the physicochemical properties of biochar

2.3.1 Effect on the surface functional groups of biochar

The FT-IR spectra of corn stalk biochar at various pyrolysis temperatures are presented in Figure 5. The characteristic absorption bands identified include C–H vibrations (880 cm⁻¹), C–O stretching (1000–1300 cm⁻¹), C=O stretching (1650–1740 cm⁻¹) and –OH stretching (3200–3500 cm⁻¹). As the temperature increased, the intensity of the C–H vibration bands attenuated, primarily due to the extensive decomposition of hemicellulose and cellulose. The weakening of the C–O stretching peaks suggests that high-temperature pyrolysis promotes the cleavage and removal of C–O bonds in phenolic and ethereal compounds^[30]. During the initial stages of pyrolysis, the decomposition of ketones, aldehydes, and carboxylic acids led to a reduction in C=O stretching intensity^[31]. Simultaneously, the dehydration of the biomass caused a gradual decrease in –OH absorption intensity, aligning with the depletion of H and O observed in the ultimate analysis. Notably, the reaction between carboxylic acids and water-soluble K (Equation (1)) to form potassium carboxylates further contributed to the reduction of –OH groups. The slight increase in –OH intensity at 500 °C may be attributed to the interaction between steam in the pyrolysis gas and the highly reactive alkali K, promoting the formation of small –OH-containing molecules.

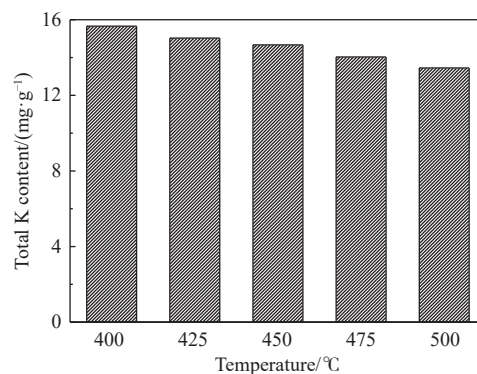


Fig. 3 Changes of potassium alkali metal content in pyrolytic carbon

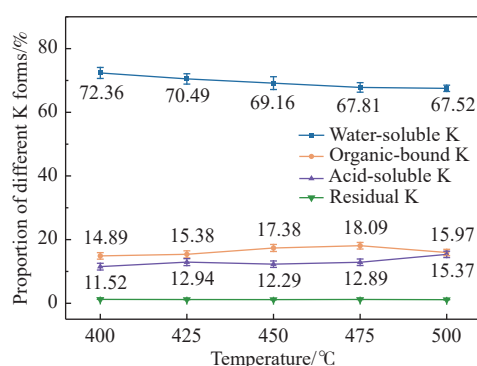


Fig. 4 Morphology changes of potassium in biochar

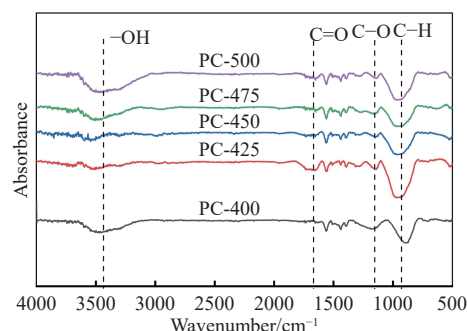


Fig. 5 FT-IR spectra of pyrolytic carbon samples

2.3.2 Effect of pyrolysis temperature on biochar morphology

The micro-morphology of the raw corn stalk and its biochar was captured *via* SEM (Figure 6). The raw biomass exhibited a smooth and integrated surface in Figure 6(a), whereas the biochar displayed fragmented fibrous structures in Figure 6(b)–(f). This fragmentation intensified with increasing temperature, manifesting as irregular cracks and the emergence of pore structures. The particle shape parameters, including sphericity and aspect ratio, are shown in Figure 7. In the 400–475 °C range, the sphericity of the biochar particles increased in Figure 7(a), suggesting that higher temperatures facilitate the transition of particles toward a more spherical morphology.

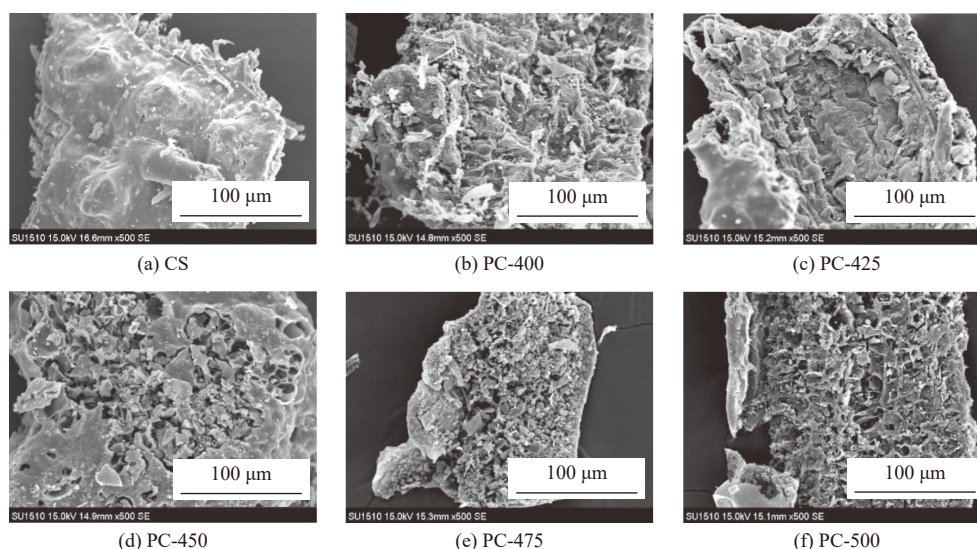


Fig. 6 SEM images of CS and biochars pyrolyzed under different temperatures

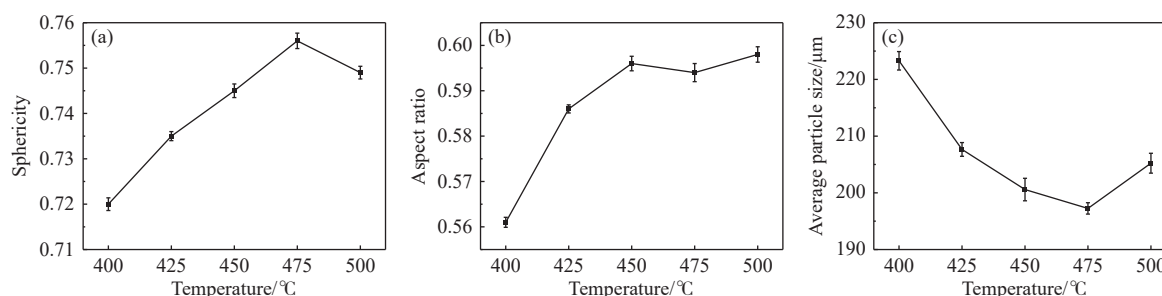


Fig. 7 Effect of temperature on the morphology of pyrolytic carbon particles

However, at 500 °C, the sphericity decreased, likely due to the adhesion of bio-oil onto the particle surfaces, creating irregularities. Despite this, the increase in the breadth-to-length ratio in Figure 7(b) indicates that higher temperatures generally promote more regular particle shapes. Regarding particle size in Figure 7(c), the average diameter decreased from 40 to 475 °C but increased at 500 °C, which is attributed to the condensation of small organic molecules and the deposition of carbonaceous minerals from the gas phase.

2.3.3 Effect of pyrolysis temperature on pore structure of biochar

The evolution of the pore structure is illustrated in Figure 8. Within the 400-475 °C range, the specific surface area (SSA) increased from 1.991 to 4.471 m²/g, indicating that elevated temperatures enhance pore development. However, at 500 °C, the SSA decreased significantly. This reduction is primarily linked to the deposition of tar and heavy organic volatiles that occlude the pores, as well as the thermal collapse of the pore walls at high temperatures. The variation in pore volume correlated with the SSA, also peaking at 475 °C. The subsequent decline in pore volume

at 500 °C is likely caused by the melting and softening of minerals that block the pore channels, alongside the polymerization of small molecular compounds within the matrix.

2.4 Investigation of the rheological properties of multicomponent slurry

2.4.1 Mechanistic study on the relationship between particle characteristics and properties of CCWS

The apparent viscosity of the multi-component biochar-coal-water slurry (CCWS), prepared by blending Shenhua coal with biochar produced at different temperatures, was measured using a rheometer (Figure 9 and Table 5). As the pyrolysis temperature increased from 400 to 475 °C, the apparent viscosity of the CCWS decreased significantly from 907.8 to 591.77 mPa·s. However, as the temperature reached 500 °C, the viscosity rose to 683.52 mPa·s. The stability of the multicomponent slurry after standing for 2–3 d was determined by the rod-drop method. Obvious sedimentation and water separation were observed, whereas the slurry could be recovered by stirring, resulting in a stability rating of Grade C.

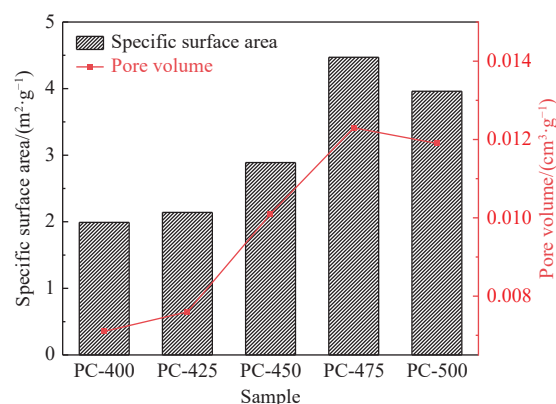


Fig. 8 Pore structure of biochar

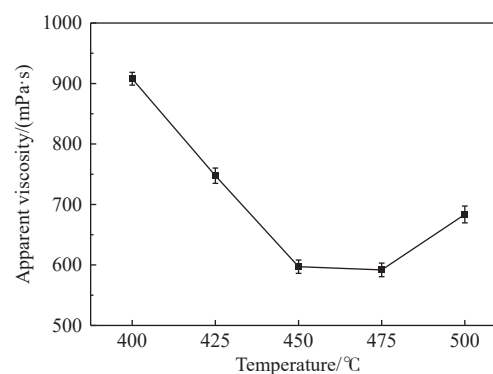


Fig. 9 Apparent viscosity of biochar mixed coal slurry at different pyrolysis temperatures

Table 5 Apparent viscosity, fluidity and stability of multi-slurry

Sample	Concentration/%	Viscosity/(mPa·s)	Fluidity	Stability
PC-400	60	907.83	B	C
PC-425	60	747.62	B	C
PC-450	60	597.15	A	C
PC-475	60	591.77	A	C
PC-500	60	683.52	B	C

The viscosity variations correlate closely with the evolution of biochar morphology (Figure 7). In the range of 400–475 °C, increasing temperature reduces the average particle size and promotes more regular particle morphology, thereby decreasing interparticle friction among the particles in CCWS. This leads to a reduction in its apparent viscosity and consequently improves its fluidity. However, when the temperature is further increased to 500 °C, polycondensation of organic small molecules occurs, with deposits forming on particle surfaces, which increases particle size and interparticle friction, ultimately impairing the fluidity of CCWS. Furthermore, FT-IR analysis (Figure 5) suggests that the reduction of hydrophilic groups (e.g., –OH) due to the reaction between K and carboxyl groups improved surface hydrophobicity, contributing to lower viscosity. At 500 °C, the regeneration of –OH groups through the interaction of reactive K with steam enhanced hydrophilicity, leading to the observed viscosity increase of CCWS.

Low-field nuclear magnetic resonance (LF-NMR) was employed to characterize the distribution of free and bound water within CCWS (Figure 10). From 400 to 475 °C, the free water content increased progressively while bound water decreased. This shift is attributed to the pore-opening effect caused by the removal of alkali metals (Figures 3 and 8), which released bound water trapped within the pores into the bulk phase as free water, thereby improving slurryability. At 500 °C, the reduction in specific surface area and pore volume inhibited the release of bound water. Additionally, the increase in hydrophilic groups (Figure 5) enhanced the adsorption capacity for bound water, further reducing the free water fraction and increasing viscosity

of CCWS. The polymerization of small organic molecules also occluded pores, hindering both the release of bound water and the entry of free water, which negatively affected the slurryability of CCWS.

2.4.2 Effect of kerosene-modified particle surfaces on properties of CCWS

The effect of kerosene dosage (0.5%–1.0%) on the rheological properties of CCWS prepared with modified PC-450 biochar (63% concentration) is shown in Figure 11. As the kerosene dosage increased from 0.5% to 0.8%, the apparent viscosity dropped from 1447.62 to 694.04 mPa·s. This indicates that kerosene formed a coating layer on the PC-450 particles, effectively enhancing hydrophobicity and preventing water absorption by the pore structures. However, excessive kerosene (beyond 0.8%) led to a viscosity increase, likely due to the formation of interparticle oil bridges and the entrapment of water within the oil phase, which reduced the lubricating effect of free water.

The maximum slurry concentration (defined at 100 s⁻¹ and 1000 mPa·s) was determined to evaluate the impact of modification (Figure 12). As shown in Figure 12, the maximum concentration of CCWS prepared with PC-450 and SH was approximately 61.6%. In contrast, after surface modification of the biochar particles with kerosene, the maximum concentration increased to about 64.2%, corresponding to an increase of 2.6 percentage points. These results indicate that kerosene modification can effectively improve the surface characteristics of biochar particles, thereby enhancing the slurryability of CCWS.

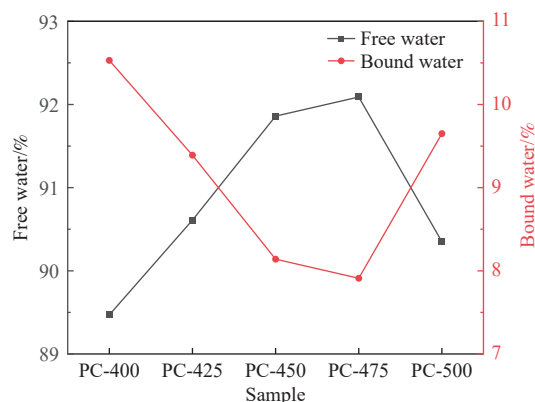


Fig. 10 The proportion of free water and bound water in multi-slurry

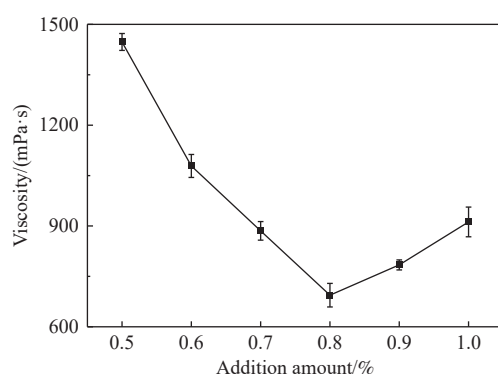


Fig. 11 Effect of kerosene on the apparent viscosity of CCWS

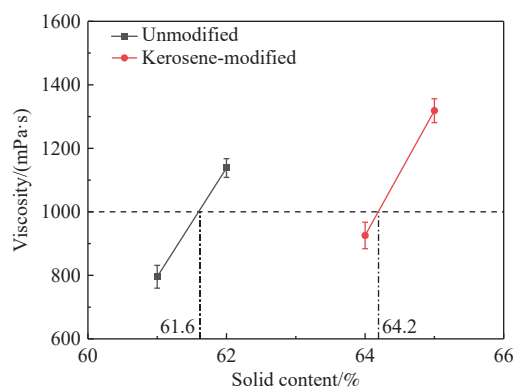


Fig. 12 Effect of kerosene on the maximum slurry concentration of CCWS

3 Conclusions

As the pyrolysis temperature increased, a portion of the K migrated into the gas phase to form volatile compounds, leading to a reduction in total K content. Concurrently, the K species transformed from a water-soluble state to an organic-bound state, eventually forming stable mineral residues at higher temperatures. The biochar surface evolved from a dense and smooth texture to a porous structure with cracks and developed pores. Both specific surface area and pore volume increased accordingly, before

declining at 500 °C due to pore occlusion caused by mineral melting. Regarding particle morphology, sphericity improved and the average particle size decreased within the 400–475 °C range; however, at 500 °C, the deposition of small organic molecules resulted in reduced sphericity and an increase in average particle size.

Within the 400–475 °C range, the reaction between water-soluble K and surface carboxyl groups to form potassium carboxylates reduced the hydrophilic group content. This enhanced the surface hydrophobicity of the particles, thereby forming a slurry with good fluidity and low apparent viscosity. Additionally, the pore-opening effect induced by alkali metal removal promoted the release of bound water from the internal pores, facilitating the formation of a low-viscosity slurry. When the temperature reached 500 °C, the transformation of K from an ion-exchangeable state to a residual state, coupled with mineral deposition on the particle surfaces, compromised particle regularity. Furthermore, the reaction between alkali metals and steam in the gas phase generated hydrophilic groups (e.g., –OH), which enhanced the adsorption of bound water. As a result, the viscosity of CCWS increases while its fluidity decreases.

Surface modification of biochar particles using kerosene significantly improved the rheological properties of CCWS, characterized by a marked reduction in viscosity and enhanced fluidity. However, excessive kerosene addition altered the inter-particle interactions within the slurry system, exerting a detrimental effect on its rheological performance. Experimental results indicated that the optimal kerosene dosage was 0.8% of the dry solids. Under these optimal conditions, the maximum slurry concentration of CCWS reached 64.2%, representing an increase of 2.6 percentage points compared to the unmodified system.

References

- [1] KRERKKAIWAN S, FUSHIMI C, TSUTSUMI A, et al. Synergetic effect during co-pyrolysis/gasification of biomass and sub-bituminous coal[J]. Fuel Process Technol, 2013, 115: 11–18.
- [2] BLANQUET E, NAHIL M A, WILLIAMS P T. Enhanced hydrogen-rich gas production from waste biomass using pyrolysis with non-thermal plasma-catalysis[J]. Catal Today, 2019, 337: 216–224.
- [3] XU L, LUO P, YAN M. Present situation of biomass energy utilization in China[J]. Guangzhou Chem, 2016, 26(11): 47–48.
- [4] YANG C, LU S. Straw and straw biochar differently affect phosphorus availability, enzyme activity and microbial functional genes in an Ultisol[J]. Sci Total Environ, 2022, 805: 150325.
- [5] CHEN L, WANG X, YANG H, et al. Study on pyrolysis behaviors of non-woody lignins with TG-FTIR and Py-GC/MS[J]. J Anal Appl Pyrolysis, 2015, 113: 499–507.
- [6] CUSTODIS V B F, BÄHRLE C, VOGEL F, et al. Phenols

- and aromatics from fast pyrolysis of variously prepared lignins from hard- and softwoods[J]. *J Anal Appl Pyrolysis*, 2015, 115: 214–223.
- [7] WANG X, YANG Z, LIU X, et al. The composition characteristics of different crop straw types and their multivariate analysis and comparison[J]. *Waste Manag*, 2020, 110: 87–97.
- [8] WANG H, WANG X, CUI Y, et al. Slow pyrolysis polygeneration of bamboo (*Phyllostachys pubescens*): Product yield prediction and biochar formation mechanism[J]. *Bioresour Technol*, 2018, 263: 444–449.
- [9] HU EF, ZHAO LX, WU J, et al. Progress in research on the influencing factors and technologies of biomass pyrolysis[J]. *Trans Chin Soc Agric Eng*, 2018, 34(14): 212–220.
- [10] BACH Q V, CHEN W H. Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review[J]. *Bioresour Technol*, 2017, 246: 88–100.
- [11] QIAN H, CHEN W, ZHU W, et al. Simulation and evaluation of utilization pathways of biomasses based on thermodynamic data prediction[J]. *Energy*, 2019, 173: 610–625.
- [12] TORRES E, RODRIGUEZ-ORTIZ L A, ZALAZAR D, et al. 4-E (environmental, economic, energetic and exergetic) analysis of slow pyrolysis of lignocellulosic waste[J]. *Renewable Energy*, 2020, 162: 296–307.
- [13] XIE Y, SUN D, PAN S, et al. Evaluating the influence of coal particle size gradation on the properties of coal–water slurry[J]. *Powder Technol*, 2024, 435: 119431.
- [14] LI Q, LIAO C, HOU J, et al. Model to predict packing efficiency in coal water slurry: Part1 construction and verification[J]. *Fuel*, 2022, 318: 123345.
- [15] SINGH H, KUMAR S, MOHAPATRA S K, et al. Slurryability and flowability of coal water slurry: Effect of particle size distribution[J]. *J Cleaner Prod*, 2021, 323: 129183.
- [16] GU S, XU Z, REN Y, et al. Energy utilization of direct coal liquefaction residue via co-slurry with lignite: Slurryability, combustion characteristics, and their typical pollutant emissions[J]. *Fuel*, 2022, 326: 125037.
- [17] HU S, LI J, LIU K, et al. Comparative study on distribution characteristics of anionic dispersants in coal water slurry[J]. *Colloids Surf Physicochem Eng Aspects*, 2022, 648: 129176.
- [18] ANTONOV D V, NYASHINA G S, STRIZHAK P A, et al. Micro-explosive droplet fragmentation of environmentally promising coal-water slurries containing petrochemicals[J]. *Fuel*, 2021, 283: 118949.
- [19] JIANG X, ZHOU Y, MENG X, et al. The effect of inorganic salt modification of sludge on the performance of sludge-coal water slurry[J]. *Colloids Surf Physicochem Eng Aspects*, 2023, 664: 131146.
- [20] GU S, XU Z, DAI Y, et al. The resource utilization of coal gasification wastewater by co-slurry with lignite: Slurryability, dispersion/aggregation behavior, and co-slurrying mechanisms[J]. *Fuel*, 2023, 352: 129114.
- [21] WANG J, CHEN J, LIU J, et al. Synergistic effects of mixing waste activated carbon and coal in co-slurrying and CO₂ co-gasification[J]. *Powder Technol*, 2022, 395: 883–892.
- [22] MAO L, ZHENG M, LI H. Acceleration effect of BDO tar on coal water slurry during co-gasification[J]. *Energy*, 2023, 262: 125432.
- [23] MAO L, LI H, ZHANG Y, et al. Preparing coal water slurry from BDO tar to achieve resource utilization: Combustion process of BDO tar-coal water slurry[J]. *Energy Fuels*, 2019, 33(10): 10297–10306.
- [24] CHEN H. Migration mechanisms of chlorine and potassium during torrefaction and subsequent pyrolysis of rice straw[D]. Shanghai: East China University of Science and Technology, 2017.
- [25] ZHANG L, LI Y, LU S, et al. Kirkendall effect synthesis of platinum group metal nanocage catalysts[J]. *Gansu Sci Technol*, 2021, 37(12): 30–32.
- [26] CAO S, MA X, LI G, et al. Study on the slurry formation characteristics of coal–water slurry prepared with anionic dispersants for different coal types[J]. *Contemp Chem Res*, 2025, 12: 1–7.
- [27] YAO D, ZHAO H, CHEN Z, et al. Preparation of high concentration coal water slurry with good fluidity based on only modified fine particles under bimodal distribution using the second fluid and the second particle[J]. *Fuel*, 2022, 317: 123461.
- [28] MA C, ZHANG W, LI Z, et al. Preparation of coal-water slurry using high-concentration inorganic saline wastewater containing microplastics — A slurry performance and particle interaction analysis[J]. *Fuel*, 2024, 375: 132660.
- [29] DAHOU T, DEFOORT F, JEGUIRIM M, et al. Towards understanding the role of K during biomass steam gasification[J]. *Fuel*, 2020, 282: 118806.
- [30] HU Y, WU Y, GAO T, et al. Evolution characteristics of surface functional groups of char residues during sewage sludge pyrolysis[J]. *Combust Sci Technol*, 2018, 24(2): 126–131.
- [31] ZHU H, YI B, HU H, et al. The effects of char and potassium on the fast pyrolysis behaviors of biomass in an infrared-heating condition[J]. *Energy*, 2021, 214: 119065.

玉米秸秆生物炭与煤共成浆的浆体构效特性机制研究

寇俊秋¹, 王春雨², 茅力龚¹, 丁 路^{1,*}, 于广锁^{1,*}

(1. 华东理工大学 洁净煤技术研究所 煤液化气化及高效低碳利用全国重点实验室, 上海 200237;

2. 盐城工学院, 江苏 盐城 224051)

摘 要: 本工作以玉米秸秆为原料, 采用卧式管式炉在 400–500 °C 进行低温热解, 研究了热解温度对生物炭理化性质及碱金属钾(K)迁移行为的影响。通过元素分析、红外光谱、扫描电镜及比表面积等表征手段研究了温度对热解炭理化性质的影响, 结果表明, 随热解温度升高, 生物炭中固定碳含量增加、挥发分和含氧官能团减少, 孔隙结构逐渐发育, 比表面积与孔容在 475 °C 达到最大值。总钾含量随温度升高而下降, 其赋存形态由水溶态逐渐向有机态和残渣态转变。将热解炭与煤混合制备炭-煤-水多元浆体, 发现在 400–475 °C, 钾离子与羧基反应生成羧酸钾盐, 减少亲水基团数量, 增强颗粒疏水性, 从而改善多元浆体的流动性并降低黏度; 当温度升至 500 °C 时, 矿物质沉积导致孔隙堵塞, 浆体黏度回升。进一步通过煤油对热解炭颗粒进行表面改性, 可显著提升浆体成浆性能, 使最大成浆浓度提高约 2.6 个百分点。研究揭示了玉米秸秆热解炭与煤共成浆的浆体成浆性能的构效机制, 为生物质炭在水煤浆及能源体系中的高效利用提供理论依据。

关键词: 生物质热解; 碱金属迁移; 多元浆体; 成浆性能; 颗粒表面改性

中图分类号: TQ536

文献标识码: A

作者简介:



寇俊秋(2001), 硕士研究生, 研究方向为掺混生物炭的炭-煤-水多元浆体成浆性能及构效机制研究, kjqiu0189@163.com。