Contents lists available at ScienceDirect

# Fuel

journal homepage: www.elsevier.com/locate/fuel

# Effect of ion-exchangeable calcium on carbonaceous particulate matter formation during coal pyrolysis

Yifan Wu<sup>a</sup>, Yu Zhang<sup>a</sup>, Jiankun Zhuo<sup>a,b,\*</sup>, Qiang Yao<sup>a,c</sup>

<sup>a</sup> Key Laboratory for Thermal Science and Power Engineering of Ministry of Education. Tsinghua University, Beijing 100084, China

larger particle size.

<sup>b</sup> Beijing Engineering Research Center for Ecological Restoration and Carbon Fixation of Saline-alkaline and Desert Land, Tsinghua University, Beijing 100084, China

<sup>c</sup> School of Electric Engineering, Xinjiang University, Urumqi 830047, China

ARTICLE INFO	A B S T R A C T				
Keywords: Ion-exchangeable calcium Soot Coal pyrolysis Mineral transformation	This work investigated the effect of ion-exchangeable calcium on the mass yield, size distribution and structural properties of carbonaceous particulate matter from coal pyrolysis. The raw, acid washed and calcium-exchanged coal samples were pyrolyzed in a flat-flame burner at 1600 K. The particulate matter was collected with a three-stage dilution sampler. Then, the particle size distributions were measured by a low pressure impactor (DLPI+) and a scan mobility particle sizer (SMPS). The results show that, with the addition of ion-exchangeable calcium, the soot yield reduces, and the size growth of soot particles is inhibited. Transmission electron microscopy (TEM) analysis shows that ion-exchangeable calcium diminishes the sizes of disordered cores in soot primary particles, accelerates the graphitization of soot and makes the soot aggregates more compact. The chemical structures derived from Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) indicate that the graphitization degree of the soot is first enhanced and then inhibited with increasing calcium loading amount. Additionally, the inorganic species in the size-segregated soot particles were characterized. The fractions of calcium and sodium in soot show opposite trend with particle size. Unlike Na, which nucleates before soot inception, Ca tends to participate in both the soot nucleation and surface growth processes, and is enriched at				

# 1. Introduction

Carbonaceous particulate matter from the thermochemical conversion of fossil fuels is a significant source of air pollution. In coal combustion facilities, soot contributes up to 35% of the total unburned carbon [1], which reduces the energy utilization efficiency. Once released into the atmosphere, soot nanoparticles can be inhaled and penetrate through the lungs into the blood, causing damage to cardiovascular and pulmonary health [2-4]. Soot is also estimated as the second largest contributor to global warming just behind CO<sub>2</sub> due to its strong light absorption effect [5,6]. In the context of carbon emission restriction, pyrolysis-based polygeneration of coal produces high-value gaseous and liquid products, and can be integrated with carbon capture and storage (CCS) to reduce CO2 emission [7]. However, pyrolysisgenerated soot might cause blockage or fouling, obstructing the continuous operation of pyrolysis facilities [8,9]. Since conventional particle removal devices are inefficient in removing submicron particulate matter [10–14], it is desirable to inhibit soot formation during coal pyrolysis.

Soot formation occurs through complex chemical and physical processes, including precursor formation, gas-to-particle transition (nucleation), surface growth, particle coalescence, and aggregation [15,16]. Pyrolysis products, especially tars, undergo secondary reactions to produce the incipient soot [17,18]. Then, the surface growth and coalescence of the incipient soot form spherical soot primary particles. The collision and aggregation of soot primary particles further leads to chain-like agglomerate structures.

In a coal pyrolysis system, soot formation is affected by the transformation of mineral species. Evaporated metals such as alkali and alkaline earth metals (AAEM) and Fe can condense and form carbonencapsulated or doped particles with soot aggregates [19-21]. Previous studies by Xiao et al. [20] and Dong et al. [22,23] suggested that the presence of Na reduces the yield and particle size of soot. The interaction between Na and soot influences the graphitization of soot [22] and enhance the soot oxidation reactivity [24]. Recent work by Ma et al. [21] and Li et al. [25] indicated that Fe also affects soot yield and

https://doi.org/10.1016/j.fuel.2021.123124

Received 17 October 2021; Received in revised form 15 December 2021; Accepted 30 December 2021 Available online 12 January 2022 0016-2361/© 2022 Elsevier Ltd. All rights reserved.



Full Length Article





<sup>\*</sup> Corresponding author at: Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China. E-mail address: zhuojk@mail.tsinghua.edu.cn (J. Zhuo).

promote the formation of iron-rich soot nuclei. The interaction mechanisms between metals and soot can be summarized as precursor reactions, nucleation mechanism, ionic mechanism, and catalytic oxidation [26–28], corresponding to different steps of soot formation. Specifically, according to Howard et al. [26], metal vapors, such as Ca, Ba and Sr, can react with gaseous species and decrease the concentration of soot precursors. Then, some cations, such as Na, Mg and Fe, can promote the polymerization of precursors through cation- $\pi$  interaction or cross-linking reactions [29,30], which accelerates soot nucleation. Due to the low ionization potential, alkali metals, such as Na and K, can neutralize the charges of the soot, decreasing the collision rate of incipient soot particles [28,31,32]. Finally, once the metal-doped soot contacts the oxidizer, the metals can catalyze the oxidation of soot [20,27,32,33].

The soot inhibition effect of Ca has also been reported in various gaseous flames. Early work by Cotton et al. [34] (on propane diffusion flame) and Haynes et al. [35] (on ethylene premixed flame) showed that alkaline-earth metal additives can decrease the soot yield. The effect was attributed to the hydroxyl radicals from the gas-phase reaction between water vapor and alkaline-earth metals. Simonsson et al. [28] investigated the influence of metal salts on soot yield and diameter in an ethylene premixed flame with optical diagnostic methods, and found that Ca can decrease the soot volume fraction and shrink the sizes of the primary soot particles. Some studies discovered the presence of Ca within soot particles from pulverized coal combustors [19], biomass gasifiers [36,37] and diesel engines [38,39], which provide concrete evidence for the Ca-soot interaction. A recent study by Wiinikka et al. [36] analyzed the spatial distributions of metallic atoms and functional groups in the soot nanostructure, and found that calcium causes oxygen functionalization of the graphitic structure. However, the role of Ca on coal-derived soot formation is still far from clear, while many studies focused on Ca transformation and the effect of Ca on pyrolysis product distribution. Ca in the water-soluble or ion-exchangeable form can be evaporated under high temperature [40-42] and has strong catalytic effect on the primary and secondary pyrolysis of coal [43-45]. Previous studies indicated that Ca can decrease the yield of polycyclic aromatic hydrocarbons (PAHs) and promote the cracking of heavy tars [40,43–48], which directly serve as soot precursors. Therefore, Ca is expected to play a significant role in soot formation during coal pyrolysis.

The present work aims to investigate the influence of Ca on the formation and structural properties of soot during coal pyrolysis. Coal samples with different Ca content were produced by acid washing and Ca ion-exchange. The coal samples were then pyrolyzed in a Hencken flat-flame burner at 1600 K and the particulate matter was collected with a three-stage dilution sampling system. The yield, size distribution, morphology and chemical properties of the particulate matter were characterized. The experimental results will provide insight into the influence of ion-exchangeable calcium on soot formation.

#### 2. Experimental

#### 2.1. Pyrolysis with Hencken burner

The pyrolysis experiments were conducted in a downward Hencken flat-flame burner, as shown in Fig. 1. The details of the burner can be found in our previous articles [20,24]. Carbon monoxide (3.54 L/min) and a small amount of methane (0.015 L/min) were selected as the burner fuels, while a mixture of nitrogen (10.2 L/min) and oxygen (1.64 L/min) were used as the oxidizer. The burner was operated under fuelrich condition, at an equivalence ratio of 1.1. The main components of the after-flame ambience were 22.4% CO2, 3.7% CO, 0.2% H2O and 73.7% N<sub>2</sub>, while the O<sub>2</sub> concentration measured with a flue gas analyzer was lower than 0.03%. The flat flame burner provided a high temperature (1600 K) and low oxygen ambience for the coal pyrolysis. A quartz chimney isolated the post-flame region from the outside air, maintaining a reductive atmosphere. Coal particles were entrained with a nitrogen flow of 0.2 L/min and fed into the post-flame zone by a central feeding tube. The coal feeding rate was set to 30 mg/min. The residence time of the coal particles was monitored by a high-speed camera. In this study, the sampling position was 54 mm beneath the burner, at a residence time of 50 ms. The temperature history along the burner centerline was measured by a B-type thermocouple considering radiation heat transfer, and is shown in Fig. 2.



Fig. 1. Schematic of the Hencken flat-flame burner and the particle sampling system.



Fig. 2. Temperature and residence time along the centerline of the flat-flame burner.

#### 2.2. Particle sampling and analysis

When sampling high-temperature aerosols, the particle size distributions (PSDs) might be distorted through several mechanisms, including the condensation of inorganic vapor and heavy tar [49–51], the collision aggregation of particles [52,53] and thermophoresis loss on the sampling probe [54]. To avoid altering the PSDs, a three-stage dilution system was established. The first-stage diluter was an annular probe where the aerosols mixed with the outer-ring nitrogen. Before mixing with aerosols, the outer-ring nitrogen had already been heated by the flue gas to suppress the condensation of vapor phase matter. The second-stage diluter exploited an orifice jet to pump out the mixture, and then the aerosols were further diluted in the third-stage diluter, reaching a suitable temperature for the measuring instruments. The dilution ratio was monitored by measuring the CO<sub>2</sub> concentration before and after dilution. In this work, the overall dilution ratio was set to 33 so that the number PSDs would no longer change with further increase of the dilution ratio. In addition, to collect all the particulate matter, a superkinetic sampling method was adopted [24]. Before size-segregated sampling with a low pressure impactor (DLPI+, Dekati) and a high flow rate impactor (DGI, Dekati), the aerosols first passed through a cyclone (type: SCC 5) to remove the coarse particles. According to the empirical correlation by Kenny et al. [55], the cut sizes of the cyclone were 10 µm for DLPI+ (at 10 L/min) and 1 µm for DGI (at 70 L/min).

The aerosols were then characterized with various methods. Sizesegregated sampling was conducted with DLPI+, which gives the total yield and the mass size distributions. The number PSDs were measured with a scan mobility particle sizer (SMPS, TSI 3936). Both the mass and number PSDs were converted into emission factors in the ratio of coal feeding rate. The morphology and nanostructures of the particulate matter were characterized with scanning electron microscopy (SEM, Zeiss Merlin) and transmission electron microscopy (TEM, Joel JEM 2100F). For chemical property analysis, all the soot samples were collected using a DGI impactor with a cut size of  $0.5 \ \mu m$ , ensuring the representation of the variously sized soot samples. The graphitization degree of soot was analyzed by a Raman spectrometer (Renishaw inVia-Reflex) with a 532 nm laser source. The functional groups in the soot samples were characterized with a Fourier transform infrared spectrometer (FTIR, Nicolet Nexus 670) by the KBr pellet method. Finally, the mineral contents in the size-segregated soot particles were analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Leeman Prodigy 7). Since each stage of particulate matter collected with DLPI+ was restricted below 1 mg, the digestion process was specially designed to satisfy the detection limit of ICP-OES. Specifically, particles collected on each teflon membrane were added into 0.4 ml of HNO3 and 0.1 ml of H2O2, heated at 240 °C for 3 h in a highpressure digester, and then diluted to 5 ml before instrumental analysis.

# 2.3. Coal properties

A Zhundong subbituminous coal was used in this study. Chemical fractionation analysis of Na, K, Ca and Fe in the raw coal was conducted following the method by Dyk et al. [56] and the result is shown in Fig. 3. The coal sample was crushed and sieved to 50–63  $\mu$ m before further treatment.

Coal samples with different Ca contents were produced by acid washing and Ca ion-exchange. To produce the acid-washed coal (ZD AW), 40 g of raw coal was soaked in 200 ml of 1 mol/L hydrochloric acid, stirred for 12 h, and then washed with deionized water to remove the redundant acid. The procedure of Ca ion-exchange is described below: 5 g of ZD AW was soaked in 50 ml of calcium acetate solutions at 0.0125, 0.025, 0.05, 0.1 and 0.2 mol/L. Then, ammonia water was added to the mixtures to reach a pH value of 8.3, the mixtures were stirred for 12 h and washed with deionized water. Cations loaded by this method have been verified to be mostly in carboxylate form [57,58]. The Ca-loaded coals were named as ZD Ca 1, ZD Ca 2, ZD Ca 3, ZD Ca 4 and ZD Ca 5 in the order of increasing solution concentration. After treatment, all the coal samples were dried at 85 °C for 24 h. The metal contents in coal were measured with ICP-OES. The pretreatment procedures are as follows, 30 mg coal samples were mixed with 3 ml HNO<sub>3</sub>, 0.6 ml HF and 0.6 ml H<sub>2</sub>O<sub>2</sub>, digested at 240 °C for 4 h, followed by aciddriving and finally diluted into 40 ml with 5% HNO<sub>3</sub>. The properties of the coal samples are listed in Table 1, and the metal contents are shown in Fig. 4.

As shown in Fig. 4, the calcium loading amount increased with the solution concentration and reached saturation at 0.1 mol/L (ZD Ca 4). Since most of the Na and Fe were removed by acid washing, the interference of other metals was weakened. In addition, except for the ash content, the proximate and ultimate properties were scarcely affected by Ca ion-exchange. In this way, the differences in the experimental results can be attributed to calcium.

# 3. Results and discussion

#### 3.1. PM yield and size distributions

Fig. 5 shows the mass size distributions of the pyrolysis-generated aerosols. For each sample, the mass PSD curve has two peaks: a fine mode peak at 40–70 nm and a coarse mode peak at 3–4.5  $\mu$ m. The fine mode particles are classified as soot agglomerates from the secondary pyrolysis of volatiles, while the coarse mode particles are dominated by char fragments [20].

As shown in Fig. 5 (a), after acid washing, the fine mode peak shifts



Fig. 3. Occurrence form of Na, K, Ca and Fe in the raw coal.

#### Table 1

Properties of the coal samples used in pyrolysis experiments.

Sample	ZD Raw	ZD AW	ZD Ca 1	ZD Ca 2	ZD Ca 3	ZD Ca 4		
Proximate analysis (wt.%, dry basis)								
Fixed Carbon	62.33	65.51	64.50	61.26	59.40	56.66		
Volatile	33.08	32.76	32.54	34.18	34.67	35.61		
matter								
Ash	4.54	2.04	2.75	4.01	4.75	5.78		
HHV (MJ/kg)	28.09	_	_	_	_	_		
Ultimate analysis (wt.%, dry ash free basis)								
С	76.51	77.47	77.75	77.72	77.42	77.04		
Н	4.34	4.15	4.17	4.18	4.26	4.25		
0	17.84	17.19	16.54	16.61	16.95	17.26		
Ν	1.08	1.00	1.37	1.29	1.19	1.24		
S	0.23	0.18	0.17	0.20	0.19	0.21		
Metal concentration (mg/kg, dry basis)								
Na	3568	114	85	91	88	86		
K	173	108	155	142	118	110		
Ca	6498	790	5963	12,553	18,532	25,339		
Fe	4404	1147	960	1088	1070	1004		



Fig. 4. Concentrations of mineral elements in the coal samples.

toward a larger size. The removal of acid-soluble minerals promoted the size growth of soot, which is accomplished by surface growth, coalescence and collision aggregation. The results of the Ca exchanged coals are shown in Fig. 5 (b). When ion-exchangeable Ca is loaded into ZD AW, the fine mode diameter decreases, and the mass concentration represented by the peak height is substantially reduced. The soot reduction effect is strengthened with increasing Ca content in coal.

Due to the bimodality of the mass PSD curves, the trough between the two peaks (0.4–0.5  $\mu$ m) is a reasonable threshold for quantifying the yield of soot and char fragments. Fig. 6 demonstrates the mass yield of soot and char fragments classified by a threshold of 0.4  $\mu$ m. Acid washing increases the soot yield from 7.59 mg/g-coal to 8.74 mg/g-coal. While with increasing Ca loading amount, the soot yield monotonically decreases to 1.59 mg/g-coal. This result signifies that both the mineral species in the raw coal and the ion-exchangeable Ca additives are effective in reducing soot yield.

For the coarse mode particles, however, the PM 0.4–10 shows a slight increase with increasing Ca content. The yield change of PM 0.4–10 is related to the enhancement of char fragmentation. As shown in Fig. 5, the major increase of PM 0.4–10 lies in the range between 0.5 and 1.2  $\mu$ m. This might be attributed to the fusion and fragmentation of the mineral-rich particles, which will be presented in Fig. 10.

Unlike the mass PSDs, which emphasize the contribution of coarse particles, the number PSDs are more sensitive to fine particles such as



**Fig. 5.** Mass PSDs of particulate matter from the pyrolysis of (a) raw coal and (b) calcium-loaded coals compared with ZD AW.



Fig. 6. Mass yield of PM 0.4 (left axis) and PM 0.4-10 (right axis).

incipient soot. Fig. 7 shows the high-resolution number PSDs of soot measured with SMPS.

As shown in Fig. 7, the number PSD of each sample also follows a bimodal distribution, with a broad aggregation mode at larger mobility diameters (70–100 nm) and a small nucleation tail below 20 nm. It is widely accepted that the bimodal distribution arises from the competition between precursor nucleation and particle aggregation [54,59], while the coalescence of the nuclei and surface growth, which make up



Fig. 7. Number PSDs of particulate matter from (a) raw coal and (b) calciumloaded coals compared with ZD AW.

the spherical primary particles, also contribute to the nucleation tail [60]. As proposed by Singh et al. [59], some characteristic points in the PSD curve, including (a) the peak trough between two modes (D<sub>p.a</sub>) and (b) the peak diameter of the aggregation mode (D<sub>p,b</sub>) can provide information about the size evolution of soot particles. The  $D_{p,a}$  is mainly affected by the size of incipient soot, while the  $D_{p,b}$  is sensitive to the incepting particle size, nucleation rate and surface growth rate [59]. The definition and values of D<sub>p,a</sub> and D<sub>p,b</sub> are shown in Fig. 8.

In concordance with the DLPI+ results, the aggregation mode diameter  $(D_{p,b})$  reaches a maximum at ZD AW and decreases with the Ca content. The soot from ZD AW also exhibits the largest trough diameter (D<sub>p,a</sub>) of 20.9 nm, while for the ZD Raw and Ca-exchanged coals, the D<sub>p,a</sub> ranged from 15.7 to 16.8 nm. Besides, Fig. 7 (b) shows that the nucleation mode concentration, represented by the height of the nucleation tail, initially increases but decreases at high Ca loading amount.

One possible explanation for the changes in the number PSDs is that a small amount of calcium could be released into the gas phase [41] and promote the polymerization of PAHs through crosslinking or metal-π interactions. Quantum chemistry calculations by Kolakkandy et al. [29] showed that metal cations can increase the binding energy of PAHs by forming a sandwich-like structure. Such a reaction stabilizes the newly formed PAH clusters, allowing physical nucleation to occur at higher temperature. Recent molecular dynamics simulation by Hong et al. [44] suggested that Ca atoms decrease the activation energy of tar polymerization from 26.6 kcal/mol to 19.7 kcal/mol. Since the polymerization of PAHs is commonly considered as the inception of soot, this effect would increase the soot nucleation rate. Thus, the height of the nucleation tail increases initially. However, at higher Ca content, the



Fig. 8. (a) Definition of characteristic diameters in the PSD curve according to ref. [59], (b) the characteristic diameters of the soot number PSDs.

catalytic effects on coal pyrolysis and tar cracking become prominent. Ca initially bonded with carboxyl groups can be connected with the char matrix and inhibit the release of tar fragments by forming cross-links between tar and char [47,61,62]. Even if tar has been released, Ca compounds can still catalyze the secondary cracking of tar [43,45], further reducing the yield of soot precursors. Consequently, both the nucleation and aggregation processes are suppressed at high Ca content. Moreover, due to the low ionization energy, Ca atoms can exchange electrons with incipient soot and inhibit the coalescence of nuclei through the ionization mechanism [26,28], which decreases the sizes of incipient soot particles. As a result, both the trough diameter (D<sub>n,a</sub>) and the aggregation mode diameter (D<sub>n,b</sub>) decreases with increasing Ca content.

## 3.2. Morphology of pyrolysis-generated particles

#### 3.2.1. Morphology of coarse mode particles

Fig. 9 shows the SEM images of the coarse mode particles collected on the 12th stage of the DLPI+ (3  $\mu$ m). The majority of the particles are char fragments in different shapes, including angular, round contours and porous shapes. As shown in Fig. 9 (a, b), some of the round contour char particles have small holes on the surface, indicating that they might arise from the swelling of coal [63]. Specifically, the char lattice softens at high temperature, and the rapidly releasing volatile matter forms bubbles inside the char and expands the char surface into a round shape [64]. Due to the high pressure of the inner volatile matter, some volatile bubbles blow holes on the char surface, leading to a porous structure [65]. Fig. 9 (d) also shows that a few soot agglomerates are attached to



**Fig. 9.** Morphology of coarse mode particles (3 µm). (a) ZD Raw, (b) ZD AW, (c) ZD Ca 3, (d) Soot attached to char surface.

the surface of some char fragments, demonstrating the coagulation between the char fragments and soot particles [20,66].

Fig. 10 (a, b) shows another type of singular, highly spherical particle generated by ZD Raw and ZD Ca 3. The EDS spectrum shows that this type of particle contains elements such as Na, Ca, Si, Al, S and Cl, which come from the fusion of inorganic species or the decomposition of organic-bonded minerals. It is also observed that some of the char fragments from ZD Raw and ZD Ca 3 have rough surfaces, as presented in Fig. 10 (c). Similar morphologies were also found from char gasification [67]. With the gasification of char, the inherent mineral species tend to be exposed on the char surface [65], and melt into a spherical shape under surface tension [68]. As shown in Fig. 10 (d), the molten mineral-rich particles collides and merges into spherical lumps on the char surface. Subsequently, the spherical mineral-rich particles could be shed by the rotation of char, which arises from the tangential thrust of the rapidly releasing volatiles [19,69].

#### 3.2.2. Soot morphology and nanostructure

Fig. 11 presents the typical TEM images of the soot collected on the 3rd stage of the DLPI+ (40 nm). All the soot samples appear to be agglomerates of spherical primary particles. As demonstrated by Mitchell [70], the primary particles arise from the collision of the nascent nuclei and the simultaneous surface growth, the latter leads to a nearly spherical shape. The collision of the spherical primary particles further leads to the fractal aggregate structures. The soot aggregates from ZD Raw and ZD Ca 3 have more compact packing form than those from ZD AW.

By measuring over 100 monomers in different images, the size distributions of the primary particles were evaluated. As shown in Fig. 12, the diameters of primary particles from ZD AW (19.9  $\pm$  3.5 nm) are larger than those from ZD Raw (16.7  $\pm$  4.2 nm) and ZD Ca 3 (15.6  $\pm$  4.5 nm). The existence of metal cation can decrease the size of soot primary particles, which also influences the results of the trough size ( $D_{\rm p,a}$ ) in Fig. 8.

The decreasing effect on the primary particle size was also found by Simonsson [28,71] in ethylene flames with KCl additives. Metal atoms with low ionization energy can exchange electrons with incipient soot nuclei through the reaction: Metal + Soot<sup>+</sup>  $\rightarrow$  Metal<sup>+</sup> + Soot. Since the coagulation rate between neutral and charged particles is higher than that of two neutral particles, charge neutralization can inhibit the coalescence of the incipient soot nuclei, leading to smaller primary particle sizes [31]. Charge neutralization might also influence the packing structure of soot aggregates. With the coalescence between charged and neutral particles, more particles are charged with the average charge density. Owing to the Coulomb repulsion force between like-charged



Fig. 10. (a, b) SEM-EDS results of mineral-containing spherical particles. (c) Morphology of mineral lumps on the char surface. (d) Melting mineral-rich lumps develop into spherical shape.



Fig. 11. HRTEM images of soot. (a and d) ZD Raw; (b and e) ZD AW; (c and f) ZD Ca 3. The black arrows mark the disordered core in the soot primary particles. The white bars mark the thickness of the graphitic layers.



Fig. 12. Size distributions of the soot primary particles.

particles, aggregates with higher charge density tend to form looser structures [72]. Hence, when the charge is partly neutralized by metal atoms, the packing structures become more compact.

Fig. 11 (d-f) shows the nanostructure of the soot obtained by HRTEM. As commonly observed in mature soot [73], soot primary particles show a core-shell structure, with an amorphous core (marked by arrows) and a graphitized shell. Typically, the amorphous core can be distinguished by its short and randomly oriented carbon segments, while the graphitized shells are recognized by the parallel oriented layers that circle around the core. Then, the sizes of the amorphous cores and the graphitized shells were measured by image processing. The soot generated by ZD AW has the largest amorphous cores, while the amorphous cores from ZD Raw and ZD Ca 3 are smaller. The core size exhibits the same trend as the primary particle size. However, the thickness of the peripheral graphitized shells (marked by white bars) only slightly differs among the three soot samples.

shell structure is dominated by the equilibrium of the curvature-induced elastic strain and the free energy gap between ordered/disordered structures [74]. With decreasing particle radius, the curvature of the shells increases, leading to larger strain force. Once the strain force overcomes the lattice energy of the ordered structures, the ordered shell would be ruptured [74]. Hence, the core-shell structure only exists in particles larger than a critical radius  $R_c$ , where  $R_c$  is the radius of the disordered core [75]. In our observation, Ca accelerates the graphitization of the soot structure, and enables the formation of graphitized shell at smaller  $R_c$ . As demonstrated by molecular dynamics simulation, metal cation could be bonded to the curved PAH molecule through cation- $\pi$  interaction, and promote the formation of onion-like structure [76]. Due to the high binding energy between cations and curved PAH layers, the ordered graphitic shell is stabilized and forms at smaller radius. Besides, the transformation from incipient soot to mature soot is also involved with the crosslinking reactions of PAHs [77]. Recent studies indicated that the crosslinking reaction between curved PAHs plays an important role in the soot nucleation and surface growth [78,79]. The strong crosslinking effect of calcium might be another reason for the increase of graphitized structure. In general, the effect of Ca on soot nanostructure might be summarized as the following two mechanisms: (i) Ca forms crosslinking bonds between aromatic layers and relieves the elastic strain force of the concentric graphitic shells. (ii) cation- $\pi$  interaction between Ca ion and the curved PAHs increases the lattice energy of the ordered shell structures [29], enlarging the free energy gap against shell rupture.

It should also be noted that in some particles, the outer layers of the ordered shells were shared by several primary particles. In other words, surface growth occurs not only on primary particles but also on aggregated particles [80]. The surface growth on aggregated particles can bury the gaps between primary particles, making the particle surface smoother [81]. Due to the smaller primary particle size of the ZD Raw and ZD Ca 3 soot, the gaps between primary particles are more likely to be filled by surface growth. This might be another possible reason for the compact aggregate structures, apart from the Coulomb effect.

The transformation from disordered core structure to concentric

# 3.3. Chemical properties of the soot

To further understand the effect of Ca on soot structures, the chemical properties of the soot were analyzed with Raman spectroscopy and FTIR. Fig. 13 (a) shows the normalized Raman spectra of the soot samples. First-order Raman curves were fitted using the 3L1G fitting method which was verified by Seong [82]. As shown in Fig. 13 (b), the G band at approximately 1590 cm-1 is attributed to the C=C stretching vibration with E2g symmetry in ideal graphitic lattices [82-85]. The D1 band at 1350 cm-1 arises from the breathing mode vibration of sp2 rings and is related to the defects or edges of the graphitic layers [83,84,86,87]. The D3 band at 1500 cm-1 refers to the amorphous carbon, such as aromatic defects, odd-membered ring linkages and functional groups [83,85,88]. The D4 band at 1200 cm-1 is involved with the mixed sp2-sp3 bond and the polyene-like structures [82,83]. In some articles, the D2 band at 1620 cm-1 is identified as a shoulder peak of the G peak and is assigned to the E2g symmetric vibration of the surface graphene layers [83,89]. However, it is difficult to distinguish the D2 band from the G band, because the overlap of D2 and G bands significantly increases the fitting uncertainty [82,85,89]. Therefore, the D1, D3, D4 and G bands will be discussed and the position of G band is used to signify the contribution of D2 band.

Fig. 13 (c) shows the area ratios of the D1, D3, and D4 bands to the G band, which can indicate the relative numbers of defects versus the ordered graphitic structures. Among all the samples, soot from ZD AW has the most disordered structure. The degree of order shows an increasing trend Ca content until 1.85%, and then decreases. Another indicator of the degree of defects, the full width half maximum (FWHM) of the G peak, shows similar trend with  $A_{\rm D1}/A_{\rm G}$ . In previous studies, the concentration dependent effect on the graphitic defects was also present for the soot from Na-loaded coals, and was attributed to the different roles of metals in soot nucleation and surface growth [23,90]. As discussed in 3.2.2, small amount of Ca decreases the sizes of the disordered cores in primary soot particles, and promotes the formation of graphitized shells at smaller radius. Hence, the fraction of amorphous carbon decreases, while the fraction of ordered graphitic structure increases.

However, when the Ca concentration continually increases, excess Ca inserts into the graphitized shells during the surface growth of soot and causes defects inside the graphitic structures. As shown in Fig. 13 (d), with increasing calcium content, the G band position shifts toward a larger wavenumber. The intrusion of calcium into graphitized layers transfers the ideal graphitic structure to defective surface graphitic structure, shifting the G band toward where the D2 band lies. The competition of the above two mechanisms might be responsible for the turning point of the order degree at ZD Ca 3.

Fig. 14 shows the baseline corrected FTIR spectra of soot samples ranging from 650 to  $3000 \text{ cm}^{-1}$ . In general, the absorbance spectra of soot are assigned to 5 bands: aliphatic C–H stretching (2800–3000 cm-1), aromatic C–H vibration (700–900 cm-1), aromatic C=C stretching



Fig. 14. FTIR spectra of soot samples from different coals.



Fig. 13. (a) Raman spectra of soot from different coals. (b) Examples of Raman curve fitting with 3L1G method. (c) Peak area ratios evaluated from the Raman spectra of soot. (d) G peak position and full width half maximum (FWHM) of the Raman spectra.

(1500–1620 cm-1), carbonyl C=O stretching (1620–1800 cm-1) and C–O stretching (1000–1300 cm-1). The detailed peak assignment refers to the work by Dong [22,90]. Each spectrum was fitted with 36 individual Gaussian peaks, and the area ratios of the functional groups to the area of aromatic C=C peaks were calculated and are presented in Fig. 15.

Since an ideal graphite lattice contains only aromatic C=C bonds, the absorbance peaks of aliphatic C-H bonds and aromatic C-H bonds signify the defects in the graphitic structures. As shown in Fig. 15 (a), A aromatic C-H/A C=C shows a decreasing trend with Ca content, while the A aliphatic C-H/A C=C shows an abrupt increase at ZD Ca 4. The trend of graphitic defects is in agreement with the Raman result. For the oxygencontaining functional groups, as shown in Fig. 15 (b),  $A_{C-O}/A_{C=C}$  first increases, reaches the peak at ZD Ca 2 and then decreases, while  $A_{C=O}/A$  $_{C=C}$  increases with Ca content. During the devolatilization process, AAEM species can be released together with tar in the carboxylate form [42] and promote the interactions between tar and oxygen-containing radicals, bringing oxygen into tar molecules [22,91]. Tar molecules with oxygen-containing groups are more likely to crack during the secondary pyrolysis [92], which leads to a lower yield of soot precursors. The oxygen-containing tars also increase the oxygen content in soot particles. As observed by Wiinikka et al. [36], Ca and oxygen tend to be enriched at the same location in soot nanostructure, and show positive correlation with the spatial distribution of ketone groups and carbonate groups. Since the above functional groups are rich in C=O, the  $A_{C=O}/A$ C=C increases with Ca content. However, some studies indicated that Ca can also catalyze the deoxygenation of oxygen-containing tar molecules, such as phenols [43,45,46], and convert the phenolic compounds into corresponding aromatics [45]. This reaction reduces the hydroxyl groups in soot precursors and thereby reduces the adjacent C-O groups in soot structure. As a result, unlike the C=O groups, the A  $_{C-O}/A$   $_{C=C}$ shows a decreasing trend at high Ca content.



**Fig. 15.** Area ratios of the FTIR absorbance peaks (a)  $A_{\text{Aromatic C-H}}/A_{\text{C=C}}$  and  $A_{\text{Aliphatic C-H}}/A_{\text{C=C}}$ ; (b)  $A_{\text{C=O}}/A_{\text{C=C}}$  and  $A_{\text{C-O}}/A_{\text{C=C}}$ .

# 3.4. Transformation of inorganic species into fine particulate matter

To investigate the transformation of mineral species from coal to soot, the mineral contents in soot from ZD Raw, ZD AW and ZD Ca 3 were analyzed by ICP-OES. As shown in Fig. 16 (b), the PM 0.5 yields of Na, K, Ca, Mg, Fe, Al and S reduces from 6.5% to 1.1% after acid washing, and then increased to 4.1% at the Ca content of 1.85%. Among the three tested samples, the total mass fractions of Na, K, Ca, Mg, Fe, Al and S only make up a small fraction of PM 0.5, while the majority of the PM 0.5 is carbonaceous.

Although the fractions of Na, K, Ca, Mg, Fe, Al and S in soot is low, the size distributions of the mineral species are still important indicators for understanding the metal-soot interactions. As shown in Fig. 17, for the raw coal, the fractions of Na, K and S show bimodal distributions, with a decreasing tail at PM 0.1. The enrichment of Na, K and S in ultrafine particles might be attributed to the homogeneous nucleation and heterogeneous condensation processes [93]. Due to the low saturated vapor pressure, mineral vapors nucleate prior to soot inception [27]. The nucleated mineral particles provide stable sites for the surface deposition of PAHs, promoting the heterogeneous nucleation of soot. Previous studies have detected encapsulated soot particles, with inorganic cores containing Na, K or Fe and graphitized layers on the periphery [19,20]. With the growth of the graphitic layers, the mass fraction of the metallic core reduces, leading to a decreasing mineral fraction in PM 0.1.

In contrast with Na, the fraction of Ca shows an increasing trend with particle size and reached maximum at approximately 0.2  $\mu$ m. According to Fig. 18 (b), ZD Ca 3 definitely released much more calcium into the particle phase than the other two coal samples, even at the finest particle

![](_page_8_Figure_10.jpeg)

**Fig. 16.** (a) PM 0.5 yields of Na, K, Ca, Mg, Fe, Al and S from ZD Raw, ZD AW and ZD Ca 3; (b) Fractions of Na, K, Ca, Mg, Fe, Al and S in the PM 0.5.

![](_page_9_Figure_1.jpeg)

Fig. 17. Fractions of the mineral elements in the size-segregated soot samples from ZD Raw, ZD AW and ZD Ca 3.

![](_page_9_Figure_3.jpeg)

Fig. 18. Mass PSDs of the mineral elements from ZD Raw, ZD AW and ZD Ca 3.

size stage. Since char fragmentation would not generate such ultrafine particles, the evaporation–condensation is still the dominant mechanism for the transformation of Ca into PM 0.1. However, Ca tend not to form nuclei before soot inception, but participates in both the nucleation and the surface growth of soot. Specifically, a small amount of Ca is bonded with PAHs and enhances the nucleation of soot, while the majority of the Ca would deposit on the soot surface or release through char fragmentation, leading to a higher Ca fraction at larger particle sizes. It should also be noted in Fig. 17 that the mass fractions of Mg and Fe from ZD Ca 3 exceeded those of ZD Raw at some size stages, although their contents in the ZD Ca 3 coal were lower. This result is attributed to the decrease of the soot yield. Since the majority of the ultrafine particulate matter is soot, the decrease of the soot yield leads to an increase of inorganic fraction.

# 4. Conclusion

This work studied the effect of ion-exchangeable Ca on particulate

matter formation during coal pyrolysis. Pulverized coal was treated by acid washing and Ca ion-exchange. The coal samples with different Ca content were pyrolyzed in a flat-flame burner at 1600 K, and the particulate matter was collected with a three-stage dilution sampling system. The mass yield, size distribution, morphology, chemical structures and inorganic content of the particulate matter were characterized. The main conclusions are as follows:

- 1. Ion-exchangeable Ca reduces the soot yield and decreases the sizes of soot aggregates. While the yield of coarse mode particles slightly increases with Ca content, indicating that Ca enhances the fragmentation of char.
- 2. Ion-exchangeable Ca decreases the sizes of soot primary particles and leads to a more compact aggregate structure. The primary soot particles show a core–shell structure. Ca exchanging shrinks the sizes of the amorphous cores, and promotes the formation of graphitized shells at smaller radius.
- 3. With the increase of Ca content in coal, the graphitization degree of soot first increases and then decreases. A small amount of Ca promotes the graphitization of soot, while a large amount of Ca increases the graphitic defects. Ion-exchangeable Ca also enhances the reaction between oxygen-containing species with soot precursors, bringing oxygen-containing groups into soot structure.
- 4. The mass fractions of Na and Ca in soot show opposite trends with particle size. Na nucleates prior to soot inception and provides sites for soot nucleation, while Ca tends to accompany the nucleation and surface growth of soot, and is enriched at larger particle size.

#### CRediT authorship contribution statement

Yifan Wu: Data curation, Investigation, Methodology, Writing – original draft. Yu Zhang: Investigation, Writing – review & editing. Jiankun Zhuo: Conceptualization, Methodology, Funding acquisition, Writing – review & editing. Qiang Yao: Conceptualization, Resources, Supervision.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgement

This work was supported by the National Key Research and Development Program of China (2018YFB0605000).

# References

- Veranth JM, Fletcher TH, Pershing DW, Sarofim AF. Measurement of soot and char in pulverized coal fly ash. Fuel 2000;79(9):1067–75.
- [2] Linak WP, Yoo J-I, Wasson SJ, Zhu W, Wendt JOL, Huggins FE, et al. Ultrafine ash aerosols from coal combustion: Characterization and health effects. Proc Combust Inst 2007;31(2):1929–37.
- [3] Michelsen HA. Probing soot formation, chemical and physical evolution, and oxidation: A review of in situ diagnostic techniques and needs. Proc Combust Inst 2017;36(1):717–35.
- [4] Lighty JS, Veranth JM, Sarofim AF. Combustion Aerosols: Factors Governing Their Size and Composition and Implications to Human Health. J Air Waste Manag Assoc 2000;50(9):1565–618.
- [5] Bond TC, Doherty SJ, Fahey DW, Forster PM, Berntsen T, DeAngelo BJ, et al. Bounding the role of black carbon in the climate system: A scientific assessment. J Geophys Res: Atmospheres 2013;118(11):5380–552.
- [6] Lohmann U, Friebel F, Kanji ZA, Mahrt F, Mensah AA, Neubauer D. Future warming exacerbated by aged-soot effect on cloud formation. Nat Geosci 2020;13 (10):674–80.
- [7] Huang Yi, Yi Q, Kang J-X, Zhang Y-G, Li W-Y, Feng J, et al. Investigation and optimization analysis on deployment of China coal chemical industry under carbon emission constraints. Appl Energy 2019;254:113684. https://doi.org/10.1016/j. apenergy.2019.113684.

Y. Wu et al.

- [8] Ferreiro AI, Segurado R, Costa M. Modelling soot formation during biomass gasification. Renew Sustain Energy Rev 2020;134:110380. https://doi.org/ 10.1016/j.rser.2020.110380.
- [9] He Q, Guo Q, Umeki K, Ding Lu, Wang F, Yu G. Soot formation during biomass gasification: A critical review. Renew Sustain Energy Rev 2021;139:110710. https://doi.org/10.1016/j.rser.2021.110710.
- [10] Helble JJ. A model for the air emissions of trace metallic elements from coal combustors equipped with electrostatic precipitators. Fuel Process Technol 2000; 63(2-3):125–47.
- [11] Yao Q, Li S-Q, Xu H-W, Zhuo J-K, Song Q. Reprint of: Studies on formation and control of combustion particulate matter in China: A review. Energy 2010;35(11): 4480–93.
- [12] Zheng C, Liu X, Xu Xi, Yan P, Chang Q, Wang Yi, et al. Experimental study on electrostatic removal of high-carbon particle in high temperature coal pyrolysis gas. Proc Combust Inst 2019;37(3):2959–65.
- [13] Zhuang Ye, Biswas P. Submicrometer Particle Formation and Control in a Bench-Scale Pulverized Coal Combustor. Energy Fuels 2001;15(3):510–6.
- [14] Chen Q, Fang M, Cen J, Zhao Y, Wang Q, Wang Y. Electrostatic precipitation under coal pyrolysis gas at high temperatures. Powder Technol 2020;362:1–10.
- [15] Schulz F, Commodo M, Kaiser K, De Falco G, Minutolo P, Meyer G, et al. Insights into incipient soot formation by atomic force microscopy. Proc Combust Inst 2019; 37(1):885–92.
- [16] Gleason K, Carbone F, Sumner AJ, Drollette BD, Plata DL, Gomez A. Small aromatic hydrocarbons control the onset of soot nucleation. Combust Flame 2021;223: 398–406.
- [17] Ma J, Fletcher TH, Webb BW. Conversion of coal tar to soot during coal pyrolysis in a post-flame environment. Symp (Int) Combust 1996;26(2):3161–7.
- [18] Apicella B, Russo C, Cerciello F, Stanzione F, Ciajolo A, Scherer V, et al. Insights on the role of primary and secondary tar reactions in soot inception during fast pyrolysis of coal. Fuel 2020;275:117957. https://doi.org/10.1016/j. fuel.2020.117957.
- [19] Zhuo J-K, Li S-Q, Yao Q, Song Q. The progressive formation of submicron particulate matter in a quasi one-dimensional pulverized coal combustor. Proc Combust Inst 2009;32(2):2059–66.
- [20] Xiao Z, Tang Y, Zhuo J, Yao Q. Effect of the interaction between sodium and soot on fine particle formation in the early stage of coal combustion. Fuel 2017;206: 546–54.
- [21] Ma P, Huang Q, Gao Q, Li S. Effects of Na and Fe on the formation of coal-derived soot in a two-stage flat-flame burner. Fuel 2020;265:116914. https://doi.org/ 10.1016/j.fuel.2019.116914.
- [22] Dong H, Zhang Y, Du Q, Li D, Feng D, Gao J, et al. Effect of different forms of Na and temperature on soot formation during lignite pyrolysis. Fuel 2020;280: 118514. https://doi.org/10.1016/j.fuel.2020.118514.
- [23] Dong H, Du Q, Li D, Feng D, Gao J, Wu S. Impact of Sodium on the Formation Mechanism and Physicochemical Properties of Coal-Derived Soot. Energy Fuels 2020;34(2):1453–66.
- [24] Xiao Z, Shang T, Zhuo J, Yao Q. Study on the mechanisms of ultrafine particle formation during high-sodium coal combustion in a flat-flame burner. Fuel 2016; 181:1257–64.
- [25] Li D, Zhang Yu, Dong H, Du Q, Gao J, Cui Z. Effects of iron on the soot formation during coal pyrolysis. Fuel 2020;270:117463. https://doi.org/10.1016/j. fuel.2020.117463.
- [26] Howard JB, Kausch WJ. Soot control by fuel additives. Prog Energy Combust Sci 1980;6(3):263–76.
- [27] Wang H. Formation of nascent soot and other condensed-phase materials in flames. Proc Combust Inst 2011;33(1):41–67.
- [28] Simonsson J, Olofsson N-E, Hosseinnia A, Bengtsson P-E. Influence of potassium chloride and other metal salts on soot formation studied using imaging LII and ELS, and TEM techniques. Combust Flame 2018;190:188–200.
- [29] Kolakkandy S, Pratihar S, Aquino AJA, Wang H, Hase WL. Properties of complexes formed by Na+, Mg2+, and Fe2+ binding with benzene molecules. J Phys Chem A 2014;118(40):9500–11.
- [30] Mao Q, Luo KH. Trace metal assisted polycyclic aromatic hydrocarbons fragmentation, growth and soot nucleation. Proc Combust Inst 2019;37(1): 1023–30.
- [31] Wang M, Mei J, You X. Effect of potassium chloride addition on soot formation during ethylene pyrolysis in a flow reactor. Combust Flame 2021;223:118–26.
- [32] Mitchell JBA, Miller DJM. Studies of the effects of metallic and gaseous additives in the control of soot formation in diffusion flames. Combust Flame 1989;75(1): 45–55.
- [33] Neeft JPA, Makkee M, Moulijn JA. Metal oxides as catalysts for the oxidation of soot. Chem Eng J Biochem Eng J 1996;64(2):295–302.
- [34] Cotton DH, Friswell NJ, Jenkins DR. The suppression of soot emission from flames by metal additives. Combust Flame 1971;17(1):87–98.
- [35] Haynes BS, Jander H, Wagner HGG. The effect of metal additives on the formation of soot in premixed flames. Symp (Int) Combust 1979;17(1):1365–74.
- [36] Wiinikka H, Hage FS, Ramasse QM, Toth P. Spatial distribution of metallic heteroatoms in soot nanostructure mapped by aberration-corrected STEM-EELS. Carbon 2021;173:953–67.
- [37] Wiinikka H, Weiland F, Pettersson E, Öhrman O, Carlsson P, Stjernberg J. Characterisation of submicron particles produced during oxygen blown entrained flow gasification of biomass. Combust Flame 2014;161(7):1923–34.
- [38] Patel M, Aswath P. Diesel soot chemical characterization using XANES. Tribol Lubrication Technol 2010;66(2):17–8.

- [39] Sharma V, Uy D, Gangopadhyay A, O'Neill A, Paxton WA, Sammut A, et al. Structure and chemistry of crankcase and exhaust soot extracted from diesel engines. Carbon 2016;103:327–38.
- [40] Li CZ, Sathe C, Kershaw JR, Pang Y. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. Fuel 2000;79(3):427–38.
- [41] Wu H, Quyn DM, Li C-Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part III. The importance of the interactions between volatiles and char at high temperature. Fuel 2002;81(8):1033–9.
- [42] Quyn DM, Wu H, Bhattacharya SP, Li C-Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part II. Effects of chemical form and valence. Fuel 2002;81 (2):151–8.
- [43] Yongbin J, Jiejie H, Yang W. Effects of Calcium Oxide on the Cracking of Coal Tar in the Freeboard of a Fluidized Bed. Energy Fuels 2004;18(6):1625–32.
- [44] Hong D, Si T, Guo X. Insight into the calcium carboxylate release behavior during Zhundong coal pyrolysis and combustion. Proc Combust Inst 2021;38(3):4023–32.
- [45] Zhou Y, Li G, Jin L, Zhou J, Wang J, Li Y, et al. In Situ Analysis of Catalytic Effect of Calcium Nitrate on Shenmu Coal Pyrolysis with Pyrolysis Vacuum Ultraviolet Photoionization Mass Spectrometry. Energy Fuels 2018;32(2):1061–9.
- [46] Tingyu Z, Shouyu Z, Jiejie H, Yang W. Effect of calcium oxide on pyrolysis of coal in a fluidized bed. Fuel Process Technol 2000;64(1-3):271–84.
- [47] Vernaglia BA, Wornat M, Li C-H, Nelson PF. The effects of pyrolysis temperature and ion-exchanged metals on the composition of brown coal tars produced in a fluidized-bed reactor. Symp (Int) Combust 1996;26(2):3287–94.
- [48] Wornat MJ, Nelson PF. Effects of ion-exchanged calcium on brown coal tar composition as determined by Fourier transform infrared spectroscopy. Energy Fuels 1992;6(2):136–42.
- [49] Lipsky E, Stanier CO, Pandis SN, Robinson AL. Effects of sampling conditions on the size distribution of fine particulate matter emitted from a pilot-scale pulverized-coal combustor. Energy Fuels 2002;16(2):302–10.
- [50] Sippula O, Koponen T, Jokiniemi J. Behavior of Alkali Metal Aerosol in a High-Temperature Porous Tube Sampling Probe. Aerosol Sci Technol 2012;46(10): 1151–62.
- [51] Gall D, Pushp M, Davidsson KO, Pettersson JBC. Online measurements of alkali and heavy tar components in biomass gasification. Energy Fuels 2017;31(8):8152–61.
- [52] Maricq MM. Coagulation dynamics of fractal-like soot aggregates. J Aerosol Sci 2007;38(2):141–56.
- [53] Kasper M, Siegmann K, Sattler K. Evaluation of an in situ sampling probe for its accuracy in determining particle size distributions from flames. J Aerosol Sci 1997; 28(8):1569–78.
- [54] Zhao B, Yang Z, Wang J, Johnston MV, Wang H. Analysis of soot nanoparticles in a laminar premixed ethylene flame by scanning mobility particle sizer. Aerosol Sci Technol 2003;37(8):611–20.
- [55] Kenny LC, Thorpe A, Stacey P. A collection of experimental data for aerosol monitoring cyclones. Aerosol Sci Technol 2017;51(10):1190–200.
- [56] van Dyk JC, Baxter LL, van Heerden JHP, Coetzer RLJ. Chemical fractionation tests on South African coal sources to obtain species-specific information on ash fusion temperatures (AFT). Fuel 2005;84(14-15):1768–77.
- [57] Schafer HNS. Chapter 7 FUNCTIONAL GROUPS AND ION EXCHANGE PROPERTIES. In: Durie RA, editor. The Science of Victorian Brown Coal. Butterworth-Heinemann; 1991. p. 323–57.
- [58] Schafer HNS. Carboxyl groups and ion exchange in low-rank coals. Fuel 1970;49 (2):197–213.
- [59] Singh J, Patterson RIA, Kraft M, Wang H. Numerical simulation and sensitivity analysis of detailed soot particle size distribution in laminar premixed ethylene flames. Combust Flame 2006;145(1-2):117–27.
- [60] Zhao B, Uchikawa K, Wang H. A comparative study of nanoparticles in premixed flames by scanning mobility particle sizer, small angle neutron scattering, and transmission electron microscopy. Proc Combust Inst 2007;31(1):851–60.
- [61] Sathe C, Hayashi J-I, Li C-Z, Chiba T. Combined effects of pressure and ionexchangeable metallic species on pyrolysis of Victorian lignite. Fuel 2003;82(3): 343–50.
- [62] Li X, Wu H, Hayashi J-I, Li C-Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VI. Further investigation into the effects of volatile-char interactions. Fuel 2004;83(10):1273–9.
- [63] Yu J, Lucas J, Strezov V, Wall T. Swelling and Char Structures from Density Fractions of Pulverized Coal. Energy Fuels 2003;17(5):1160–74.
- [64] Solomon PR, Fletcher TH. Impact of coal pyrolysis on combustion. Symp (Int) Combust 1994;25(1):463–74.
- [65] Chen Yi, Luo Z, Fang M, Wang Q. Migration and transformation of sodium during staged coal combustion of Zhundong coal and influence of carbon coating. Fuel Process Technol 2020;203:106382. https://doi.org/10.1016/j. fuproc.2020.106382.
- [66] Apicella B, Senneca O, Russo C, Heuer S, Cortese L, Cerciello F, et al. Separation and characterization of carbonaceous particulate (soot and char) produced from fast pyrolysis of coal in inert and CO2 atmospheres. Fuel 2017;201:118–23.
- [67] Yu Ge, Yu D, Liu F, Han J, Yu X, Wu J, et al. Different impacts of magnesium on the catalytic activity of exchangeable calcium in coal gasification with CO2 and steam. Fuel 2020;266:117050. https://doi.org/10.1016/j.fuel.2020.117050.
- [68] Ma Z, Bai J, Li W, Bai Z, Kong L. Mineral Transformation in Char and Its Effect on Coal Char Gasification Reactivity at High Temperatures, Part 1: Mineral Transformation in Char. Energy Fuels 2013;27(8):4545–54.
- [69] Helble JJ, Sarofim AF. Influence of char fragmentation on ash particle size distributions. Combust Flame 1989;76(2):183–96.

#### Y. Wu et al.

- [70] Mitchell P, Frenklach M. Particle aggregation with simultaneous surface growth. Phys Rev E 2003;67(6):061407.
- [71] Simonsson J, Olofsson N-E, Bladh H, Sanati M, Bengtsson P-E. Influence of potassium and iron chloride on the early stages of soot formation studied using imaging LII/ELS and TEM techniques. Proc Combust Inst 2017;36(1):853–60.
- [72] Chen S, Li S, Liu W, Makse HA. Effect of long-range repulsive Coulomb interactions on packing structure of adhesive particles. Soft Matter 2016;12(6):1836–46.
- [73] Ishiguro T, Takatori Y, Akihama K. Microstructure of diesel soot particles probed by electron microscopy: First observation of inner core and outer shell. Combust Flame 1997;108(1-2):231–4.
- [74] Hurt RH, Crawford GP, Shim H-S. Equilibrium nanostructure of primary soot particles. Proc Combust Inst 2000;28(2):2539–46.
- [75] Kholghy MR, Veshkini A, Thomson MJ. The core-shell internal nanostructure of soot – A criterion to model soot maturity. Carbon 2016;100:508–36.
- [76] Bowal K, Martin JW, Misquitta AJ, Kraft M. Ion-Induced Soot Nucleation Using a New Potential for Curved Aromatics. Combust Sci Technol 2019;191(5-6):747–65.
  [77] Pascazio L, Martin JW, Botero ML, Sirignano M, D'Anna A, Kraft M. Mechanical
- Properties of Soot Particles: The Impact of Crosslinked Polycyclic Aromatic Hydrocarbons. Combust Sci Technol 2021;193(4):643–63.
- [78] Commodo M, Kaiser K, De Falco G, Minutolo P, Schulz F, D'Anna A, et al. On the early stages of soot formation: Molecular structure elucidation by high-resolution atomic force microscopy. Combust Flame 2019;205:154–64.
- [79] Pascazio L, Martin JW, Menon A, Hou D, You X, Kraft M. Aromatic penta-linked hydrocarbons in soot nanoparticle formation. Proc Combust Inst 2021;38(1): 1525–32.
- [80] Davis J, Molnar E, Novosselov I. Nanostructure transition of young soot aggregates to mature soot aggregates in diluted diffusion flames. Carbon 2020;159:255–65.
- [81] Balthasar M, Frenklach M. Monte-Carlo simulation of soot particle coagulation and aggregation: the effect of a realistic size distribution. Proc Combust Inst 2005;30 (1):1467–75.
- [82] Seong HJ, Boehman AL. Evaluation of Raman Parameters Using Visible Raman Microscopy for Soot Oxidative Reactivity. Energy Fuels 2013;27(3):1613–24.

- [83] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. Carbon 2005;43(8):1731–42.
- [84] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B 2000;61(20):14095–107.
- [85] Russo C, Ciajolo A. Effect of the flame environment on soot nanostructure inferred by Raman spectroscopy at different excitation wavelengths. Combust Flame 2015; 162(6):2431–41.
- [86] Ferrari AC, Robertson J. Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. Physical Review B 2001;64(7):075414.
- [87] Baldelli A, Trivanovic U, Sipkens TA, Rogak SN. On determining soot maturity: A review of the role of microscopy- and spectroscopy-based techniques. Chemosphere 2020;252:126532. https://doi.org/10.1016/j. chemosphere.2020.126532.
- [88] Commodo M, Joo PH, De Falco G, Minutolo P, D'Anna A, Gülder ÖL. Raman Spectroscopy of Soot Sampled in High-Pressure Diffusion Flames. Energy Fuels 2017;31(9):10158–64.
- [89] Beyssac O, Goffé B, Petitet J-P, Froigneux E, Moreau M, Rouzaud J-N. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. Spectrochim Acta Part A Mol Biomol Spectrosc 2003;59(10): 2267–76.
- [90] Dong H, Zhang Yu, Du Q, Li D, Feng D, Gao J, et al. Roles of Ion-Exchangeable Sodium in the Conversion Process of Tar to Soot during Rapid Pyrolysis of Two Brown Coals in a Drop-Tube Reactor. ACS Omega 2020;5(16):9078–92.
- [91] Feng D, Zhao Y, Zhang Yu, Xu H, Zhang L, Sun S. Catalytic mechanism of ionexchanging alkali and alkaline earth metallic species on biochar reactivity during CO2/H2O gasification. Fuel 2018;212:523–32.
- [92] Zeng D, Hu S, Sayre AN, Sarv H. On the rank-dependence of coal tar secondary reactions. Proc Combust Inst 2011;33(2):1707–14.
- [93] Deng C, Liaw SB, Wu H. Fundamental investigation into characteristics of particulate matter produced from rapid pyrolysis of biochar in a drop-tube furnace at 1300 °C. Proc Combust Inst 2021;38(4):5229–36.