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Morphology and nanostructure of flame-formed soot particles from combustion of typical municipal solid waste

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ABSTRACT

The structural property of soot particles released during the pellet combustion of different municipal solid waste (MSW) was comparatively investigated through high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and X-Ray diffraction (XRD). The results showed under the same combustion condition, soot particles generated from different waste components have the same typical core-shell shape. But soot mass and aggregate morphology were strongly dependent on waste component material. When plastic (textiles) waste was burned, the soot obtained featured a much higher mass and more compact morphology with larger particle size compared to that from burning biomass and kitchen waste. Nanostructural characterization results revealed that paper and kitchen waste possessed the highest graphitization degree in soot, followed by wood waste, textiles, and plastic. Additionally, with the increasing addition of plastic in the mixed waste, the flame temperature was slightly reduced. And the soot was formed a lot and became more disordered in the nanostructure with shorter, more tortuous fringes and larger separation distances, which suggested a higher oxidation tendency. The A_{D1}/A_G ratio had a linear relationship with the fringe separation distance and fringe tortuosity, with R² values of 0.824 and 0.847, respectively.

1. Introduction

The output of municipal solid waste (MSW) is increasing yearly because of China's economic development and fast urbanization [1]. Waste to energy is widely used for the disposal of MSW. However, incomplete combustion of hydrocarbon fuels results in frequent emissions of soot particles [2,3], which is closely related to temperature and oxygen [4]. On one hand, soot aggregates participate in the radiative heat transfer process in the flame, depending on their physicochemical property and morphology [5]. Moreover, soot released into the environment takes an important part of the atmospheric aerosol, and its effect on the climate warming is only second to the well-known CO₂ [6]. On the other hand, soot particles with nano size and large specific areas are fine carriers for highly poisonous substances, such as heavy metals and surface-absorbed polycyclic aromatic hydrocarbons (PAHs), which have adverse effects on the atmospheric environment and human health [7–9]. Also, de novo synthesis of dioxins relates to soot formation in the MSW combustion zone [10,11]. Previous work has revealed that the nanostructural characteristics of soot materials significantly affect their reactivity [12–15], which is crucial to determining toxicity. Therefore, understanding the morphology and nanostructural characteristics of soot particles is crucial for their formation mechanism and emission control.

Numerous investigations have been conducted focusing on the formation, physicochemical features, and reactivity of soot particles derived from the combustion of coal [16], gas [13,17], and liquid fuels [12,18]. But to the author's best knowledge, the understanding of the soot formation and physical characteristics based on the combustion of municipal solid waste is still limited so far. In essence, combustible MSW is a mixture of various biomass-based products (i.e., paper and wood waste), plastics, and kitchen waste [1]. During combustion, soot formation involves highly complex reactions including nucleation,

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condensation, coalescence, surface growth, and oxidation [4], where PAHs are potential precursors. For cellulosic or plastic soot, the formation of initial benzene rings takes place through the Diels-Alder reaction with light olefins produced by the thermal degradation of alkanes [19-21]. William et al. [8] stated that soot particles from biomass solid fuels were formed from small aromatics or large molecules of heavy tar, where and 'H-abstraction-C2H2-addition' (HACA) mechanism take the form as the dominant pathway for further surface growth of the particles throughout the whole process. In their study, soot properties were found to be strongly affected by combustion conditions and fuel properties [8]. In contrast, soot formation during plastic pyrolysis features a similar mechanism but seems to follow a simpler formation route, due to the simple chemical structures of plastics [21]. High-resolution Transmission electron microscopy (HRTEM) combined with other analytical technics permits soot observation at the nanoscale [22]. And the image processing algorithms enable the quantification analysis of the morphology and nanostructure [23]. It reveals that mature soot particles are heterogeneous in particle size ranging between 20 nm and 200 nm [4] and the aggregates are clustered of dozens and hundreds of soot nanoparticles. Trubetskaya et al. [24] analyzed the particulate soot emissions from fast pyrolysis of lignocellulosic compounds and found that soot from lignin content showed a larger particle size than that from cellulose. Weinbruch et al. [25] found the significant size differences of soot primary particles emitted from wood, diesel, and coal sources, as well as the differences in the graphene sheet separation distances. Shemwell and Levendis [26] discovered the yield and size distributions of particulates derived from burning several common plastics were remarkably different, yet not provided more detailed information on the nanostructure. A study by Sawant et al. [27] gave the diameters of soot particles from plastic pyrolysis which mainly concentrated in the range of 50–70 nm. Despite these effects, the above results are obtained based on the different experimental setups, characterization methods, and solid fuels. Therefore, it is very hard to efficiently compare the physical features of soot between these biomass materials and plastics.

To address this knowledge gap, the present work aimed to investigate the effect of common municipal solid waste fractions on the morphological and nanostructural properties of flame-formed soot particles. The experiments were performed in a laboratory-scale combustion setup where a flat-flame burner was applied to generate a stable high-temperature combustion atmosphere. In each trial, the man-made single waste pellet was firstly combusted in the chamber with a temperature of 1073 K to produce sooty flames. Then the soot samples were collected via a thermophoretic sampling method and a quartz plate collection method. Last, HRTEM and X-ray diffraction (XRD) were combinedly used to explore the structure and crystallite characteristics of the soot samples in terms of the particle size, fractal dimension, and fringe characteristics. And Raman spectroscopy was adopted for the

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evaluation of the soot graphitization degree. The new information obtained in this study was helpful in better understanding the nanostructure and reactivity of soot particles from different waste sources.

2. Materials and methods

2.1. Material preparation

In this work, fractions of several common mixed solid wastes, including paper, waste wood, kitchen waste, plastic, and textiles, were selected as experimental samples. Prior to the experiment, all the samples were firstly dried in an oven at 105 °C overnight. After that, paper, waste wood, and kitchen waste were milled into powders with desired diameters less than 250 µm, while plastic and textiles were smashed into small flakes with sizes less than 1 mm [28,29]. The ultimate analysis and proximate analysis of each sample on air-dried basis were given in Table 1. Note that mixture 1 was the mixture of wood and paper (mass ratio: 1:4) with no plastic addition [1]. The mass percentages of plastic added to mixture 1 were set to be 10%, 30%, 50%, 70%, respectively (denoted as Mixtures 2–5). Since kitchen waste would be no longer used for incineration in the future due to China's garbage classification policy, kitchen waste was excluded for the mixtures 1-5. Table 1 showed that these samples differed largely in chemical compositions, especially the share of fixed carbon and volatile matter.

2.2. Experimental setup and analysis methods

The schematic diagram of the laboratory-scale setup used for wastepellet combustion is depicted in Fig. 1. For consistency, approximately 100 mg (\pm 1 mg) of each waste sample was manually pressed into 6 mmdiameter cylindrical pellets. A Hencken burner was used to produce hundreds of flat flames, providing a stable high-temperature atmosphere [30]. The flow rates of methane (fuel gas) and air (oxidant) were set to be 0.6 L/min and 8 L/min, respectively. In theory, the post-combustion gas compositions were 73.4% N₂, 13.9% H₂O, 7.0% CO₂, and 5.6% O₂. The single waste pellet was suspended on two ceramic rods (d = 0.8 mm) and then combusted in the chamber. The temperature of the hot gas stream at the pellet position was approximately 1073 K (\pm 10 K).

Usually, the combustible pellet was firstly heated up to pyrolysis under high-temperature condition; and then, the volatiles released to the gas phase was ignited to further form visible flames after being mixed with surrounding air/oxygen. A similar phenomenon can be seen in other reports [16,30] based on biomass/coal burning, in which the combustion behavior was divided into three distinguished periods as the devolatilization, char oxidation, and ash stage. The whole pelletcombustion process was monitored using a CCD camera at a speed of 30 frames per second. In the stable flame stage [16], soot particles were

Num.	Materials	Proximate analysis (wt% on air dried basis)			Ultimate analysis (wt% on air dried basis)					
		M ^a	A ^b	V ^c	FC^{d}	С	Н	0	Ν	S
1	Paper	1.70	5.60	81.90	10.80	41.10	5.40	43.90	0.10	0.20
2	Waste Wood	1.70	4.40	77.10	16.80	44.10	6.10	41.80	0.15	0.16
3	Kitchen waste	4.50	10.20	64.80	20.50	39.20	6.80	45.20	0.45	0.09
4	Plastic	1.60	2.10	91.50	4.80	59.20	6.00	33.50	0.20	0.56
5	Textiles	0.70	3.20	89.90	6.20	45.60	3.50	40.10	1.20	0.85
6	Mixture 1	1.70	5.30	80.70	12.30	41.85	5.58	43.38	0.11	0.19
7	Mixture 2	1.69	4.98	81.78	11.55	43.59	5.62	42.39	0.12	0.23
8	Mixture 3	1.67	4.34	83.94	10.05	47.06	5.70	40.41	0.14	0.30
9	Mixture 4	1.65	3.70	86.10	8.55	50.53	5.79	38.44	0.16	0.38
10	Mixture 5	1.63	3.06	88.26	7.05	54.00	5.87	36.46	0.17	0.45

^a Moisture.

^b Ash content.

^c Volatile matter.

^d Fixed carbon.



Fig. 1. Main steps of material preparation and schematic diagram of combustion setup.

thermophoretically sampled from the hot soot-laden flames (approximately a height of 10 mm above the pellet) onto a cold copper TEM grid (3 mm diameter, 200 mesh) for HRTEM characterization. The residence time of the micro-grid in flame was set to be approximately 30 ms. In addition, a 90 mm-diameter water-cold quartz glass plate [17], fixed at a height of 50 mm above the pellet, was used to collect enough samples for X-ray diffraction (XRD) and Raman spectroscopy analysis [15]. For each sample, at least three parallel tests were required to ensure the good repeatability and reproducibility of measurements. And standard deviation was calculated based on the measurements.

2.3. Analysis methods

Soot samples on the TEM grid were imaged using the HRTEM technique, and then, the software Image-J was applied to quantify the physical characteristics of soot particles. The morphological properties of soot particles were evaluated by the parameters primary particle size (d_p) and fractal dimension (D_f) , while the nanostructure was characterized by three fringe parameters of graphitic carbon, namely the fringe separation distance (straight-line distance between two adjacent graphene layers), fringe length (size of the carbon layer), and fringe tortuosity (ratio of the fringe length and the endpoint distances). The sampling bias was evaluated and the results (see Fig. S1) indicated that the large enough sample size provided reliable results for determining the particle size and fractal dimension. Hence, at least 700 individual mature soot particles with clear boundaries were selected to obtain the mean particle size (d_p); at least 100 soot aggregates from different locations of the grid were selected to determine the mean particle number per aggregate (N) and the fractal dimension (D_f) of aggregates. Fringe parameters were obtained according to the reported procedures [22]. It was noted that the overlap between the individual particles was not considered in the quantitative measurements and the fringe length less than 0.3 nm, commonly regarded as noise, was also excluded [22]. Apart from HRTEM analysis, X-ray diffraction (XRD) and Raman spectroscopy were used to investigate the crystalline characteristics and graphitization level of the soot samples, respectively.

3. Results and discussion

3.1. Soot collection and flame temperature

The average soot mass (collected on the plate) and typical



Fig. 2. Collected soot mass according to the waste samples.

combustion images (taken at 20s after ignition in the stable flame stage [16]) from burning ten waste samples are shown in Fig. 2. Compared to biomass materials, plastics featured volatiles-dominant combustion with more luminous yellow flames [29], suggesting the presence of higher soot loadings. It was interesting for the mix. 1–5 that the plastic fraction (Stage I) would quickly melt because of a high heating rate, forming a liquid coating on the pellet surface (Stage II). Following closely, biomass and plastic co-combusted at the devolatilization stage, after which the remained biomass char continued the oxidation (Stage III) before reaching the ash stage. Since some volatiles released from fuel pyrolysis may be trapped inside the molten layer, the formation of secondary char probably occurred via interactions between the volatiles and residue char/other volatile species [31].

As shown in Fig. 2, the soot mass varied largely across the waste materials, which was inferred to be caused by the differences in fuel compositions. Previous studies [32,33] revealed that the condensed heavy PAHs act as crucial precursors in particle inception and size/mass growth. PAH growth usually undergoes two reaction routes, one is via the conventional HACA mechanism regarding benzenes as an intermediate [34], while the other is through the polymerization of pyrolysis fragments [8]. The two pathways are interactive and co-construct the growth mechanism of PAHs. A study conducted by Zhou et al. [20] showed that compared to biomass, plastic fractions were more likely to release large molecule species such as PAH from the large organic components via pyrolysis, which accounted for the high soot productions from textiles and plastic in this work. Moreover, the 'ring-ring condensation' interaction probably occurred under such sufficient aromatic species concentration to form larger PAHs [35]. The soot mass from paper fraction was quantitatively comparable to that from kitchen waste, yet both were lower than that from wood waste. A possible reason was that lignin content in biomass with abundant aromatic structures [24] increased the rate of PAH formation, which, in turn, increased the soot-volume fractions in flame. Also, when the plastic blending ratios rose from 10 to 30%, the soot mass showed no significant trend; whereas it increased drastically as the ratio reached 50%; after that, it continued to increase but with a slowing amplitude. This was because the plastic addition enabled the formation of more precursors, which then promoted the soot growth via the HACA mechanism. On the other hand, the portion of oxygen content in the mixtures reduced as the plastic blending ratios increased. For this reason, the oxidative reactions were weakened.

The temperatures at axial heights of 10, 20, 30, and 40 mm above the pellet were measured using a type-K thermocouple to discuss its effect on soot emission. The temperatures were corrected for radiation loss [36]. After each experiment, the soot deposit on the thermocouple

surface was removed by the blue flame. It can be observed from Fig. 3 that the differences in flame temperature are very small, only 0–30 K. Plastic and textiles exhibited slightly lower flame temperatures than other waste fractions. The reason may be that the high soot volume fractions in plastic burning flames increased the soot radiative losses, which resulted in a subtle decrease in temperature. In addition, a slight decrease in flame temperature was found with an increase in plastic addition in the waste mixture. A decreased flame temperature, in turn, led to higher soot concentrations [17]. And therefore, the present observation of the higher soot production from the mixed waste with the addition of plastic may partly be due to a temperature effect. In contrast, the fuel composition is likely a more critical factor influencing the soot features.

3.2. Morphological characteristics

Fig. 4 presents the quantitative results of soot morphology in terms of the fractal dimension and particle size. Generally, tens to hundreds of mature soot particles with approximately spherical shapes were randomly clustered to form the aggregates, which featured various fractal-like morphologies, such as chains, rings, flakes, etc. (see Fig. S2). The fractal dimension (D_f) was extensively used to assess the compactness degree of the soot aggregates [37]. Fig. 4 showed that the mean D_f values of the soot samples mainly lay within the range between 1.5 and 1.9, similar to the values reported in [12]. A larger D_f indicated, for instance, that plastic (~1.87) produced soot particles with more compact morphology in contrast to those generated by other waste fractions, which inclined to exhibit elongated chain-like structures that were more easily attacked by oxygen. It was found that the D_f values were greater than 1.8 for plastic and textile soot, implying a clustercluster collision mode during particle growth [38].

The mean particle size (d_p) of soot samples was ranged from 30.0 to 46.0 nm, as shown in Fig. 4. The d_p values obtained were slightly smaller than those of the particles from waste open burning [15]. On one hand, the higher environmental temperature understudy promoted the cracking of PAHs species and limited their contributions to the surface growth of soot particles; on the other hand, the carbonization and oxidation of the particles were strengthened, thereby resulting in a decrease in particle size. In essence, particle oxidation and aggregate formation with the growth process take place concurrently in flames, and the competition between them determines the size of soot particles. Molecular oxygen is considered the primary contributor to oxidation under fuel-lean conditions [39]; while under fuel-rich conditions, OH plays a more important role. As reported in Ref. [2], large amounts of the oxygenated species released during biomass pyrolysis/combustion could



Fig. 3. Measured flame temperature distribution along with the height of flame centerline for typical waste fractions (a) and mixtures with different blending ratios of plastic (b).



Fig. 4. Particle size and fractal dimension according to the MSW fractions (a) and mixed samples (b); Linear correlation of the particle size with fuel properties (c); Plot of the particle size, fractal dimension and mean particle number per aggregate.

accelerate the oxidative reactions on the soot surface, which is a plausible explanation for the smaller particle size of paper and wood soot than that of plastic soot. In contrast to plastic soot, biomass soot is more susceptible to being oxidized because of the higher specific surface areas. Real-time observation of the oxidation behaviors of soot particles revealed that a decrease in particle size, usually caused by surface oxidation, could break the sphericity of soot particles and then weaken the bridges among the particles [39], which ultimately resulted in the fragmentation of aggregate structures.

In short summary, soot particles from plastic (textiles) exhibited larger values of D_f and d_p compared with the particles from biomass fractions (paper and waste wood) and kitchen waste. In addition, upon increasing the plastic blending ratio in the mixture from 10 to 70%, the inception and surface growth of soot particles were strengthened, viewing from an increase of the particle size from 31 nm to 41 nm. Further, the linear correlation coefficients between d_p and fuel compositions were calculated to explore the dependence of soot morphology on fuel chemistry. The results in Fig. 4c showed that the particle size was negatively correlated with the O/C ratio, with an R² value of 0.811. This revealed that high oxygen content in solid fuels suppressed the soot formation with smaller-sized particles. The phenomenon was similar to what has been observed for diesel soot [40]. Notably, more fixed carbon can be released into the flaming environment at the devolatilization

stage of plastic combustion compared to biomass combustion, due to the overlap between volatile and char combustion [29]; with this, soot concentrations inside the flame were therefore increased. For the plastic addition ratios of 10, 30, 50, and 70%, the average fractal dimension values were 1.65, 1.69, 1.81, and 1.80, respectively. Clearly, larger soot particles were formed with more compact morphology. Last, a 3-dimensional plot of the three morphological parameters (N, d_p , and D_f) is presented in Fig. 4d. An evident grouping was identified in the graph because of the differences in fuel compositions, where the morphological characteristics of kitchen waste soot were closer to that of biomass soot.

3.3. Fringe analysis

Fig. 5 shows presentative soot images taken at a resolution of 45, $000 \times$. It is observed that regardless of the waste type, the particles exhibited the same 'onion-like' shape. Close inspection of the nano-structure demonstrated that inner cores (highlighted by arrows) were almost amorphous while fringes in the outer shell, in recognizable shapes of undulations or twisting, constituted the majority of particle volume. Compared with plastic soot, paper and kitchen waste soot seemed to show tighter packed graphene layers and fewer core numbers. The formation of these multi-core structures was attributed to the fast,



Fig. 5. Typical images of soot nanostructures.

random coalescence of nuclei before growing into a bigger particle, which meanwhile led to the different straight-line distances between these cores. On the other hand, the presence of cores could make the particles more reactive because of large amounts of short carbon streaks [23] with high reactivity, as observed in HRTEM images. Around the particles, edge defects were found in the shape of armchairs or zigzags, suggesting the disordered regions in soot. It is reported that O₂ molecules are easily bounded in these dislocations and vacancies [41], where dioxins are potentially formed [11]. In addition, the overlap between the particles, which can be easily observed, implied that the agglomeration process was ongoing.

Fig. 6a provides the baseline-removed XRD spectra of soot samples in the angle range of 10-60°, where two broad peaks can be identified at $\sim 25^{\circ}$ (002 peaks) and $\sim 44^{\circ}$ (100 peaks) respectively. All soot samples showed lower values of the diffraction angle $(2\theta_{002})$ than graphitic carbon (26.8°), suggesting the nanostructure in high disorder [42]. This was in line with the observations in HRTEM images. Notably, the additional reflections corresponding to the inorganic matter of potassium chloride (KCl) were evidently detected in the XRD spectra of wood soot. These alkali species were vaporized into the flame during combustion and then participated in soot formation, taking as an inhibitor to soot growth [24]. Wang et al. [43] found that an increase of gaseous KCl concentrations in the reaction zone had a negligible effect on the nucleation of the soot particles. However, the further size growth was suppressed because the neutralization of multi-charged particles lowered the coagulation rates. In addition, the interlayer distance (d_{002}) between PAHs from the XRD spectra was determined using Bragg's law [42], as presented in Table 6d. It was found that the values of d_{002} were slightly lower for the soot produced by paper and kitchen waste, indicating a higher graphite-like nanostructure compared to the soot from the other waste fractions. With the plastic addition in the mixtures rising from 10 to 70%, the d₀₀₂ became larger from 3.44 to 3.63 Å, unveiling an increasing trend in oxidation reactivity.

For the purpose of quantitative analyses in the nanostructure, the fringe length, separation distance, and tortuosity were measured. As shown in Fig. 6b, paper soot exhibited the largest value of 1.56 nm among the samples, followed by wood waste, kitchen waste, and plastics (textiles), corresponding to the values of 1.50 nm, 1.44 nm, and 1.2 nm, respectively. A smaller fringe length implies a higher population of

reactive carbon atoms in the edge sites [44]. And the reactivity of these carbon atoms is reported to be 100–1000 times greater than that of the atoms in the basal planes [45]. In contrast to the fringe length, the separation distance in Fig. 6b featured an inverse pattern, where plastic soot attained the largest value of 0.44 nm among the samples. The soot reactivity increases with larger separation distances between carbon layers for a reason that oxygen molecules are more likely to access the edge positions because of more loosely arranged nanostructures [44]. Compared with the parameter d_{002} which reflected a bulk average level, the separation distance was determined by local measurements of HRTEM images. Therefore, the two parameters were basically consistent in the trend but possessed not equal values because of the differences in techniques.

Regarding the tortuosity (τ) derived as the ratio of fringe length and endpoint distances, the τ values in the soot samples were in the range of 1.11–1.145. Large tortuosity implies the presence of more curved graphene segments in soot, and from a structural viewpoint, these graphene layers are more easily to be broken under strain [46,47]. It is seen that most of the fringes, independent of the waste type, were nearly flat ($\tau <$ 1.15) or present a low degree of tortuosity (1.15 < τ < 1.35). The fringes with low tortuosity reflect the presence of a maximum of one or two pentagonal rings in the PAH [48], while the formation of highly tortuous fringes is linked to the incorporation of 5- or 7- membered rings in PAHs. Similarly, rarely fringe tortuosity was larger than 1.35 for these soot samples.

Overall, with the increasing plastic addition in the mixed waste, the less graphitic nanostructures developed with an increase in the fringe tortuosity and separation distance and a decrease in the fringe length. To some extent, the slightly lower flame temperatures in the cases of plastic addition inhibited the graphitization of the soot and made them be less dense in the nanostructure and more easily to be oxidized. As can be seen, the three parameters all changed not significantly at low plastic blending ratios, yet varied largely when the ratio exceeded 30%. For instance, the tortuosity increased by 3.0%, 12.2%, and 18.3% for the soot samples from the mixtures with plastic blending ratios of 30, 50, 70%, respectively. This trend was similar to that observed for the particle size and fractal dimension. From another respective, since the plastic fraction would form a liquid coating on the pellet surface during the co-combustion of biomass and plastic fractions, it was likely that



Fig. 6. XRD spectra (a); Fringe quantification according to the MSW fractions (b) and mixed samples (c) with standard deviations less than 10%; and d₀₀₂ from XRD spectra and distributions of fringe tortuosity (d).

some volatiles derived from waste pyrolysis were trapped inside the molten plastic layer. Especially for the mixtures with high plastic blending ratios, the combustion chemical characteristics tended to be dominated by the plastic fraction. Hence, the physical properties of the soot, such as particle size and fringe characteristics, became closer to that of plastic soot with the increasing addition of plastic.

3.4. Raman spectroscopy

The raw Raman curve obtained was fitted into five bands commonly known as D1 (\sim 1360 cm⁻¹), D2 (\sim 1620 cm⁻¹), D3 (\sim 1500 cm⁻¹), D4 (\sim 1180 cm⁻¹), and G (\sim 1580 cm⁻¹) [49], as presented in Fig. 7a, b. In this work, the peak area of D bands was compared to the peak area of G band to evaluate the graphitization degree of the soot samples.

Herein, the G band is commonly associated with the ideal graphitic structure in soot, while D1 and D3 bands are ascribed to the presence of

disordered graphitic lattice and amorphous carbon respectively [49]. Fig. 7c presents the variations in the values of A_{D1}/A_G , A_{D3}/A_G , and A_{D4}/A_G A_G ratios for ten soot samples. The area ratio between D1 and G indicates the graphitic crystalline structure of soot, and smaller A_{D1}/A_G manifests the increasing structural order [17,50,51]. Specifically, the values of A_{D1}/A_{C} were 1.59 for paper soot, 1.73 for wood soot, 1.64 for kitchen waste soot, 2.05 for plastic soot, and 1.82 for textile soot, suggesting that plastic was the most structurally disordered sample. This also unveiled that the soot from plastic-containing materials (plastic and textiles) featured a high fraction of amorphous structures and edge defects, which provided available active surfaces for fast oxidation. The finding agreed well with the fringe analysis. In addition, the graphitization degree of soot gradually decreased with the increasing plastic addition in the mixtures, manifesting the more disordered nanostructures in crystallite arrangement. The A_{D3}/A_G ratio reflected the portion of the amorphous carbon in the soot and its variation showed a similar trend to



Fig. 7. Raw Raman data (a); Fitting of the Raman spectra with a five-band approach (more seen in Fig. S3) (b); Peak area ratios for the ten soot samples (c); correlation of the A_{D1}/A_G ratio with three fringe parameters (d-e); and correlation between the fringe parameters (f).

 A_{D1}/A_G ratio [49]. However, no large differences were discovered in A_{D4}/A_G ratios across the soot samples, which were related to C—C and C=C stretch such as ionic impurities or polyene-like structures [49].

Raman and fringe results were contradictory to the analysis based on the morphological data in section 3.2. For example, paper soot exhibited a much smaller particle size (30.6 nm) and a lower fractal dimension value (1.58) compared with plastic soot ($d_p = 45.1 \text{ nm}, D_f = 1.87$). Paper soot was expected to be more reactive because of higher specific surface area and less compact aggregate morphology. However, the fringe separation distance and tortuosity of plastic soot were greater than that of the former, suggesting a higher reactivity [44-48,52]. A comparison of the A_{D1}/A_G ratio versus three fringe parameters for all samples was further given in Fig. 7(d-e). Overall, as the A_{D1}/A_G ratio increased, both the fringe separation distance and tortuosity increased, whereas the fringe length decreased. The A_{D1}/A_G ratio owned strong linearity with the fringe separation distance and fringe tortuosity, with R² values of 0.824 and 0.847 respectively. In contrast, the linear correlation was less evident between the A_{D1}/A_G ratio and the fringe length only with an R^2 value of 0.752. This implied that soot particles with more disordered nanostructure were likely to exhibit looser aligned carbon layers and highly curved fringes. Hence, XRD and Raman spectral analysis verified the HRTEM observation and fringe analysis, unveiling that the reactivity

of the soot samples seemed to be more correlated with their nanostructures, and less with the particle size and fractal properties of aggregates [44,46,47]. That also implied that the oxidation took place more likely from the inside of particles than from the outside, in agreement with the observation by Sediako et al. [39].

In addition, the relationship between the three fringe parameters was also explored, as plotted in Fig. 7f. It revealed that fringes with large size and low tortuosity tended to show a smaller separation distance between the graphene layers, which could be attributed to greater packing factors they owned [18].

4. Conclusions

The present work mainly characterized the particle size, fractal dimension, and nanostructure of soot particles from burning a range of municipal solid waste fractions, namely paper, waste wood, kitchen waste, plastic, and textiles. Besides, the effect of plastic addition in the mixed waste on soot structural properties was comparatively investigated. Some main findings can be obtained as follows:

The observation from HRTEM images showed under the same combustion condition, soot particles from different waste components exhibited the same typical core-shell shape. However, the collected soot mass and aggregate morphology varied depending on the type of waste materials, where plastic produced soot particles with larger particle size and more compact structure compared to the soot from biomass materials and kitchen waste. Subsequent qualification of the nanostructure by fringe analysis revealed the order of graphitization degree from high to low: paper \approx kitchen waste > wood waste > textiles \approx plastic. This indicated that biomass (waste wood and paper) and kitchen waste soot exhibited more stable nanostructures than plastic soot, which, in turn, tended to show a higher oxidation tendency because of more loosely stacked layers. Besides those, with the increasing addition of plastic in the mixtures, soot particles were formed a lot and their nanostructures became more disordered with shorter fringe length, higher fringe tortuosity, and larger fringe separation distances. This implied an increase in the oxidation reactivity of soot. The Raman and XRD results confirmed the HRTEM observation and fringe analysis. Further, the A_{D1}/ A_G ratio was found to correlate linearly with the fringe tortuosity and fringe separation distance, with R² values of 0.847 and 0.824, respectively. It was also found that due to the greater packing factor, the smallsized fringes with low tortuosity were likely to possess smaller separation distances.

Overall, the results in the present work revealed a significant influence of waste compositions on the physical properties of flame-formed soot particles and a high correlation between the fringe characteristics and graphitization degree. The detailed statistics could provide valuable information for the modeling of soot nanostructures and heat transfer in the furnace.

CRediT authorship contribution statement

Junjie He: Conceptualization, Investigation, Project administration, Writing – original draft. Lianming Li: Formal analysis. Hong Feng: Data curation. Mingnan Jiang: Validation, Methodology. Jiayu Li: Writing – review & editing. Linlin Guo: Software. Jie Zhang: Software. Pingheng Zhang: Validation, Methodology. Jun Gong: Validation, Methodology. Qunxing Huang: Funding acquisition, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2022.107269.

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