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High Time- and Size-Resolved Measurements of PM and Chemical Composition from Coal Combustion: Implications for the EC **Formation Process**

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Supporting Information

ABSTRACT: Inefficient coal combustion is a significant source of elemental carbon (EC) air pollution in China, but there is a limited understanding of EC's formation processes. In this study, high time-resolved particle number size distributions (PNSDs) and size-resolved chemical compositions were obtained from the combustion of four bituminous coals burned in a quartz tube furnace at 500 and 800 °C. Based on the distinct characteristics of PNSD, the flaming stage was divided into the first-flaming stage (with a PNSD peak at 0.3–0.4 μ m) and the second-flaming stage (with a PNSD peak at 0.1–0.15 μ m). For the sizesegregated EC and OC measurements, more soot-EC was observed in particles larger than 0.3 μ m, whereas the smaller ones possessed more char-EC. The results indicated that gas-phase and direct-conversion EC generation mechanisms dominate different burning stages. The analysis of 16 parent PAHs showed more



high-molecular-weight PAHs in the second-flaming stage particles, which supports the idea of different formation processes for char-EC and soot-EC. For all four coals, the PNSD and chemical compositions shared a similar trend, confirming that the different formation processes of EC in different flaming stages were common. This study provides novel information concerning EC formation.

INTRODUCTION

Elemental carbon (EC), which may be considered a surrogate for black carbon (BC), is an environmental pollutant that greatly impacts regional climate and human health and is generated from the incomplete combustion of fuel. China is the largest contributor of EC in the world,¹ and 28% of EC emissions in China can be ascribed to residential coal combustion (RCC), which is considered to be a typically inefficient combustion.² According to previously conducted emission estimates, the burning condition and coal type can be significant factors for EC emission. For example, a variation of several orders of magnitude for EC emission factors (EFs)

produced by RCC was observed in different stoves.^{3,4} In these studies, the volatile content was shown to be a crucial factor for EC emission, but there was a nonlinear function between volatile content and EC emission.⁵⁻⁷ A reasonable explanation is that the volatile component usually consists of complex compositions, such as light gases (CO and CO₂), light hydrocarbons, and tars,⁸ and each component would go

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through different transformation processes during different RCC phases, resulting in the complex EC production processes.

The coal combustion process is usally divided into four burning stages: (1) ignition stage; (2) flaming stage; (3) solid burn stage; and (4) burnout stage.^{3,7,9–11} A large amount of organic matter is released during the first stage through volatilization, and then most of the volatile contents subsequently burn out at the end of the second stage, leaving the fixed carbon to burn in the next two stages. The volatile contents (mostly coal tar), are considered to be the primary precursors of EC;¹² hence, the flaming stage produces the most EC emitted from RCC. However, it is likely that the flaming stage includes many different EC formation processes because of the complex composition of coal tar.

Two formation pathways are accepted for the transformation of tars to solid carbon: one is the gas-phase H-abstract reactions between light organic molecules, 13-16 and the other is the direct conversion of tar.¹⁷ Although carbonaceous particles generated through these two kinds of pathways are both defined as EC, it is worth noting the existing morphological and constituent differences between them. Scientists often separate EC into two categories: char-EC and soot-EC. Char-EC is generated from the partial oxidation of fuel and has a morphology similar to the source. Soot-EC is formed via the gas-phase condensation of hydrocarbons,¹⁸ and tends to form chainlike aggregates assembled by small soot particles. When analyzed by the thermal/optical reflectance (TOR) method,¹⁸ it was observed that char-EC contained a higher EC1 fraction (the first fraction of EC in TOR measurement that was oxidized first when the temperature was 550 °C), while soot-EC possessed significantly higher EC2 and EC3 (the last two fractions of EC that were oxidized successively when the temperature reached 650 and 850 °C in TOR measurement).

There are notably few studies focused on EC formation during the coal combustion flaming stage. The typical description of coal combustion usually takes the flaming stage as a whole phase. Actually, different components of coal tar go through different reactions during the coal combustion flaming stage, which results in different flaming stages with distinct characteristics. In addition, the EC generated from different coal tar components may have different size distributions or compositions. It is meaningful to investigate EC emissions in the flaming stage during coal combustion.

Because of the complicated burning condition of RCC, the EC formation process is affected by many factors including combustion temperature, oxygen supply and fuel property. It is necessary to simplify the burning condition to highlight the EC emission process during coal combustion. Compared to the actual RCC, which usually includes many burning stages at the same time, coal combustion in a quartz tube furnace can reveal the actual EC emission process in each burning stage. Moreover, many previous studies demonstrated that the quartz tube furnace was serviceable in coal combustion research.^{19,20} Therefore, four bituminous coals with different volatile contents were tested in a quartz tube furnace to perform the RCC experiment. Two combustion temperatures (500 and 800 °C) were set to simulate the actual ignition process and stable combustion phase of RCC. Together with a dilution sampling system (FPS-4000, Dekati Inc., Finland), an electrical lowpressure impactor (ELPI⁺, Dekati Inc., Finland) was used to obtain highly time-resolved particle number size distribution (PNSD) and highly size-segregated particle samples. Next, the particle samples were analyzed for EC/OC and PAHs offline.

The EC/OC and PAH contents of different size particles, as well as PNSD, were examined to investigate the differences in EC morphology and composition. This work extends our previous research on RCC emission pollutants and provides a further understanding of EC formation during different burning stages.

EXPERIMENTAL SECTION

Coal Combustion and Dilution Sampling Measurement System. For the coal combustion tests, a coal combustion and dilution sampling measurement system were built in our laboratory, which contained a quartz tube furnace, a dilution sampling system, and a flue gas monitor system. The sketch of the whole system is shown in Figure S1 in Supporting Information (SI), and details are given in SI Text S1.

Coal Samples and Experiment Setup. Four coal types with different geological maturities were tested in this study, with V_{daf} (the volatile matter content on a dry and ash-free basis) ranging from 30% to 40% (SI Table S1). These four coal types have been demonstrated to be the largest contributors to ambient air pollutants (PM OC EC and PAHs).⁶ Combustion experiments of three types of coal were repeated three times (one coal combustion experiments under 800 °C and combustion experiments of two types of coal include YM and SH coal under 500 °C). The reproducibility is presented in SI Table S2 together with the PM, OC, and EC EFs (emission factors). The values of Coefficient of Variation (CV) of EF_{PM} EF_{OC} , and EF_{EC} for the repeated experiments range from 0.8% for YM coal in 500 °C combustion to 4.7% for SH coal in 500 °C combustion, but the variation between different volatile content coals were comparable with previous work, which indicated that the combustion technology was reliable. For each coal combustion experiment, a 5 g coal sample was burned at both 500 and 800 °C. During the coal combustion process, gaseous pollutants were detected by a flue gas analyzer (Photon-II, Madur, Italy). The particle number and size distribution were monitored by an electrical low-pressure impactor plus (ELPI⁺, Dekati Inc., Finland) in the size range from 0.006 to 9.88 μ m. The particle number concentration and size distribution of mean values of repeat trials are shown in SI Figure S2 and S3, and detailed information can be found in SI Text S2. The particle samples for EC/OC and PAHs analysis were collected by ELPI+ at the same time with size ranging from 0.016 to 9.88 μ m during the entire combustion cycle. The detailed experimental setup information can be found in SI Text S3.

Particle Mass Measurement and Organic and Elemental Carbon Determination. The EC, OC and TC concentrations of QFF (quartz fiber filter) samples were obtained by an improved thermal/optical reflectance (Improved TOR) protocol (Atmoslytic Inc. model 2001A).²¹ Eight EC and OC fractions (EC1, EC2, EC3 OC1, OC2, OC3, OC4, and POC) were obtained during the analysis (SI Text S4). The EF_{EC} , EF_{OC} and EF_{PM} for each coal/temperature combination were calculated according to the EC, OC, and PM masses of the QFF samples combined with the sampled fractional ratio and coal weight in this test.

Thermal Desorption PAHs Analysis and Quality Control. An optical-4 thermal desorption (TD) sample injection port coupled with an Agilent GC7890B/MS5977A (Agilent Technologies; Santa Clara, CA) system was used in this study. The thermal desorption method was similar to a previous work reported by Ding et al.²² and detailed



Figure 1. Variations in particle number size distribution and gaseous pollutants during burning Xuzhou bituminous coal in high ignition temperature combustion: (a) particle number size distribution; (b) variations in particle number concentration for typical sizes; (c) carbon dioxide, carbon monoxide, and sulfur dioxide concentrations; (d) particle size distribution in each burning stage.

information can be found in SI Text S5. The desorption efficiency was greater than 90%. The detection limit for the TD-GC/MS method ranged from 0.2 pg/mm² (Ace) to 0.6 pg/mm² (Incdp).

Morphology Analysis. The photographs of sample morphologies were acquired by means of a field emission scanning electron microscope (FESEM S-4800, Hittachi, Japan) and transmission electron microscopy (TEM, Jeol JEM 2100, Japan, operating at 200 kV). The FESEM analysis was carried out by observing the size segregated and time-resolved particle samples on the quartz fiber filters, and the TEM analysis was performed by observing the particles collected on TEM grids using the single particle sampler (DKL-2, Genstar, China).

RESULTS AND DISCUSSION

Emission Characteristics of PM, OC and EC during RCC. The EFs of PM, OC and EC of coal combustion, including the comparative experiments for high ignition temperature combustion and low ignition temperature combustion (denoted as HIC and LIC, respectively), are shown in SI Table S2 (the EC and OC emission calculation can be found in SI Text S6).

Variations of EF_{PM} , EF_{OC} , and EF_{EC} values of more than 1 order of magnitude were observed between the two combustion processes. It was found that the EF_{PM} values of HIC and LIC in this study are approximate to the lower and upper values reported by previous work (SI Figures S4). For OC EFs, the range between HIC and LIC could cover almost

all of the recently reported EFs for coals with the same geological maturity (SI Figure S5).^{3,23–29} This indicates that the real-world RCC (combustion temperature ranges from 400 to 900 °C) PM and OC emissions were mostly a mixture of the emissions from these two combustion phases. Several studies that reported extremely high OC EFs that were ascribed to specific poor conditions of combustion are not comparable with the results of this study.³⁰ The average EFs of PM and OC (5.49 g/kg and 3.64 g/kg) are similar to the mean values of previously reported EFs of RCC, ^{3,5,23,24,29–35} indicating that our results are comparable. Therefore, the scale of HIC and LIC phases in real-world coal combustion greatly affects the composition of emitted particles because of the different burning conditions, burning temperatures, and coal types.

The EC emissions are more complex than PM and OC in this study (SI Figure S6). The ratios of EF_{EC} to EF_{OC} (referred to as EC/OC) are presented in SI Table S2. This table shows that HIC (EC/OC = 10.7 ± 4.62) emitted a higher fraction of EC than LIC (EC/OC = 0.016 ± 0.003), which was ascribed to the high burning temperature leading to a high EC generation rate. However, the ratios of EF_{TC}/EF_{PM} for HIC and LIC are 0.408 and 0.738, respectively, and reveal that the fraction of total carbonaceous components emitted from HIC declined dramatically. As expected, the higher burning temperature promotes the generation of EC, but the decomposition of OC and EC were promoted simultaneously. Compared to previous studies, the results given in this study lack the range to cover the variations of all the reported EC EFs and are more similar to the median values. This means that the formation process of

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EC was affected by not only temperature, but also some other crucial factors, such as the coal composition. Despite significant differences of EFs in different combustion conditions, the bell-shaped trends for EC emission similar to previous work³⁶ are observed under both HIC and LIC conditions. Previous studies^{4,6} observed that the coal volatile content was an important factor for EC emission from RCC; the moderately and highly volatile bituminous coals were shown to emit the most EC.⁶ Dong et al.³⁷ found that the moderately and highly volatile bituminous coals emitted more high-molecular-weight PAHs. Therefore, the nonlinear function between EC emission and volatile contents of coal suggested that EC generation was not related to the volatile total contents but was determined by the volatile composition.

Segmentation of Flaming Stage Based on High Temporal- Particle Number Size Distributions. Generally, the solid fuel combustion processes are separated into four stages by flue gas analysis or pollutant composition evaluation, including (1) ignition stage, (2) flaming stage, (3) solid burning stage, and (4) burnout stage. Nielsen et al.¹¹ divided the wood combustion process into three phases depending on the concentration of oxygen and carbon monoxide. Zhou et al.³⁸ classified different coal combustion stages according to the pollutant emissions variation, which has obvious differences in the furnace temperature. These segmentations of the combustion stage satisfy the real-world RCC process but are insufficient to reveal the differences in the EC formation processes during the flaming stage. Coal combustion is a complex process that includes (1) evaporation of light organic matters, (2) gasification of coal, (3) burning of gasification products, and (4) burning of fixed carbon. Moreover, these gasification products (including tar) can be divided into five fractions and produced in the different devolatilization periods of coal burning because of the different volatilities.³⁹ Therefore, the process of the burning of gasification products exhibits distinct characteristics when different fractions of tar (the light organic fraction and the heavy tar fraction) are burned. Hence, the flaming stage defined previously should include both the burning of light organic matter and heavy tar matter. It may be difficult to distinguish these two burning phases using traditional methods. In contrast, the highly time-resolved PNSD is useful to differentiate the different flaming stages because the particles generated from different tar fractions form different size distributions.

The evolution of PNSD from XZ coal combustion at HIC is presented in Figure 1a. The tendencies of the other three coal types are similar to that of XZ coal, and the data are not presented in this article. The gaseous data, including concentrations of CO₂, CO and SO₂, are shown in Figure 1c. In these figures, time "0" indicates the fuel addition time. The coal combustion process can be divided into four stages depending on the different particle size distribution characteristics: Stage 1, the ignition stage; Stage 2, the first flaming stage; Stage 3, the second flaming stage; and Stage 4, the burnout stage. As shown in Figure 1d, the ignition stage produces a very high average number concentration of particles with a wide size range from 0.006 to 1 μ m. Small particles with the diameter in the range of 0.03–0.15 μ m were the most abundant particles during this stage. Then, large particles with the diameter in the range of 0.25-1 μ m were dominant in the second burning stage. Particles emitted in the third stage have a similar size distribution to that of the first stage but with a relatively low number concentration. At the fourth stage, particles were barely

generated. The first stage and the fourth stage are not so important to EC generation; hence, the first and the last burning stages are not discussed in this study. In the following discussion, the first flaming stage and the second flaming stage are discussed in detail.

The first flaming stage (stage 2) was when the vast majority of lightweight organic components were burned, and it lasted for approximately 2-3 min after the ignition stage (lasting approximately 0.5 min). During this stage, many aggregated particles (range from 0.094–0.66 μ m in diameter with peak values occurring at 0.26–0.38 μ m) were emitted. Simultaneously, a significant increase in particle diameter was observed, which distinguishes stage 2 from stage 1 (with peak values occurring at 0.05–0.09 μ m). Moreover, as shown in Figure 1b, a sharp decrease in the concentration of particles smaller than 0.03 μ m occurred immediately after the flames appear. This finding suggests that a different formation process occurred due to the presence of flames. Figure 1d shows that aggregate particles with a diameter in the range of 0.25–1 μ m were the most abundant during this stage, while the average produced emission of small particles ($\sim 10^5$) was lower than that of stage 1 (~10⁶). Another characteristic of this stage was that CO_2 and CO were barely detected (Figure 1c) because of the low generation rate; this indicates that the combustion temperature was relatively low, and most light volatile components were burned in this stage. Generally, unburned light volatile contents transform into small soot particles (0.03–0.1 μ m in diameter), which is in contrast to the observations of this stage. An explanation for this result is that small particles readily formed large size aggregates by polymerization and aggregation.⁴⁰ A large amount of light volatile contents that escaped from coal contributed to particle growth, resulting in the large particle size in this stage. The SO₂ concentration started to increase at the end of this stage, indicating that the combustion temperature started to increase and the burn process was developing into another stage. Therefore, a rapid decrease of particle size was observed at the end of this stage.

The second flaming stage (stage 3) was when the vast majority of heavy weight organic components were burned, and it lasted for approximately 3 min after stage 2. During this stage, a clear decrease in particle size distinguished this stage from stage 2, even though it was also a flaming stage. Clearly, as shown in Figure 1a, two PNSD modes with peak values occur at ~0.006–0.03 and 0.094–0.15 μ m during this stage. The average particle number concentration of particles smaller than 0.15 μ m in this stage are usually higher than that of stage 2 (shown in Figure 1d), which means that the deep devolatilization of coal contributed a large amount of the smaller particles (0.094–0.15 μ m), even in the absence of light volatiles. However, the absence of light volatiles resulted in a lower average number concentration of large particles (larger than 0.15 μ m in diameter) compared with stage 2. In addition, the CO and CO₂ concentrations began to rise at the beginning of this stage, because of the increasing combustion rate. This result suggests that the gasification and combustion of the carbon skeleton became the dominant process during this stage. It must be noted that the flaming phase combustion and solid phase combustion occurred at the same time in this stage, because of the high heating rate, which resulted in these two PNSD modes. Another important indicator was SO₂ generated by the high-temperature oxidation of pyrite. The SO₂ concentration exhibited a peak in the middle of this stage, indicating that the combustion temperature increased to its



Figure 2. Profiles of carbon fractions produced from Xuzhou coal combustion under different combustion conditions: (a) size-resolved emission factors of EC fractions under high-temperature burning, (b) sizeresolved emission factors of EC fractions under low-temperature burning, (c) size-resolved emission factors of OC fractions under high-temperature burning, (d) size-resolved emission factors of OC fractions under low-temperature burning, (e) size-resolved ratios of soot-EC to char-EC and ratios of EC to OC and sizeresolved ratios of high-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high-molecular-weight PAHs from the HIC, and (f) size-resolved ratios of soot-EC to char-EC to C and size-resolved ratios of high-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high-molecular-weight PAHs to low-molecular-weight PAHs together with the emission factors of high and low-molecular-weight PAHs from the LIC. The left scales for the right panel are the same as for the left panel.

peak in this stage, and large amounts of inorganic compounds (such as sulfate) were produced to form the smallest particles less than 0.03 μ m in size.^{41,42} Along with the rate of combustion decreasing, the concentrations of all the gaseous pollutants and particles exhibited a decreasing trend at the end of this stage.

Compared with the HIC case, the PNSD of XZ coal in LIC (SI Figure S7) can also be divided into four stages, similar to HIC but with significant overlap. The same variation trends were observed, confirming that the four stages' separation was suitable for characterizing the combustion process of all of these four bituminous coals. However, the emissions of particles produced in LIC for each stage were approximately three times higher than those in HIC (SI Figure S7c), indicating that both the generation and decomposition of particles occurred at the same time during the coal combustion process, and the higher combustion temperature would specifically promote decomposition.

In this study, we separate coal combustion stages depending on PNSD, which is different from previous research focusing on the pollutant concentrations variation. The result shows that the burning of different coal volatile components generates particles of different sizes. As a consequence, particles produced in each burning stage should also have different compositions.

Potential EC Formation Processes Based on Size Distribution of Carbon Fractions and PAHs. According to the decomposition temperatures of the OC and EC measurements, the OC and EC fractions were separated into eight groups, including OC1, OC2, OC3, OC4, EC1, EC2, EC3, and POC. The OC fractions were organic carbon detected when the TOR protocol stepwise heated the sample to 120, 250, 450, and 550 °C in the pure He atmosphere. The EC fractions were elemental carbon detected when the TOR protocol stepwise heated the sample to 550, 700, and 850 $^{\circ}$ C in the 2% O₂/98% He atmosphere. Among these fractions, OC1+OC2 was classified as volatile organic compounds and OC3+OC4 was categorized as refractory organic compounds. EC was typically divided into char and soot. EC1 was classified as char-EC and EC2+EC3 was classified as soot-EC.

Size-Resolved OC and EC Distribution. The quantities of seven carbon fractions are presented in Figure 2. As we can see from Figure 2a and b, the carbonaceous contents are highly dependent on particle size. Most EC was emitted as particles ranging from 0.090 to 10 μ m in diameter for both HIC and LIC. Additionally, more than 90% of carbonaceous matter in smaller HIC particles (<0.030 μ m) was OC, whereas the proportion of OC in larger partilces was only 9% (shown in Figure 2e). Huge differences in EC to OC ratios between different size particles suggest a clear distinction between the formation processes. In contrast, the ratios of EC to OC (shown in Figure 2f) in small (with diameter in range of 0.010–0.030 μ m) and large particles (with diameter in range of $0.030-10 \ \mu m$) in LIC are 0.1 and 0.15, respectively, which have very minor variation, indicating that the evolution of EC emission was bedimmed because of the large amount of OC emission. The HIC processes are discussed in detail to describe the EC formation during coal combustion, while the LIC processes are compared with HIC processes.

As discussed above, the HIC coal combustion was divided into four stages depending on the particle size distribution. Among them, the flaming stages (first flaming stage and second flaming stage) emitted most of the carbonaceous matter, especially EC. Distinct characteristics were observed between particles emitted from these two burning stages. Particles

generated in stage 2 were usually larger than 0.3 μ m, whereas smaller diameter particles (less than 0.3 μ m in diameter) were observed in stage 3. Furthermore, the composition of these particles was also different. As seen from Figure 2a, larger particles (with diameter larger than 0.30 μ m) contained a large amount of soot-EC, whereas the composition of smaller particles (with diameter in range of 0.01–0.30 μ m) were dominated by char-EC.

Two mechanisms are normally described for EC formation, the gas-phase condensation and direct conversion. Chen et al.,¹ found that at least one-third of EC produced in coal combustion was generated by gas-phase condensation. Previous studies of the soot formation mechanism reported that soot was produced in regions close to the main flame zone where H atoms are abundant.^{14,40} The H atoms generated through the H-abstraction reactions were a critical factor for the soot production reaction between aromatic and aryl radicals. Furthermore, in the study of the evolution of primary particles in a premixed laminar flame, Feenklach et al.⁴³ found that there exists a transition point for the transformation of nucleation to surface growth. In the nucleation zone, ultrafine particles coagulate with each other to form the nascent particles. After that step, surface growth dominates the diameter growth. This finding appeared to explain well the core-shell structure of soot-EC. However, gas-phase condensation cannot explain the formation of large particles, which can be ascribed to the aggregation between small soot particles. For the first flaming stage, the gas-phase condensation mechanism was apparent. It is clearly shown in Figure 2a that more than half of the carbonaceous matter in the particles larger than 0.30 μ m (mostly generated from the first flaming stage) was soot-EC, and the ratio of soot-EC to char-EC increased with particle size (in range of 0.2–2.5 μ m) until the diameter reached 4 μ m (shown in Figure 2e). This finding indicates that soot-EC formation was the major EC formation process during this burning stage. Another distinguishing feature of this burning stage was the relatively stable ratio of EC/OC (approximately 14), which meant that the organic compounds were almost completely converted or decomposed.

Another EC formation mechanism considers that coal tar can be turned into EC by a direct conversion. Studies conducted by A. L. Brown et al.⁴⁴ reported that tar (products of coal devolatilization) was the only precursor of EC that could be turned into EC directly by polymerization or could be turned into light gas-phase organics by decomposition.¹⁷ In this study, these two types of tar pyrolysis products were both important to EC generation. The first type could form tar-ball-like EC directly, and the second type could take part in the gas-phase reaction. The tar ball was first found in ambient air and consisted of spherical particles from biomass burning with a diameter range of 0.03–0.5 μ m.⁴⁵ However, the particles were somewhat aged, resulting in the increase in diameter. Fresh generated tar balls in burning biomass smoke were observed by Reid et al.⁴⁶ within the 0.05–0.3 μ m size range, which is in concordance with our observation of second flaming stage particles. We can infer that, after being generated from coal devolatilization, repolymerization could turn these tar ball into graphitized particles. Based on this hypothesis, the direct transformation of coal tar could produce single spherical EC particles (0.05–0.3 μ m in diameter). Different from gas-phase condensation, the EC converted from tar balls was more likely to be char-EC without the gas-phase condensation-formed core-shell structure that exists in soot-EC.

During the second flaming stage (stage 3), the soot-EC generation was depressed, because most of the light organic matter was consumed in the first flaming stage (stage 2). In contrast, char-EC generated in the second flaming stage (stage 3) showed a peak value at 0.2–0.3 μ m in diameter. As Figure 2e shows, for particles smaller than 0.30 μ m, the ratio of soot-EC to char-EC decreased with increasing particle size until the particle size reached 0.2 μ m and then started to increase,the ratio was 0.04 for particles with diameter of 0.015 μ m, indicating that almost all the carbonaceous matter produced in this stage was char-EC. As expected, that when the particle size approached that of the first flaming stage particles, the particles containing soot-EC increased again. Moreover, the ratio of EC/ OC increased with the particle size (the ratios in range of 0.2-20) to its peak, when the particle size reached 0.3 μ m. This result is in agreement with our hypothesis, because particles generated in the second flaming stage contained more OC than EC, which can be ascribed to the incomplete polycondensation of coal tar.

Notably, the soot-EC and char-EC generation processes were not strictly isolated, as a little peak of char-EC emission was observed in the first flaming stage (as shown in Figure 2a). The results suggest that it is not possible to draw clear boundaries between different coal combustion phases; however, the observations in this study present the existence of different EC generation processes during the HIC experiment, which are usually not investigated in RCC.

Compared with the HIC case, clearly different size-resolved distributions were observed for EC and OC in the LIC process (unimodal distributions with peak values occurring at 0.5–0.6 μ m) (shown in Figures 2b and d), which means that LIC particles grow through a similar coagulation between EC and OC. This result suggests that all the EC formation and OC emission processes occurred at the same time during LIC. The ratio of soot-EC to char-EC presented in Figure 2f showed that the soot-EC content increased slowly with particle size, indicating that the soot-EC formation process was not the major driving force for the particle size growth during the LIC process. The ratio of EC to OC in LIC showed a relatively stable trend (approximately 0.1), more than 90% of the mass fraction of total carbon was contributed from OC, confirming that the LIC emission was dominated by OC.

Size-Resolved PAH Distribution. In previous studies, the PAHs were considered to be the most important precursor of EC.⁴⁷ Studies that focused on the soot emitted from the premixed flame^{13–16} reported that inception of the nuclei formation could be considered as a pure chemical reaction between light organic matter or a physical condensation between heavy organic matter. Recent studies revealed that these two growth mechanisms played an equally important role in the EC formation process; hence, we can infer that the composition of PAH can be used as an indicator to the EC production mechanisms during coal combustion.

The ratios for high molecular weight (HMW) PAHs to low molecular weight (LMW) PAHs (HWM = 4–6 ring PAHs, LWM = 2–3 ring PAHs) of the XZ coal are presented in Figure 2e and f, it is apparent that LIC emitted substantially more PAHs than HIC—approximately 2 orders of magnitude more. It is generally known that coals contain some free PAHs bonded to the carbon skeleton by weak bonds.⁴⁸ Free PAHs in coal begin to rupture at low temperatures resulting in the rapid emission observed in LIC. However, the decomposition and cyclization reaction increased with the temperature causing a



Figure 3. (a) The size distribution of ratios of high-molecular-weight PAHs to low-molecular-weight PAHs in different size sections in particles of HIC of three coals, (b) The size distribution of ratios of high-molecular-weight PAHs to low-molecular-weight PAHs in different size sections in particles of LIC of three coals.



Figure 4. (a)–(d) FESEM images of time-resolved particles from HIC of XZ coal, (a')–(d') Low magnification FESEM images of time-resolved particles from HIC of XZ coal, (e)–(g) FESEM images of size-resolved (three particle samples collected by ELPI+ with typical size for 0.10 μ m, 0.30 μ m, and 1.0 μ m were observed) particles from HIC of XZ coal, (e')–(g') Low magnification FESEM images of size-resolved (three particle samples collected by ELPI+ with typical size for 0.10 μ m, 0.30 μ m, and 1.0 μ m were observed) particles from HIC of XZ coal, (e')–(g') Low magnification FESEM images of size-resolved (three particle samples collected by ELPI+ with typical size for 0.10 μ m, 0.30 μ m, and 1.0 μ m were observed) particles from HIC of XZ coal, (h) and (h') TEM images of char-EC, (i) and i') TEM images of soot-EC.

decrease in free PAH emission,⁴⁸ especially for HWM PAHs, which are easier to turn into EC.

Furthermore, the EFs of PAHs were observed to be sizedependent in this study. From Figure 2e we can see that the ratio of HMW to LMW in HIC decreased with particle size up to approximately 0.3 um and then increased. Whereas, the ratio in LIC increased first and then decreased when the particle size reached 0.09 μ m (Figure 2f). The differences between HIC and LIC can be ascribed to the different burning temperatures. The LIC process yielded more OC generated during the evaporation and gasification of the coals. During the lowtemperature combustion, most fine particles contained significantly more LMW PAHs that formed from the condensation of organic materials. For the particles ranging from 0.09 to 0.16 μ m in diameter (most particles generated in the second flaming stage), the ratio of HWM to LWM was relatively high (approximately 10) because of the deep coal devolatilization. Compared with the second flaming stage, the first flaming stage produced less HMW (the ratio of HWM to LWM for the first stage was approximately 5).

The measured variations of HWM/LWM ratios from three coal combustions were very similar (YZ coal was not included due to a detection failure). For all these coals, the finer the particles are, the higher the content of high-molecular-weight PAHs is. As seen in Figure 3a, the particles with diameter in the range of $0.3-1 \ \mu$ m contained more LMW PAHs than in the smaller particles ($0.03-0.3 \ \mu$ m). Therefore, we can infer that low-molecular-weight organic matter was the largest contrib

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utor to soot-EC, generated via gas-phase condensation, whereas the HMW PAHs were more inclined to turn into char-EC, which is in agreement with our previous hypothesis about EC formation.

Morphological Properties of Time- and Size-Resolved EC Particles. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analyses have been carried out to fully characterize the morphological properties of the collected particles. Generally, Char is defined as a kind of carbonaceous matter with randomly organized aromatic rings formed directly from fuel gasification. Soot is a kind of graphited carbon, which is a crystalline phase, and formed via gas-to-particle conversion of molecular precursors.^{18,49} The most evident distinction between char and soot in structure is that soot usually has a chain-like form while char usually has a spherical morphology.

Figure 4 shows several FESEM and TEM images of the timeand size-resolved particle samples. Figures 4a-d show the variation of particular morphologies in the first 7 min of HIC. It is clearly shown that in the first 3 min (Figure 4a), most of the emitted carbonaceous particles have a chain-like morphology which can be considered as soot-EC;¹⁸ however, the observed spherical particles (usually considered as char-EC) increased with the combustion time. In addition, the morphologies of size-resolved particles presented in Figure 4e-g show that the small particles with diameter approximate to 0.1 μ m were single spherical char-EC, while, the larger particles were soot-EC assembled by small soot particles. Detailed structure information was obtained by the TEM observation and shown in Figure 4h, i and Figure 4h',i'. In the TEM images we can see that the char-EC is a spherical particle surround by a shell, and it can be inferred that the char-EC was generated from the incomplete oxidation of tar. However, the soot-EC has a distinct different shape composed of many small particles with diameters in the range of 0.03– 0.05 μ m; this finding indicates the significantly different formation processes. These results confirmed our hypothesis that the EC generation process during RCC is dominated by different formation mechanisms.

IMPLICATIONS

EC emitted from coal combustion is usually formed by many complex mechanisms. The homogeneous and heterogeneous combustion of vaporized and nonvolatile organic matter are considered as two crucial formation processes. Our study focused on the formation and composition characteristics of carbonaceous particles produced in different coal combustion stages and at different burning temperatures. The results are useful in helping to understand the EC generation process that has implications on the environmental and health impact of RCC emitted particles.

In this study, we divided the coal burning flaming stage into two different stages with different types of EC emitted. The first flaming stage produced particles with a high soot-EC content, and the second flaming stage emitted char-EC particles containing more organic matter. The low-molecular-weight volatile organic matter tended to take part in the homogeneous reaction to form soot-EC, but the refractory organic compounds were more likely to turn into char-EC by heterogeneous conversion. For the whole coal combustion process, these different EC formation mechanisms dominated different burning stages, and the proportion of each period of burning stage was affected by the combustion conditions and coal properties. Previous works reported that the EC emission of different coal types with different volatile contents in several specific combustion experiments showed a bell shape tendency—the medium-volatile bituminous coal has the largest emission factors of ambient air pollutants (PM, EC, and OC), while the lower and higher volatile content coal have lower emission factors.⁶ A reasonable explanation for this result is that differently constituted coals with different volatilities transform into different EC types through different processes, and the RCC EC emission was a mixture of these different EC formation processes.

The distinct characteristics of Char-EC and Soot-EC, including composition, size, morphology, and mixed state, can result in different environmental impacts. For example, fresh particles generated by low-temperature burning contain more OC and scatter light more significantly; whereas the high-temperature-produced particles with more EC strongly absorb solar radiation that causes global warming. Moreover, EC particles formed in different combustion stages have clearly different compositions and OC mixing states, which could also result in different environmental impacts.^{8,50}

Therefore, we believe that the aspects of RCC generated EC should be considered when doing environmental risk assessment or human health evaluation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b05786.

A sketch of the combustion system, experimental details, analytical values of four coals, organic and elemental carbon determination, thermal desorption PAHs analysis and quality control, OC and EC emission calculation, particle number concentration with uncertainty information, comparative EFs of OC, PM and EC of coal combustion for high ignition temperature combustion and low ignition temperature combustion with studies, PNSD of XZ coal from LIC, and mass distribution of particles emitted from four coal combustion in two temperature conditions(PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Bond, T. C.; Streets, D. G.; Yarber, K. F.; Nelson, S. M.; Woo, J.-H.; Klimont, Z., A technology-based global inventory of black and organic carbon emissions from combustion. *J. Geophys. Res.* **2004**, *109*, (D14), 10.1029/2003JD003697.

(2) Wang, R.; Tao, S.; Wang, W.; Liu, J.; Shen, H.; Shen, G.; Wang, B.; Liu, X.; Li, W.; Huang, Y.; Zhang, Y.; Lu, Y.; Chen, H.; Chen, Y.; Wang, C.; Zhu, D.; Wang, X.; Li, B.; Liu, W.; Ma, J. Black Carbon Emissions in China from 1949 to 2050. *Environ. Sci. Technol.* **2012**, *46* (14), 7595–7603.

(3) Li, Q.; Jiang, J.; Qi, J.; Deng, J.; Yang, D.; Wu, J.; Duan, L.; Hao, J. Improving the Energy Efficiency of Stoves To Reduce Pollutant Emissions from Household Solid Fuel Combustion in China. *Environ. Sci. Technol. Lett.* **2016**, 3 (10), 369–374.

(4) Zhi, G.; Peng, C.; Chen, Y.; Liu, D.; Sheng, G.; Fu, J. Deployment of Coal Briquettes and Improved Stoves: Possibly an Option for both Environment and Climate. *Environ. Sci. Technol.* **2009**, *43* (15), 5586–5591.

(5) Shen, G.; Tao, S.; Wei, S.; Chen, Y.; Zhang, Y.; Shen, H.; Huang, Y.; Zhu, D.; Yuan, C.; Wang, H.; Wang, Y.; Pei, L.; Liao, Y.; Duan, Y.; Wang, B.; Wang, R.; Lv, Y.; Li, W.; Wang, X.; Zheng, X. Field Measurement of Emission Factors of PM, EC, OC, Parent, Nitro-, and Oxy-Polycyclic Aromatic Hydrocarbons for Residential Briquette, Coal Cake, and Wood in Rural Shanxi, China. *Environ. Sci. Technol.* **2013**, 47 (6), 2998–3005.

(6) Chen, Y.; Zhi, G.; Feng, Y.; Liu, D.; Zhang, G.; Li, J.; Sheng, G.; Fu, J. Measurements of Black and Organic Carbon Emission Factors for Household Coal Combustion in China: Implication for Emission Reduction. *Environ. Sci. Technol.* **2009**, *43* (24), 9495.

(7) Li, Q.; Jiang, J. K.; Zhang, Q.; Zhou, W.; Cai, S. Y.; Duan, L.; Ge, S.; Hao, J. M. Influences of coal size, volatile matter content, and additive on primary particulate matter emissions from household stove combustion. *Fuel* **2016**, *182*, 780–787.

(8) Bond, T. C.; Covert, D. S.; Kramlich, J. C.; Larson, T. V.; Charlson, R. J. Primary particle emissions from residential coal burning: Optical properties and size distributions. *J. GEOPHYS RES Atmos.* **2002**, *107* (D21), ICC9–1–ICC 9–14.

(9) Atiku, F. A.; Mitchell, E. J. S.; Lea-Langton, A. R.; Jones, J. M.; Williams, A.; Bartle, K. D. The Impact of Fuel Properties on the Composition of Soot Produced by the Combustion of Residential Solid Fuels in a Domestic Stove. *Fuel Process. Technol.* **2016**, *151*, 117–125.

(10) Hong, L.; Liu, G.; Zhou, L.; Li, J.; Xu, H.; Wu, D. Emission of organic carbon, elemental carbon and water-soluble ions from crop straw burning under flaming and smoldering conditions. *Particuology* **2017**, *31*, 181–190.

(11) Nielsen, I. E.; Eriksson, A. C.; Lindgren, R.; Martinsson, J.; Nyström, R.; Nordin, E. Z.; Sadiktsis, I.; Boman, C.; Nøjgaard, J. K.; Pagels, J. Time-resolved analysis of particle emissions from residential biomass combustion – Emissions of refractory black carbon, PAHs and organic tracers. *Atmos. Environ.* **2017**, *165*, 179–190.

(12) Gai, Z.; Zhang, R.; Bi, J. Characteristics of Soot from Rapid Pyrolysis of Coal and Petroleum Coke. *Energy Fuels* **2017**, *31* (4), 3759–3767.

(13) Celnik, M. S.; Sander, M.; Raj, A.; West, R. H.; Kraft, M. Modelling soot formation in a premixed flame using an aromatic-site soot model and an improved oxidation rate. *Proc. Combust. Inst.* **2009**, 32 (1), 639–646.

(14) Frenklach, M. Reaction mechanism of soot formation in flames. *Phys. Chem. Chem. Phys.* **2002**, *4* (11), 2028–2037.

(15) Guo, Z.; Lou, C.; Liu, Z.; Zhou, H. The impact of combustion characteristics and flame structure on soot formation in oxy-enhanced and oxy-fuel diffusion flames. *Sci. China: Technol. Sci.* **2013**, *56* (7), 1618–1628.

(16) Wang, H.; Zhao, B.; Wyslouzil, B.; Streletzky, K. Small-angle neutron scattering of soot formed in laminar premixed ethylene flames. *Proc. Combust. Inst.* **2002**, *29* (2), 2749–2757.

(17) Chen, J. C.; Castagnoli, C.; Niksa, S. Coal devolatilization during rapid transient heating. 2. Secondary pyrolysis. *Energy Fuels* **2002**, *6* (3), 264–271.

(18) Han, Y.; Cao, J.; Chow, J. C.; Watson, J. G.; An, Z.; Jin, Z.; Fung, K.; Liu, S. Evaluation of the thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere* **2007**, 69 (4), 569–574.

(19) Wang, X.; Williams, B. J.; Wang, X.; Tang, Y. Characterization of organic aerosol produced during pulverized coal combustion in a drop tube furnace. *Atmos. Chem. Phys. Discuss.* **2013**, *13* (2), 3345–3377.

(20) Jones, J. M.; Ross, A. B.; Mitchell, E. J. S.; Lea-Langton, A. R.; Williams, A.; Bartle, K. D. Organic carbon emissions from the co-firing of coal and wood in a fixed bed combustor. *Fuel* **2017**, *195*, 226–231.

(21) Chow, J. C.; Watson, J. G.; Chen, L. W. A.; Arnott, W. P.; Moosmüller, H.; Fung, K. Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols. *Environ. Sci. Technol.* **2004**, *38* (16), 4414– 4422.

(22) Ding, L. C.; Ke, F.; Wang, D. K. W.; Dann, T.; Austin, C. C. A new direct thermal desorption-GC/MS method: Organic speciation of ambient particulate matter collected in Golden, BC. *Atmos. Environ.* **2009**, 43 (32), 4894–4902.

(23) Chen, Y.; Sheng, G.; Bi, X.; Feng, Y.; Mai, B.; Fu, J. Emission Factors for Carbonaceous Particles and Polycyclic Aromatic Hydrocarbons from Residential Coal Combustion in China. *Environ. Sci. Technol.* 2005, 39 (6), 1861–1867.

(24) Chen, Y. J.; Tian, C. G.; Feng, Y. L.; Zhi, G. R.; Li, J.; Zhang, G. Measurements of emission factors of PM2.5, OC, EC, and BC for household stoves of coal combustion in China. *Atmos. Environ.* **2015**, *109*, 190–196.

(25) Chen, Y. J.; Zhi, G. R.; Feng, Y. L.; Tian, C. G.; Bi, X. H.; Li, J.; Zhang, G. Increase in polycyclic aromatic hydrocarbon (PAH) emissions due to briquetting: A challenge to the coal briquetting policy. *Environ. Pollut.* **2015**, *204*, 58–63.

(26) Shen, G. F.; Wang, W.; Yang, Y. F.; Zhu, C.; Min, Y. J.; Xue, M. A.; Ding, J. N.; Li, W.; Wang, B.; Shen, H. Z.; Wang, R.; Wang, X. L.; Tao, S. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmos. Environ.* **2010**, *44* (39), 5237–5243.

(27) Shen, G. F.; Xue, M.; Chen, Y. C.; Yang, C. L.; Li, W.; Shen, H. Z.; Huang, Y.; Zhang, Y. Y.; Chen, H.; Zhu, Y.; Wu, H. S.; Ding, A. J.; Tao, S. Comparison of carbonaceous particulate matter emission factors among different solid fuels burned in residential stoves. *Atmos. Environ.* **2014**, *89*, 337–345.

(28) Shen, G. F.; Tao, S.; Wei, S. Y.; Chen, Y. C.; Zhang, Y. Y.; Shen, H. Z.; Huang, Y.; Zhu, D.; Yuan, C. Y.; Wang, H. C.; Wang, Y. F.; Pei, L. J.; Liao, Y. L.; Duan, Y. H.; Wang, B.; Wang, R.; Lv, Y.; Li, W.; Wang, X. L.; Zheng, X. Y. Field Measurement of Emission Factors of PM, EC, OC, Parent, Nitro-, and Oxy- Polycyclic Aromatic Hydrocarbons for Residential Briquette, Coal Cake, and Wood in Rural Shanxi, China. *Environ. Sci. Technol.* **2013**, *47* (6), 2998–3005. (29) Li, Q.; Jiang, J.; Cai, S.; Zhou, W.; Wang, S.; Duan, L.; Hao, J. Gaseous Ammonia Emissions from Coal and Biomass Combustion in Household Stoves with Different Combustion Efficiencies. *Environ. Sci. Technol. Lett.* **2016**, *3* (3), 98–103.

(30) Chen, Y.; Zhi, G.; Feng, Y.; Fu, J.; Feng, J.; Sheng, G.; Simoneit, B. R. T. Measurements of emission factors for primary carbonaceous particles from residential raw-coal combustion in China. *Geophys. Res. Lett.* **2006**, 33 (20), 382–385.

(31) Chen, Y.; Bi, X.; Mai, B.; Sheng, G.; Fu, J. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. *Fuel* **2004**, 83 (7–8), 781–790.

(32) Chen, Y.; Tian, C.; Feng, Y.; Zhi, G.; Li, J.; Zhang, G. Measurements of emission factors of PM 2.5, OC, EC, and BC for household stoves of coal combustion in China. *Atmos. Environ.* **2015**, *109*, 190–196.

(33) Chen, Y.; Zhi, G.; Feng, Y.; Chongguo, T.; Bi, X.; Li, J.; Zhang, G. Increase in polycyclic aromatic hydrocarbon (PAH) emissions due

to briquetting: A challenge to the coal briquetting policy. *Environ. Pollut.* **2015**, *204*, 58-63.

(34) Li, Q.; Jiang, J.; Zhang, Q.; Zhou, W.; Cai, S.; Duan, L.; Ge, S.; Hao, J. Influences of coal size, volatile matter content, and additive on primary particulate matter emissions from household stove combustion. *Fuel* **2016**, *182*, 780–787.

(35) Shen, G.; Chen, Y.; Xue, C.; Lin, N.; Huang, Y.; Shen, H.; Wang, Y.; Li, T.; Zhang, Y.; Su, S.; Huangfu, Y.; Zhang, W.; Chen, X.; Liu, G.; Liu, W.; Wang, X.; Wong, M.-H.; Tao, S. Pollutant Emissions from Improved Coal- and Wood-Fuelled Cookstoves in Rural Households. *Environ. Sci. Technol.* **2015**, *49* (11), 6590–6598.

(36) Chen, J. P.; Deng, C. P.; Wang, H. T. A comparison of geochemical features of extracts from coal-seams source rocks with different polarity solvents. *Energy Explor. Exploit.* 2009, 27 (1), 29–46.

(37) Dong, J.; Li, F.; Xie, K. C. Study on the source of polycyclic aromatic hydrocarbons (PAHs) during coal pyrolysis by PY-GC-MS. *J. Hazard. Mater.* **2012**, *243*, 80–85.

(38) Zhou, W.; Jiang, J.; Duan, L.; Hao, J. Evolution of Submicrometer Organic Aerosols during a Complete Residential Coal Combustion Process. *Environ. Sci. Technol.* **2016**, *50* (14), 7861–7869.

(39) Guan, G.; Kaewpanha, M.; Hao, X.; Abudula, A. Catalytic steam reforming of biomass tar: Prospects and challenges. *Renewable Sustainable Energy Rev.* **2016**, *58*, 450–461.

(40) Wang, H. Formation of nascent soot and other condensedphase materials in flames. *Proc. Combust. Inst.* 2011, 33 (1), 41-67.

(41) Kulmala, M.; Riipinen, I.; Sipilä, M.; Manninen, H. E.; Petäjä, T.; Junninen, H.; Maso, M. D.; Mordas, G.; Mirme, A.; Vana, M. Toward Direct Measurement of Atmospheric Nucleation. *Science* **2007**, *318* (5847), 89–92.

(42) Andreae, M. O. The Aerosol Nucleation Puzzle. *Science* 2013, 339 (6122), 911–912.

(43) 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), 1467–1475.

(44) Brown, A. L.; Fletcher, T. H. Modeling Soot Derived from Pulverized Coal. *Energy Fuels* **1998**, *12* (4), 745–757.

(45) Pósfai, M.; Gelencsér, A.; Simonics, R.; Arató, K.; Li, J.; Hobbs, P. V.; Buseck, P. R., Atmospheric tar balls: Particles from biomass and biofuel burning. *J. Geophys Res., Atmos.* **2004**, *109*, (D6), n/a10.1029/2003JD004169.

(46) Reid, J. S.; Koppmann, R.; Eck, T. F.; Eleuterio, D. P. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* **2005**, *5* (3), 799–825.

(47) Park, S.; Wang, Y.; Chung, S. H.; Sarathy, S. M. Compositional effects on PAH and soot formation in counterflow diffusion flames of gasoline surrogate fuels. *Combust. Flame* **2017**, *178*, 46–60.

(48) Peng, N.; Li, Y.; Liu, Z.; Liu, T.; Gai, C. Emission, distribution and toxicity of polycyclic aromatic hydrocarbons (PAHs) during municipal solid waste (MSW) and coal co-combustion. *Sci. Total Environ.* **2016**, *565*, 1201–1207.

(49) Nedjalkov, I.; Yoshiie, R.; Ueki, Y.; Naruse, I. Tar and soot generation behaviors from ABS, PC and PE pyrolysis. *J. Mater. Cycles Waste Manage.* **2017**, *19* (2), 682–693.

(50) Bond, T. C. Spectral dependence of visible light absorption by carbonaceous particles emitted from coal combustion. *Geophys. Res. Lett.* **2001**, 28 (21), 4075–4078.