INTRODUCTION

Biomass is the only renewable and sustainable carbon resource, expected to be a promising clean alternative to traditional fossil fuels because of carbon-neutral, low pollutant emission, and wide distribution. To solve the drawback of low energy density, thermochemical conversion techniques were applied, including pyrolysis, gasification and combustion, by which multiple high-grade energy products can be produced. However, the industrial application of such materials still faces serious obstacles in terms of technical issues and economic competitiveness. On the other hand, coal
is still dominant in the current national energy consumption structure of China, taking up more than 50% of world coal consumption in 2018. Due to the similarity in thermochemical conversion facilities, co-processing of biomass and coal has attracted much attention, attempting to figure out their limitations and technical issues to acquire higher economic benefits.

For thermochemical conversion, pyrolysis is the first step that has a significant impact on the overall process, and of course, co-processing is no exception. Thus, the knowledge of interactions during co-pyrolysis is essential. Most early studies have focused on three-phase yields, which were considered the direct indicator of co-pyrolysis synergy. However, even though different kinds of biomass and coal were extensively examined, the benefits of co-pyrolysis synergy are still unclear. For example, a high heating rate was once believed in favor of positive synergy because of the strengthened free radical reaction during simultaneously evolved volatiles from both biomass and coal; however, some researchers did not support such point. Afterwards, synergy under slow heating rates was also claimed. Due to the urgent desire for taking full advantage of co-pyrolysis synergy covering various working conditions and materials, it is necessary to find suitable interpretations and build correct understandings of these findings.

Char is basically a carbonaceous solid material derived from carbonization, pyrolysis, and gasification. It is well established that the overall combustion rate of biomass and coal is usually limited by char conversion, which is much slower than devolatilization. Based on this, the evolution of char from various carbonaceous fuels has been widely studied, uncovering many major differences between biomass- and coal-derived chars, such as structural order, porosity, and reactivity. That is, the distinctions are also helpful in revealing the hidden process and synergy during co-pyrolysis. Many informative progresses have been made in this way to identify the role of co-pyrolysis synergy. Wu et al studied the effects of cellulose on the co-pyrolysis char and found promoted pore uniformity as well as the negative synergistic effect in char gasification reactivity. Krerkkaiwan et al and Guo et al found that the morphology of co-pyrolysis char was changed into a loose packed and more porous structure. Chen et al validated significant differences in gasification reactivity between simple char blends and co-pyrolysis char. Wei et al investigated the impact of co-pyrolysis synergy on char structure evolution, alkali and alkaline-earth metal (AAEM) transformation. Kastanaki et al assessed the combustion reactivity and kinetics of co-pyrolysis char from various biomass, lignite, and hard coal. Hu et al investigated the volatile–char interactions between biomass and coal, and their influences on CO₂ gasification reactivity.

However, the relationship between char evolution and co-pyrolysis synergy is still not clear. In addition, investigation on thermal behaviors during combustion of co-pyrolysis char is insufficient, especially for distinguishing the influential effect from co-combustion of char blends. The unexplored issues might confuse further application of co-processing of these fuels. Thus, in this work, physicochemical properties of the chars derived from co-pyrolysis of cornstalk (CS) and bituminous coal (BC) were characterized. The chars were prepared at 600°C and 800°C, and the characterization methods included N₂ and CO₂ adsorption-desorption, X-ray diffraction (XRD), ultimate analysis, inductively coupled plasma optical emission spectrometer (ICP-OES), scanning electron microscope equipped with energy-dispersive X-ray spectrometer (SEM-EDS), and non-isothermal thermogravimetric-differential scanning calorimeter (TG-DSC). The results were expected to provide in-depth physicochemical information, including pore structure, carbon structure, surface morphology, elemental distribution, AAEMs migration, and combustion reactivity of co-pyrolysis char, which contributed to bringing insights into their understandable relationship with co-pyrolysis synergy.

### EXPERIMENTAL SECTION

#### 2.1 Raw materials

CS and BC were chosen as the raw materials in this work. They were obtained from a bioenergy company in Shandong Province and a coalfield located in Shaanxi Province in China.
respectively. All raw materials were ground and sieved to over 80 meshes (<0.18 mm), and dried in the oven at 105°C for at least 4 hours. Afterwards, CS and BC were premixed by different mass blending ratios, including 3:1, 1:1, and 1:3 from one to another. Proximate and ultimate analysis of CS and BC is shown in Table 1.

2.2 | Char preparation

Considering the difference between the thermal behaviors of biomass and BC, the method for char preparation was designed to simulate the condition of fast co-pyrolysis, which was expected to strengthen the volatile release and potential synergistic effects. A tubular resistance furnace equipped with a quartz tube reactor was employed. The reactor was sufficiently swept in advance by high-pure nitrogen (≥99.99%) to ensure the inert atmosphere and then preheated to the desired temperatures before feeding raw materials. Pyrolysis temperatures were 600°C and 800°C, which was left isothermal for at least 10 minutes to stabilize the temperature field. Afterwards, single or premixed materials (10 g) were loaded in a porcelain container and rapidly fed to the middle of the heating zone, which was blown by nitrogen (100 mL min⁻¹). After holding the temperature for at least 1 hour, the reactor cooled down naturally, and the newly produced char was removed from the container and preserved for further investigation.

2.3 | Char characterization

Adsorption-desorption tests by N₂ at 77 K and CO₂ at 273 K were carried out using Autosorb-IQ2-MP (Quantachrome Instruments). The char samples were degassed in vacuum at 300°C for 6 hours before the tests. Owing to different pore sizes and adsorbates, different methods were applied for specific surface area (SA) and pore size distribution: (1) based on N₂ isotherms, Brunauer– Emmett– Teller (BET) method, t-Plot method, and Barrett– Joyner– Halenda (BJH) model were employed for total SA, micropore area, and mesopore size distribution, respectively; and (2) based on CO₂ isotherms, Grand Canonical Monte Carlo (GCMC) method was employed for SA and pore volume of ultramicropore. The above-mentioned methods were built-in models of ASiQwin software (Quantachrome Instruments), which was used for data analysis. Due to the heterogeneity of char, all calculations were based on the adsorption branches.

XRD experiment was conducted by D8 Advance (Bruker Corporation) for the sake of identifying the phase of carbon and mineral matters using Cu Kα radiation at 40 kV and 40 mA. The intensities of X-rays were recorded against the diffraction range at 5° ≤ 2θ ≤ 95° with a scan rate of 5° min⁻¹.

Ultimate analysis was performed for the contents of C, H, N and O according to the Chinese National Standard GB476-91. ICP-OES analysis (Varian 720-ES, Agilent Technologies) was applied for the quantitative measurement of the major metal elements including K, Ca, Na, Mg, Al, and Fe.

Surface morphology and elemental distribution of char were investigated by SEM-EDS (Sigma 500, Zeiss). In addition to individual char samples, the images of CS and BC char particles in each co-pyrolysis char sample were also captured. The magnification was set at 10 000x, and EDS analysis was conducted at spot mode. Five point locations for each SEM image were randomly chosen, whose average values of elemental contents were demonstrated.

In this work, abbreviations were used for description of the experimental or test schemes in the format of “material (blending ratio when blended) - pyrolysis temperature”, for example, C-600 meant CS char prepared at 600°C, B-800 meant BC char prepared at 800°C, and CB31-800 referred to char of 75 wt%CS + 25 wt%BC from 800°C co-pyrolysis. For the evaluation of co-pyrolysis synergy based on SA and elemental analysis, the calculated values (cal.) by simply adding the values from single chars proportionally were introduced compared with the real experimental values (exp.) of co-pyrolysis char. CS and BC have different mass residues after pyrolysis; therefore, the theoretical proportions of CS char and BC char in blended scenarios were no longer linear as those adopted in raw materials (3:1, 1:1 and 1:3), which were calculated and shown in Table 2.

2.4 | TG experiment for char combustion reactivity

Non-isothermal TG-DSC measurement dealing with char combustion was conducted using STA449 F5 Jupiter Simultaneous Thermal Analyzer (NETZSCH Instruments). Air (40 mL min⁻¹) was introduced as the combustion agent.

### Table 2: Theoretical proportions of CS char and BC char adopted in calculated groups [wt%]

| Scenarios | From CS char | From BC char | Scenarios | From CS char | From BC char |
|-----------|--------------|--------------|-----------|--------------|--------------|
| CB31-600  | 61.76        | 38.24        | CB31-800  | 62.43        | 37.57        |
| CB11-600  | 34.99        | 65.01        | CB11-800  | 35.65        | 64.35        |
| CB13-600  | 15.21        | 84.79        | CB13-800  | 15.59        | 84.41        |
Meanwhile, nitrogen (40 mL min$^{-1}$) was used as protective gas. In each test, char sample (~10 mg) was loaded in an aluminum oxide crucible. The heating program was performed from the ambient temperature (~27°C) to 800°C with a constant heating rate (10°C min$^{-1}$). In order to decrease potential concerns of overlapping impacts from additional devolatilization of the char, only the char from 800°C pyrolysis was studied. Besides, a control group was particularly introduced to distinguish whether the synergistic effects were from co-pyrolysis of the raw materials, or co-combustion of the chars. These control groups were named by a prefix “C-” to differentiate them from co-pyrolysis char. For example, C-CB31-800 represented “the char blend theoretically had the same char blending ratio as CB31-800”. The blending ratios of the char blends conform to those in Table 2.

3 | RESULTS AND DISCUSSION

3.1 | N$_2$ and CO$_2$ adsorption-desorption analysis

N$_2$ and CO$_2$ adsorption-desorption isotherms of the chars are shown in Figures 1 and 2, by which the SA and porosity of the chars could be figured out and shown in Table 3. N$_2$ isotherms generally followed multiple categories of type I, II, and III according to the standard of IUPAC (International Union of Pure and Applied Chemistry), indicating complex structures of the char. When char preparation temperature increased from 600°C to 800°C, $S_{N_2-BET}$ of CS char increased from 82.6 m$^2$ g$^{-1}$ to 135.6 m$^2$ g$^{-1}$, but that of BC char decreased from 50.6 m$^2$ g$^{-1}$ to 3.3 m$^2$ g$^{-1}$. However, as
suggested by the parameters in Table 3, BC char had pretty high microporosity, which was beyond the scope of N₂-BET analysis. It validated the importance of CO₂ as a molecular probe at ultra-micro scale and also shed some light on co-pyrolysis synergy, which could not be interpreted well by single N₂-BET analysis.

By comparing the experimental and calculated values of SA_{N₂-BET}, positive or negative synergy brought by co-pyrolysis could be identified. As observed, co-pyrolysis at 800°C was consistently in favor of reducing SA_{N₂-BET} of the char, whose relative differences [100% × (exp./cal. − 1)] were always minus, ranging from −79.0% (CB11-800) to −43.1% (CB13-800). These results are consistent with some previous studies, but the situation was quite different for co-pyrolysis char obtained at 600°C since the relative difference became very unstable and fluctuant, ranging from −92.7% (CB11-600) to +136.3% (CB31-600). On the other hand, SA_{CO₂-GCMC} of co-pyrolysis char presented much less differences between experimental and calculated values, whose ranges were from −5.0% (CB31-600) to +12.6% (CB11-600) for 600°C chars and −3.1% (CB11-800) to −1.5% (CB13-800) for 800°C chars. The fact clearly revealed that volatile–volatile and volatile–solid interactions during co-pyrolysis impacted on meso- and large micropores more seriously than ultramicropores. It is well known that the volatile might crack into gas or condense at the high-temperature surface because of secondary reactions, and those which form larger ring systems would be charred and became carbonaceous deposits, or called secondary char.

Therefore, the final performance of the SA and pore volume depended on the competition between primary char matrix and secondary char. Compared with individual pyrolysis, different void spaces and free radical reactions in co-pyrolysis would lead to different distributions of secondary char.
char deposits. Depending on the above factors, the results indicated that the porous channels at around 1-3 nm were severely influenced by co-pyrolysis synergy, which contributed to the majority of SA BET. To be specific, for co-pyrolysis at 800°C, the primary effect of secondary char might be simply blocking these porous channels, reducing SA BET and the proportion of micropore SA. However, at 600°C, the variation was more sophisticated. Considering that 600°C was a pretty moderate temperature for pyrolysis, there were quite a lot of uncertainties for char evolution and volatile release which were still in progress. However, it is noteworthy that the char from 1:1 blended materials always had the lowest SA BET compared with other blended cases. On the other hand, the variations of SA GCMC were much less compared to those of SA BET, which was probably because the nascent secondary char itself had very abundant microporous structures. Therefore, the change of SA BET did not count much to SA GCMC. The results would be meaningful for CO$_2$ gasification of char because of the strong correlation between CO$_2$ gasification reactivity and micropore SA.

### Table 3

| Scenarios | Exp. | Cal. | Exp. | Cal. | Exp. | Cal. |
|-----------|------|------|------|------|------|------|
| C-600     | 82.6 | -    | 71.4 | 86.4 | 260.7| -    |
| CB31-600  | 111.6| 70.4 | 103.6| 92.8 | 286.8| 302.0|
| CB11-600  | 4.5  | 61.8 | 4.3  | 95.6 | 372.5| 330.8|
| CB13-600  | 130.9| 55.4 | 124.5| 95.1 | 356.2| 352.2|
| B-600     | 50.6 | -    | 43.3 | 85.6 | 368.6| -    |
| C-800     | 135.6| -    | 121.2| 89.4 | 248.4| -    |
| CB31-800  | 27.8 | 85.9 | 17.5 | 62.9 | 313.5| 314.4|
| CB11-800  | 10.6 | 50.5 | 5.7  | 53.8 | 361.9| 373.5|
| CB13-800  | 13.6 | 23.9 | 8.8  | 64.7 | 406.4| 412.5|
| B-800     | 3.3  | -    | 1.9  | 57.6 | 442.8| -    |

**Notes:**

- SA: surface area.
- BET: Brunauer-Emmett-Teller.
- GCMC: Grand Canonical Monte Carlo.
- Exp.: experimental values.
- Cal.: calculated values.

### Figure 3

XRD patterns of chars from pyrolysis at (A) 600°C and (B) 800°C.
3.2 | XRD patterns

XRD patterns were expected to provide more information about the carbon phase and mineral matters in the char, which are shown in Figure 3. The carbon structures in the char could be divided into amorphous carbon and turbostratic carbon. Amorphous carbon generally refers to non-crystalline forms of carbon, and turbostratic carbon is an intermediate state between amorphous and graphite structures. The background intensity of XRD spectrum is closely connected to the presence of amorphous carbon. The notable features of turbostratic carbon are (002) band at around 20 ≈ 44°, 30 which were originally the characteristic peaks of graphite-like carbon but presented as diffused bands which are marked in Figure 3. The intensity of (10) band distributed in 20 ≈ 38-50°. Meanwhile, due to the overlapping of γ band (20 ≈ 15-25°) which suggested the existence of saturated aliphatic chains, (002) band was asymmetric and distributed in 20 ≈ 15-32°. Apparently, the background as well as the intensity of (002) and (10) bands increased gradually in the case of higher BC fraction, indicating that BC char was richer in both amorphous and turbostratic carbon. No conclusive change in characteristic bands of carbon was found in co-pyrolysis scenarios, suggesting that no fundamental change occurred in the carbon structure.

The key components of mineral matters detected in CS char were quartz (SiO2, 2θ = 20.86°, 26.64°, 36.54°, 39.46°, 50.13°, 55.32°, 59.95°, and 68.13°) and potassium chloride (KCl, 2θ = 28.35°, 40.52°, and 50.19°). In BC char, quartz was also found important along with the presence of some CaCO3 (2θ = 29.48°). No clue of other mineral contents was observed. The spectra indicated that there were still considerable contents of KCl retained, which makes sense because devolatilization could only lead to a minimal release of inorganic-K. It has been reported that AAEMs in biomass were likely to interact with the mineral matter in coal and form specific aluminosilicates during gasification or combustion, such as KAlSiO4, KAlSi3O8, and Ca3Al2(SiO4)3. This interaction was regarded as negative synergy for thermochemical co-conversion because of catalytic deactivation of AAEMs. Nevertheless, the observation of XRD patterns indicated the lack of such interaction, which meant it probably occurred during subsequent char combustion, since the carbon matrix would be further destroyed.

3.3 | Elemental analysis

The identification of the elemental composition of the char is summarized in Figure 4. The one-side error bar referred to the gaps between measured values of real co-pyrolysis char and corresponding calculated values from individual char. Interestingly, compared to the calculated values, the experimental values of carbon content were always slightly higher. It might be considered as a side effect of free radical reactions during devolatilization. As indicated by previous researches, small free radicals such as H radical and OH radical from biomass would interact with the fragments from coal pyrolysis, preventing them from increment, stabilizing as light tar products, or secondary char. Reversely, the redundant fragments from biomass pyrolysis would combine, which resulted in the growing of aromatic rings. As a result of competing with being released, more carbon was retained in the char. Compared with the raw materials, hydrogen content has been extremely reduced. Thus, further conversion of the char, such as co-gasification or co-combustion, could no longer rely on the hydrogen donation mechanism, which was considered to exist in co-pyrolysis. The release of nitrogen was in the form of gaseous nitrogen species, which was accompanied by the release of volatile. However, co-pyrolysis under 800°C led to considerably less release of N, which meant the relationship between co-pyrolysis synergy and N release needs further exploration.

K, Ca, Mg, and Al appeared to be the main AAEM species in CS char, while only Ca and Al were of high content in BC char. Many studies have reported that pyrolysis would lead to notable losses of AAEMs, sometimes even more than in an oxidizing atmosphere. K+ would become highly mobile and volatile under high-temperature conditions combined with chloride emissions, and its interaction with H radical also promoted its removal. In addition, water-soluble K tended to form organic-K with carboxyl acids and methoxyl, and then released or was captured by char matrix. Ca and Mg, usually serving as a crosslinking-point of the char matrix, were likely to form carboxylate and phenolate ester with carboxylic acid and phenolic groups, and evolved at the molecular level rather than retained inside the mineral structures. Based on the mechanism, it was interesting to find that the experimental AAEMs contents of co-pyrolysis chars were always higher compared to the calculated values, suggesting that co-pyrolysis synergy was strongly in favor of retaining AAEMs in the solid phase. The results mostly agreed with those previously reported by Zhang et al. and Chen et al.

According to the observations, AAEMs from biomass were probably captured and stabilized by the char matrix of BC. However, it was worth discussing why the variations of experimental AAEMs contents became different with the change of temperature and blending ratio. Starting from individual pyrolysis cases, the gaps of AAEMs contents between 600°C and 800°C scenarios were very small, indicating that the release of AAEMs was basically in proportion to the release of volatiles between 600°C and 800°C. Nevertheless, for co-pyrolysis, AAEMs contents were found much higher when the char preparation temperature was 600°C, except for the cases when the blending ratio between CS and BC
was 1:3. The results revealed some clues for finding the optimum blending ratio for AAEMs retention under different co-pyrolysis temperatures, but the information for explaining the mechanism is still not enough. It would be further discussed in the next section combined with EDS elemental analysis.

3.4 Macro-morphology and surface elemental distribution

The SEM images presenting char surface morphology are shown in Figure 5. Several distinct features were regarded as the basis to distinguish the source of particles in co-pyrolysis char. From the view of morphology, CS char was highly twisted and irregular with many cavities, pores, and wrinkles, which was deeply connected with softening and melting during pyrolysis. BC char was composed of tight aromatic ring systems, mostly with smoother surfaces and sharp edges, and the cracks were due to the shrink during devolatilization. However, it was not easy to distinguish whether the particle was from individual pyrolysis or co-pyrolysis, even though many groups from different scenarios were compared. The above-mentioned secondary char deposits might be helpful; however, the macro-morphologies of the char were extremely diverse as the raw materials. The changes were not enough for identification since there was no consistent standard to follow in this case.

EDS tests were employed to further study the elemental distribution on the surface of the char, which were normalized and shown in Table 4. Since BC char had very few potassium contents, it was selected as an index representing AAEMs migration. As expected, there was a strong positive correlation between CS fraction and potassium content detected in co-pyrolyzed BC char. By comparing two charring temperatures, the amounts of captured potassium in co-pyrolyzed BC char from 600°C pyrolysis were basically lower than 800°C scenarios. This result was logical because the high temperature could promote the release of inorganic-K, and the potassium release was the precondition of being captured by char. However, overall elemental contents provided by Figure 4 suggested that the influence of co-pyrolysis interaction on the migration of K should be more than just release and capture, because much more AAEMs were detected in co-pyrolysis char compared to those in individual CS char. To understand this phenomenon, the mechanism of K release during biomass pyrolysis must be first clarified. In former literatures, it has been proved that organic-K and inorganic-K have different release paths. For organic-K, 300-400°C would be enough for its release because of the thermal decomposition of organic structure, such as alkaline carboxylates and phenol-associated K. KCl was the primary form of inorganic-K in this case, which could directly release through sublimation at >700°C, or react with char to form char-K and evolved.
like organic-K. Thus, given the fact that AAEMs contents of the char from 600°C co-pyrolysis were abnormally high, a possibility should be considered that co-pyrolysis with BC might inhibit the organic-K in CS to release. That is, there might be some potential synergies cutting off the evolving path of organic-K. Based on the free radical reaction mechanism, a lot of CS volatile fragments were consumed in free radical reactions with BC volatile fragments, some of which were supposed to be the carrier of organic-K. On the other hand, H radical from CS was also more consumed, which might also suppress the release of potassium. When such synergies occurred, associated potassium was forced to stay on the surface of co-pyrolyzed CS char. However, with the increasing temperature, it would be much easier for inorganic-K to directly evaporate in chloride; thus, the consumption of organic carriers or H radical was no longer crucial for the overall AAEMs contents in 800°C scenarios.

3.5 Char combustion reactivity

Derivative thermogravimetric (DTG) analysis and DSC profiles of co-pyrolysis char (black curves) and char blends (red curves) during combustion were demonstrated and compared, as shown in Figure 6. The solid curves referring to the left axis represented DTG and DSC curves, and the dashed curves referring to the right axis represented the cumulative conversion (percentage in the total weight loss) and heat release. It was observed that DTG and DSC curves matched quite well for every single test, indicating the weight loss was mostly from combustion. Based on TG profiles, typical characteristic values were introduced (Table 5) for the description of their thermal behaviors, including $T_i$ (Initial temperature), $T_o$ (Onset temperature), $T_p$ (Peak temperature), $T_e$ (End temperature), $T_f$ (Final temperature), burn out time, $D_{max}$ (Maximum weight loss rate), and final mass residue. Detailed illustration about these characteristic values could
be found in ref. 47. In this work, $T_i$ and $T_f$ were regarded as the beginning and end of the combustion reactions, respectively. Combining the results of Table 5 with Table 3, it was confirmed that the combustion temperature was not directly correlated with the SA and porosity of the char. The possible reason is that the combustion continued to be kinetic controlled during the accelerating stage; thus, the combustion rate was more dependent on temperature. Obviously, BC- and CS-derived chars presented significant differences in thermal behavior and characteristic values. For BC char, about 150°C higher was required for its combustion associated with a higher weight loss rate, which was because coal char consisted of compact aromatic carbon clusters. 15 Naturally, the cleavage of such structures required a much higher temperature than that of the oxy-containing ring systems in biomass char. Once the temperature met the requirement, high-density carbon would contribute to higher combustion intensity.

More importantly, a crucial feature of co-pyrolysis char was revealed: the curves of co-pyrolysis char combustion presented only one major peak and notably resembled the thermal behavior of pure BC char, which was much different from those of char blends. In contrast, the thermal behavior of char blends revealed a typically mixed fuel with double major peaks. In addition, the TG curves of co-pyrolysis char had remarkably higher $T_i$ and lower $T_f$ compared with those of char blends, which could be confirmed by higher $D_{max}$ and shorter burn out time. Evidently, the combustion conversion of co-pyrolysis char was concentrated in a narrower temperature interval. These characteristic values implied the cause for the single-peak performance: due to some kind of synergy, DTG and DSC curves were shifted, which made their peaks more overlapped and eventually merged into a single peak. Based on the discussions in previous sections, two factors were supposed to take effect: (1) the combustion of BC char was catalyzed by the AAEMs, which were captured during co-pyrolysis, and as a result, the peaks were shifted to lower temperatures; and (2) the consequence of secondary char formation. It is well known that the volatile of CS contained a series of O-containing species, such as carboxylic acids, ketones, aldehydes, and furans. In contrast, the volatile of BC consisted of a bunch of polycyclic aromatic hydrocarbons. The compositions of secondary char on the external surface were thus different. As indicated by Chen et al. 48 H- and O-containing reactive species in volatile-solid interactions would decrease and enhance char reactivity, which was exactly in accordance with the nature of volatiles between BC and CS, respectively. That is, to be specific, the reactivity of CS char was suppressed by the secondary char condensed from BC volatile and that of BC char was enhanced by the secondary

| TABLE 4 | EDS elemental analysis of char samples [wt%] |
|---------|---------------------------------------------|
| Scenarios & C & N & O & Na & Mg & Al & Si & P & S & Cl & K & Ca |
| CS char from 600°C pyrolysis |
| (a) | 39.07 | 1.35 | 28.09 | 0.10 | 2.19 | 2.40 | 7.28 | 3.34 | 2.02 | 4.91 | 3.98 | 5.25 |
| (b) | 47.32 | 0.56 | 25.91 | 0.09 | 1.39 | 0.81 | 10.88 | 2.71 | 1.81 | 0.49 | 2.05 | 5.98 |
| (c) | 44.97 | 1.44 | 25.82 | 0.15 | 1.87 | 2.99 | 8.29 | 3.42 | 2.13 | 0.37 | 3.70 | 4.85 |
| (d) | 45.21 | 0.50 | 24.40 | 0.51 | 2.64 | 2.79 | 8.49 | 5.12 | 1.22 | 0.64 | 5.03 | 3.45 |
| CS char from 800°C pyrolysis |
| (e) | 48.90 | 0.00 | 25.97 | 0.43 | 1.74 | 1.27 | 7.02 | 2.33 | 1.53 | 0.98 | 4.60 | 5.25 |
| (f) | 45.39 | 0.43 | 25.61 | 0.32 | 4.45 | 0.15 | 9.83 | 3.62 | 2.47 | 0.46 | 2.79 | 4.48 |
| (g) | 55.36 | 0.00 | 18.35 | 0.14 | 1.61 | 1.84 | 8.88 | 2.71 | 1.90 | 0.58 | 0.84 | 7.80 |
| (h) | 67.96 | 0.00 | 14.62 | 0.15 | 2.49 | 1.44 | 4.71 | 3.09 | 2.27 | 0.40 | 0.52 | 2.34 |
| BC char from 600°C pyrolysis |
| (i) | 81.88 | 0.00 | 8.22 | 0.06 | 0.10 | 0.39 | 1.09 | 2.47 | 2.25 | 0.77 | 2.27 | 0.51 |
| (j) | 83.91 | 0.00 | 7.24 | 0.01 | 0.18 | 0.44 | 1.50 | 2.51 | 2.07 | 0.54 | 0.77 | 0.83 |
| (k) | 84.68 | 0.00 | 7.28 | 0.01 | 0.02 | 0.40 | 1.03 | 2.82 | 2.26 | 0.83 | 0.31 | 0.37 |
| (l) | 80.53 | 0.00 | 9.14 | 0.09 | 0.10 | 1.67 | 2.81 | 3.09 | 2.62 | 0.77 | 0.58 | 0.37 |
| BC char from 800°C pyrolysis |
| (m) | 81.89 | 0.00 | 5.78 | 0.06 | 0.07 | 0.09 | 0.65 | 1.91 | 1.82 | 2.86 | 4.36 | 0.50 |
| (n) | 87.26 | 0.00 | 5.05 | 0.02 | 0.03 | 0.16 | 0.65 | 2.31 | 2.12 | 0.58 | 1.22 | 0.63 |
| (o) | 83.63 | 0.15 | 6.81 | 0.08 | 0.02 | 0.63 | 2.04 | 3.11 | 2.21 | 0.55 | 0.27 | 0.52 |
| (p) | 73.43 | 0.64 | 11.12 | 0.13 | 0.22 | 1.71 | 4.94 | 3.91 | 2.93 | 0.59 | 0.02 | 0.37 |

The same order as that in Figure 5: CS char from (a) C-600, (b) CB31-600, (c) CB11-600, (d) CB13-600, (e) C-800, (f) CB31-800, (g) CB11-800, (h) CB13-800 and BC char from (i) CB31-600, (j) CB11-600, (k) CB13-600, (l) B-600, (m) CB31-800, (n) CB11-800, (o) CB13-800 and (p) B-800.
char condensed from CS volatile. It was consistent with the report that carbonaceous deposit reformed from biomass had better reactivity than the inherent carbon structure of BC char.\(^4^9\)

By integrating DSC curves against time, total heat released during char combustion was demonstrated. The results are summarized in Table 6, confirming that total heat releases of co-pyrolysis char and char blends were both higher than the corresponding calculated values. Since the experimental carbon content of co-pyrolysis char (Figure 4) was not significantly higher, the catalytic role of AAEMs was supposed to give rise to this phenomenon. For co-pyrolysis char, as indicated by ICP-OES and EDS analysis, BC char captured potassium as organic-K and chloride from CS volatile,
which were both catalytically active for combustion. For char blends, considering the non-isothermal heating program, CS char was mostly burnt out before the main combustion stage of BC char, which made it possible for the alkali metals in CS ashes to release, contact BC char, and catalyze its conversion. It was also proved by observing the variation with the change of blending ratio. The gaps between experimental and calculated values reached the maximum in CB31-800/C- CB31-800 and minimum in CB13-800/C- CB13-800, respectively, which perfectly fitted the blending ratio associated with the concentrations of catalytic AAEMs captured from CS. It was also found that the heat release of C- CB31-800 was advantageous compared with that of CB31-800. However, it would be on the contrary for CB13-800 and C- CB13-800. This finding seemed illogical: the burn out time of char blends was basically longer than that of co-pyrolysis char, thus the heat release should always be higher. However, according to the previous discussion, BC contributed to shifting the combustion of co-pyrolysis char to a higher temperature interval, which was probably in favor of complete combustion and heat release for CB11-800 and CB13-800. In contrast, for CB31-800, the fraction of BC was not enough for such a phenomenon to occur. Since char combustion reactivity is highly dependent on the carbon structure and surface chemistry, the results above certainly evidenced the influence of co-pyrolysis synergy on char evolution, which were expected instructive for not only the understanding about co-pyrolysis mechanism, but also the utilization of biomass-coal blends and co-pyrolysis char.

4 | CONCLUSIONS

In this work, the co-pyrolysis synergy between biomass and coal was assessed focusing on the physicochemical properties of char products. Several characterization methods were combined for the evaluation, and conclusions were as follows:

1. Co-pyrolysis hardly influenced macrosurface morphology and structure of mineral matters.
2. Specific SA and pore structures of large micropores and mesopores were more impacted than those of ultramicropores, indicating that the influence was mainly from the formation of secondary char.
3. Elemental analysis revealed excessive contents of carbon and AAEMs in co-pyrolysis char. Co-pyrolysis under moderate temperature strongly favored inhibiting potassium from releasing, probably by interfering with free radical reactions.
4. The combustion profiles of co-pyrolysis char resembled a single fuel rather than a mixture, which was very different from those of char blends. It was mostly attributed to the distinct compositions of secondary char reformed from the volatiles of cornstalk and BC, which remarkably shifted the temperature intervals of combustion. In addition, co-pyrolysis chars and char blends favored enhancing heat release compared with individual chars. The cause was supposed to be the catalytic AAEMs captured by BC.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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| TABLE 6 | Total heat release of chars and comparison between experimental and calculated values [MJ kg⁻¹] |
|----------|--------------------------------------------------|
|          | C-800    | CB31-800 | C-CB31-800 | CB11-800 | C-CB11-800 | CB13-800 | C-CB13-800 | B-800 |
| Exp.     | 10.69    | 14.93    | 15.61      | 17.20    | 17.31      | 19.01    | 18.77      | 20.05 |
| Cal.     | -        | 14.20    | 14.20      | 16.71    | 16.71      | 18.59    | 18.59      | -     |
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