Characterization and reactivity of soot from fast pyrolysis of lignocellulosic compounds and monolignols

Anna Trubetskaya^{a,*}, Avery Brown^b, Geoffrey A. Tompsett^b, Michael T. Timko^b, Jens Kling^c, Markus Broström^a, Mogens Larsen Andersen^d, Kentaro Umeki^e

^a Thermochemical Energy Conversion Laboratory, Umeå University, 90187 Umeå, Sweden

^b Chemical Engineering Department, Worcester Polytechnic Institute, 01609 Worcester, MA, USA

^c Center for Nanoscience, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

^d Department of Food Science, University of Copenhagen, Rolighedsvej 26, 1958 Copenhagen, Denmark

^e Energy Science Division, Luleå University of Technology, 97187 Luleå, Sweden

HIGHLIGHTS

- Biomass soot samples were generated at fast pyrolysis conditions in a DTF at 1250 °C.
- The reactivity of soot was determined in 40 vol.% CO₂ gasification by TGA.
- The most reactive was cellulose soot with the largest separation distance.
- The least reactive CH₃OH extracted lignin soot had the smallest separation distance.
- The particle size and radical concentration of soot influenced the reactivity less.

ARTICLE INFO

Keywords:

Fast pyrolysis

Lignocellulosic compounds and monolignols

Soot

Reactivity

Nanostructure

ABSTRACT

This study presents the effect of lignocellulosic compounds and monolignols on the yield, nanostructure and reactivity of soot generated at 1250 °C in a drop tube furnace. The structure of soot was characterized by electron microscopy techniques, Raman spectroscopy and electron spin resonance spectroscopy. The CO₂ reactivity of soot was investigated by thermogravimetric analysis. Soot from cellulose was more reactive than soot produced from extractives, lignin and monolignols. Soot reactivity was correlated with the separation distances between adjacent graphene layers, as measured using transmission electron microscopy. Particle size, free radical concentration, differences in a degree of curvature and multi-core structures influenced the soot reactivity less than the interlayer separation distances. Soot yield was correlated with the lignin content of the feedstock. The selection of the extraction solvent had a strong influence on the soot reactivity. The Soxhlet extraction of softwood and wheat straw lignin soot using methanol decreased the soot reactivity, whereas acetone extraction had only a modest effect.

1. Introduction

Biomass gasification utilizes biomass in an efficient and sustainable way for a wide variety of applications such as heat, electricity, chemicals and transport fuels [1]. During pulverized biomass firing and gasification, particles first undergo rapid drying and devolatilization, leading to the formation of char and volatiles. The volatile compounds are the primary precursors of tar and coke (or soot) at low and high temperatures, respectively [2]. At temperatures less than 1000 °C, secondary reactions of volatiles produce mainly tars and small amounts of soot; at higher temperatures (1100–1400 °C) these reactions produce

soot and almost no tars [3,4]. The high soot yields often obtained in a high-temperature entrained flow gasifier require extensive gas cleaning and can necessitate periodic plant shut down for soot removal [5]. Soot particle size plays an important role, with larger soot particles building up more rapidly than smaller ones and requiring greater effort to remove. Likewise, the intrinsic oxidation activity of biomass soot determines the severity of conditions required to recover from soot accumulation problems. Reducing soot formation combined with production of highly active soot therefore increases overall process efficiency and improves the economic feasibility and reliability of gasification plants.

* Corresponding author.

E-mail address: anna.trubetskaya@umu.se (A. Trubetskaya).

The formation of soot produced by combustion of gaseous fuels has been described in the literature. A common feature of many soot formation models is initial formation of highly reactive radicals that combine to form larger polyaromatic hydrocarbons (PAH) which then undergo condensation, carbon addition, and hydrogen abstraction reactions to form soot [6]. Several types of species may act as potential precursors, leading to soot particle inception via formation of polyacetylene or polyene intermediates. The importance of C_2H_2 in thermal decomposition reactions was emphasized by Berthelot and Lewis [7,8], whereas another hypothesis suggests the carbon formation from acetylene through its simultaneous polymerization and dehydrogenation [9]. In biomass gasification, PAHs are mainly formed from phenoxy radicals produced by decomposition of lignin and extractive compounds, producing cyclopentadienyl radicals, PAHs, and eventually soot [10–12]. Previous investigations showed that low lignin-containing wheat straw generated less soot than pinewood with high content of extractives and lignin [13]. Lignin is mainly composed of 3 different monolignol monomers, namely p-coumaryl, coniferyl and sinapyl alcohols [14,15]. These monolignols are incorporated into lignin aromatic cores in the form of p-hydroxyphenyl (H), guaiacyl (G) and 2,6-dimethylphenol (S) units, respectively. Different types of lignin (softwood, hardwood, herbaceous biomass) contain various amounts of methoxy groups depending on how much of each of the three monolignols has been incorporated into the lignin macromolecules [16]. Atmospheric aerosols produced from biomass combustion contain considerable oxygenated species, including components associated with levoglucosan and other anhydrosugars derived from cellulose pyrolysis [17–19]. Lastly, the high concentration of resin acids in wood may increase soot yields in addition to increasing the formation of PAH precursors [20,21].

In addition to improving gasifier operations, understanding soot characteristics is important for the optimization of gasification processes because low soot yield and complete conversion of soot maximize syngas yields [4]. The chemical and structural variance of biomass make it difficult to identify how the soot yield and composition are affected by specific operating parameters and feedstock composition to optimize entrained-flow gasifiers. The heat treatment temperature and gasification agent have a strong influence on soot formation and conversion [22]. Steam gasification leads to complete conversion of soot at temperatures greater than 1300 °C, whereas at temperatures less than 1300 °C soot formation is determined by O_2 concentration, to which it is inversely proportional [23]. Soot oxidation reactivity and particle size are important and interrelated considerations. In general, larger graphene layer planes, larger crystallites, and concentrically orientated crystallites decrease soot reactivity [24]. The nanostructure of soot was previously characterized by high-resolution transmission electron microscopy (HRTEM), and the results indicated large differences in soot nanostructure and reactivity with increasing heat treatment temperature [22,25]. Knauer et al. [25] demonstrated the combined use of temperature-programmed oxidation (TPO), Raman microspectroscopy and HRTEM for soot characterization. Previous results from fast pyrolysis indicate that pinewood soot generated at 1250 °C had a broader particle size range (27.2–263 nm) than either beechwood soot (33.2–102 nm) or wheat straw soot (11.5–165.3 nm); likewise, pinewood soot contained mainly multi-core structures, indicating a significant influence of feedstock on the soot nanostructure [26]. The origin of the feedstock effect on soot composition and reactivity is not clear. Volatiles deposited on the soot particles are known to increase soot reactivity in entrained-flow gasification [27]. Accordingly, X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) were carried out to gain information on the surface composition of the carbonaceous soot and alkali metals deposited on the soot surface. However, XPS and EELS showed that the differences in organic composition of pinewood and wheat straw soot are small [26].

To reduce aerosol emissions, gasification and wood stove industries require basic data to understand how soot yields and particle properties

are correlated with fuel composition and operating conditions. The initial fuel structure affects aerosol transformation processes (coagulation, fragmentation, etc.) and thus, the aerosol particle size, nanostructure, and viscosity [28]. Lignin rich feedstocks present challenges for gas cleaning units of wood stoves, and require optimization based on differences in feedstock composition. Knowledge about influence of lignocellulosic compounds on the soot particle size and nanostructure is important to prevent outlet blockages and to ensure steady syngas production. Many soot formation studies are based on combustion of coal [29], liquid [30,31], or gaseous hydrocarbons [32], but only a few have focused on biomass soot. Compared to soot produced from hydrocarbon fuels, soot from biomass pyrolysis contains greater concentrations of oxygen functional groups and more readily adsorbs primary, secondary and tertiary pyrolysis products such as organic acids, aldehydes and phenolics [33]. To address this knowledge gap, soot from pyrolysis of lignocellulosic compounds and monolignols was produced in a drop tube reactor at 1250 °C. The resulting soot materials were then characterized for yield, structure, and reactivity. The specific objectives of this study were to: (1) identify relationships between biomass feedstock characteristics and soot yield and (2) identify relationships between soot characteristics and reactivity. The results of this study provide a clear basis for understanding the effects of biomass selection on soot production and potential impacts on process design and operation.

2. Materials and methods

The effects of lignin type, extractives (resin acids), holocelluloses and monolignols on the soot yields and composition were studied in a drop tube reactor. Soot samples were generated at 1250 °C in a drop tube reactor. Two types of organosolv lignin made from softwood and wheat straw (purity > 94%) were provided by BOC Sciences. Cellulose Avicel® (purity > 99.9%) and xylan from beechwood (purity > 90%) were supplied by Sigma-Aldrich. The purity of xylan was increased from 90% to 96.6% by a three step procedure involving strong alkali treatment, bleaching, and acetylation. Monolignols (2,6-dimethylphenol, guaiacol, and p-hydroxyphenol) were acquired from Sigma-Aldrich and used without purification.

Lignocellulosic compounds were reacted in the drop tube furnace (DTF) at 1250 °C, as described in detail by Trubetskaya et al. [13]. The high heating rate and short residence times obtained with the drop tube furnace simulate the conditions in entrained-flow gasifiers. Based on previous work [26], operation at 1250 °C was selected to maximize the soot yield. The reactor consists of an alumina tube (internal diameter: 54 mm, heated length: 1.06 m) heated by four heating elements with independent temperature control. Gas flow rate into the reactor was regulated by mass flow controllers (EL-FLOW® Select, Bronkhorst High-Tech B.V.). The feeding system was based on a syringe pump that displaces a bed of fuel that falls directly into the high temperature zone in the reactor through a water-cooled probe. The syringe pump was vibrated to ensure stable feeding of the fuel particles, as described by Bach-Oller et al. [34]. In each experiments, ≈5 g of biomass were fed to the reactor at a rate of 0.2 g min⁻¹. Both primary (0.18 l min⁻¹ measured at 20 °C and 101.3 kPa) and secondary (4.8 l min⁻¹ measured at 20 °C and 101.3 kPa) feed gases were N_2 . The residence time of fuel particles was estimated to be about 1 s, taking into account density changes during pyrolysis [35]. Both the samples (extractives, monolignols) and the syringe pump feeder were kept in a freezer at -18 °C overnight and in each experiment to ensure that extractives and monolignols entered the reactor at a consistent feeding rate. Reaction products were separated into coarse particles (mainly char and fly ashes), fine particles (mainly soot and ash aerosols), permanent gases, and tars. Coarse particles were captured in a cyclone (cut size 2.5 μm). Soot particles exited the cyclone and were collected on a grade QM-A quartz filter with a diameter of 50 mm (Whatman, GE Healthcare Life Science).

Table 1

Proximate and ultimate analysis of cellulose, xylan from beechwood (hemicellulose), extractives, lignin from softwood and lignin from wheat straw and monolignols (hydroquinone; guaiacol; 2,6-dimethylphenol).

	Cellulose	Xylan beechwood	Lignin softwood	Lignin wheat straw	Extractives	H	G	D
<i>Proximate and ultimate analysis (% on dry basis)</i>								
Moisture ^a	6	6	4.1	3.8	0.5	1	6	0.2
Ash (550 °C)	0.3	2	1.5	4.3	0.4	0.2	0.3	0.2
Volatiles	94.9	81.6	67.3	66.3	99.8	100	100	100
HHV ^b	18	14	26.4	26.7	35	25.5	29	26.3
LHV ^b	16.1	12.2	24.9	25.2	33	24.1	27.3	24.7
C	42.3	39.6	59.9	61.1	73.2	65.2	66.7	62.1
H	6.3	6	5.5	5.6	8.9	5.2	6.1	6.4
O	50.9	52.3	31.9	28.2	17.5	29.4	27	31.3
N	0.3	0.2	1.2	0.8	–	–	–	–

H: Hydroquinone; G: Guaiacol; D: 2,6-Dimethylphenol.

^a wt.% (as received).

^b In MJ kg^{−1}.

Soxhlet extraction using either acetone and methanol as the solvent was performed on soot samples from pyrolysis of both lignin types by extracting 0.1 g of the solid placed within a 100 ml Soxhlet apparatus for 12 h. The reactivity of soot in CO₂ gasification was investigated by thermogravimetric analysis. The structure of soot samples was characterized by transmission electron microscopy and Raman spectroscopy. The concentrations and types of free radicals remaining in the soot matrix after pyrolysis (at the decay stage) were determined using electron spin resonance spectroscopy.

2.1. Original fuel characterization

The ultimate and proximate analysis of the lignocellulosic compounds was carried out at University of Agder and at Celignis Limited. The results are shown in Table 1 and supplementary Table S-1. The ash content of lignocellulosic compounds was determined using a standard ash test at 550 °C, according to the procedure described in DIN EN 14775. The ash composition was calculated on the dry basis. Lignin from wheat straw was rich in Na, Si and Fe (Na: 2.2 wt.%; Si: 1.3 wt.%; Fe: 0.5 wt.%), whereas lignin from softwood contained a smaller fraction of Na (1 wt.%). Xylan from beechwood after purification contained low amounts of Na and Ca (Na: 1.5 wt.%; Ca: 0.4 wt.%).

2.2. Soot analysis

2.2.1. Thermogravimetric analysis

The reactivity of soot was analyzed by exposing samples to 40% volume fraction CO₂ (14 cm³ min^{−1} of CO₂ and 21 cm³ min^{−1} of N₂ at 20 °C and 101.3 kPa) in a thermogravimetric instrument Q5000 (TA Instrument, USA) by loading 4 mg of sample in an Al₂O₃ crucible and heating from 30 to 1200 °C in CO₂ at a constant heating rate of 10 °C min^{−1}.

2.2.2. Soot pretreatment for microscopy

Prior to microscopy, soot samples were kept at 350 °C for 4 h in a thermogravimetric instrument to reduce the volatile content. Samples were dry dispersed on a lacey carbon copper grid.

2.2.3. Transmission electron microscopy

Soot morphology was studied using a FEI Titan transmission electron microscope operated at 120 keV.

2.2.4. Particle size distribution analysis using TEM

The particle size of soot samples was estimated manually from TEM images using the ImageJ software [36,37]. Only clearly visible primary particles were selected for accurate analysis. The data were assessed to establish particle size distributions. For size analysis, soot particles were

assumed spherical. Particle size analysis was conducted on 200 particles at each operating condition. Standard deviation was calculated for curvature, fiber length (see definition below) and separation distance of graphene layers as described in the [supplemental material \(Eq. \(1\)\)](#). The curvature of a single graphene sheet was calculated as shown in the [supplemental material \(Eq. \(2\)\)](#).

2.2.5. Raman spectroscopy

Raman spectra of the soot samples were obtained using a XploRa Raman microscope (Horiba Scientific, USA) operating with a 532 nm laser line at a power of 10 mW. 2 s scan time was used with an accumulation of 100 scans. An 1800-line grating was used with an aperture of 100 μm and slit width of 300 μm. Laser light was focused on the sample using a 100 magnification lens from Olympus. The collected spectra are presented here as averages of three experiments. Raman spectra were averaged, subtracted and then normalized by the most intense band. Deconvolution of the Raman spectra were conducted using the peak fit pro tool in the OriginPro software (OriginLab, USA) by combination of six Gaussian-shaped bands (D5, D4, D3, D2, D1, and G) following Sadezky et al. [38]. The assignment of Raman bands was conducted as shown in the [supplemental material \(Section S-2.3\)](#). The mean crystal size in the *a*-direction (*L_a*), that is valid for the laser wavelength from 400 to 700 nm, is given by [39]:

$$L_a = \frac{C_0 + C_1 \lambda_L}{A_{D1}/A_G} \quad (1)$$

with the fitting constants *C*₀ = −12.6 nm and *C*₁ = 0.033.

2.2.6. Electron spin resonance spectroscopy

The concentration and type of free radicals formed in soot during the decay stage of pyrolysis at 1250 °C were studied using the electron spin resonance (ESR). ESR spectra were recorded on a Magnetech MS-5000 ESR spectrometer (Freiberg Instruments, Germany). Samples were placed in a closed-bottom quartz capillary tube with a wall thickness of 0.75 mm and an outer diameter of 5 mm. The measurements were carried out at room temperature with a microwave power of 10 mW, and a modulation width of 0.2 mT, sweep width of 6200 G, sweep time of 1 min, magnetic field modulation of 100 kHz. A solid sample of CuSO₄·5H₂O of known weight was used as a standard for calculating the number of spins in the sample signals. To minimize bias introduced by radical recombination, ESR was performed less than 24 h after soot generation and compared with results 7 months later. The radical concentration showed negligible differences (<5%) over a period of 7 months, and was therefore judged to be independent of storage time [40]. More details are provided in the [supplemental material \(Section S-6.1\)](#).

(a) Cellulose soot

(b) Hemicellulose soot

(c) Extractives soot

(d) Monolignol soot

(e) Softwood lignin soot

(f) Wheat straw lignin soot

Fig. 1. (a)–(f) DTG curves of soot from pyrolysis of cellulose, hemicellulose, extractives, monolignols (guaiacol, hydroquinone, 2,6-dimethylphenol), softwood lignin, wheat straw lignin, and Soxhlet extracted softwood and wheat straw lignin soot using acetone and methanol as solvents reacted in 40% volume fraction CO_2 + 60% volume fraction N_2 .

3. Results

3.1. Soot reactivity

Fig. 1 shows differential weight loss curves (DTG) for the gasification of soot samples (40% volume fraction CO_2). The relative importance of external diffusion on the overall soot gasification in the TG experiments was evaluated by comparison of the observed maximal reaction rate (r_{max} , % min^{-1}) with the calculated diffusion rate (r_{diff} , % min^{-1}) of CO_2 in the supplemental material (Eq. (5)). The calculated $r_{\text{max}}/r_{\text{diff}}$ ratio showed that the gasification reaction in the TG analysis was influenced only by chemical kinetic limitations, as shown in the supplemental material (Table S-3). The DTG curves show both a single broad peak and a double peak in CO_2 gasification, indicating a heterogeneous soot mixture with respect to the composition and particle size as suggested by Russell et al. [41] and a combination of two constituents with different reactivity as observed by Abian et al. [42]. The CO_2 gasification of most soot samples took place at nearly the same temperature range from 850 to 920 °C while soot from monolignols and Soxhlet extracted softwood and wheat straw lignin soot using methanol as a solvent reacted at higher temperatures. The reactivities of soot from lignocellulosic compounds were nearly identical with that of beechwood and wheat straw soot samples [26]. The maximum reaction rate of soot from monolignols in the CO_2 gasification was about 100 °C greater than lignocellulosic soot samples. The cellulose, hemicellulose and monolignol (hydroquinone) soot exhibited a double peak, indicating the presence of a carbon constituent with similar reactivity to other soot samples and a less reactive carbon structure approaching the reactivity of commercial graphite, as shown in the supplemental material (Fig. S-4). The elemental analysis of soot samples in the supplemental material (Figs. S-2 and S-3) showed that carbon was the most abundant element observed on all soot samples (≈ 98 –99.5%). Instead, differences in a carbon structure probably led to the formation of a double peak in CO_2 gasification of cellulose, hemicellulose and hydroquinone soot samples, as shown later. The maximal reaction rate of softwood and wheat straw lignin soot after Soxhlet extraction with acetone changed only slightly, as shown in the supplemental material (Table S-4). In contrast, the results showed that the Soxhlet extraction using methanol decreased the reactivity of both lignin soot samples. The maximum reaction rate of methanol extracted lignin soot was about 250 °C greater than for the other biomasses, and thus, the methanol extracted softwood and wheat straw soot were clearly less reactive. Interestingly, the mass loss of organic compounds after Soxhlet extraction of softwood and wheat straw lignin soot using both acetone and methanol as solvents was in the range 0.01–0.02 wt.%. The present results show that differences in carbon chemistry of soot samples may also influence the soot reactivity, and will be discussed below.

3.2. Soot yields

Soot yields from pyrolysis of lignocellulosic compounds at 1250 °C were similar to soot yields of monolignols, as shown in Fig. 2. Low soot yields were obtained from pyrolysis of cellulose and hemicellulose, consistent with their lack of aromatic rings [17–19]. Lignin and extractives are major compounds in biomass that enhance soot formation at high heating rates and high temperatures. The highest soot yield was obtained from pyrolysis of wheat straw lignin and quantitatively comparable with the soot yield of hydroquinone. The soot yields from wood and herbaceous biomass pyrolysis were lower than the soot yields from lignin and extractives due to the high content of holocelluloses in original pinewood, beechwood and wheat straw, as shown in the supplemental material (Table S-2). The high concentrations of lignin and resin acids in wood increased formation of PAH precursors and thus, increased soot yields from the wheat straw pyrolysis. Therefore, Fig. 2 suggests that soot yields are correlated with the lignin content of the feedstock. The effect of ash on lignin soot yields was investigated.

Fig. 2. The total yield of soot from pyrolysis of lignocellulosic compounds, monolignols and biomass at 1250 °C shown in wt.% relative to the original compound (g g^{-1} on dry basis).

Previous results showed that the alkali rich wheat straw soot yield was almost twice as low as that of softwood lignin soot, indicating the catalytic effect of alkali on the soot formation [43]. However, the yield of low ash containing softwood lignin soot was less than that of Na^+ rich wheat straw lignin soot in the present study. This indicated that the ash content has less influence on the soot yield than the organic content of lignin.

Soot yields obtained from pyrolysis of the monolignols (hydroquinone, 2,6-dimethylphenol, and guaiacol) were quantified to understand the effects of the organic content of lignin on soot production in more detail. Fig. 2 shows that the soot yields from the individual monolignols were typically less than that observed for lignin, with the exception being hydroquinone. Radicals generated from the primary pyrolysis reactions of hydroxyquinone are stabilized by the delocalized unpaired electrons and are not highly reactive with other molecular species [44]. Phenoxyl radicals can undergo radical–radical recombination reactions to form PAHs and possibly soot at temperatures greater than 600 °C [45,46]. Phenyl radicals can decompose via hydrogen loss to yield benzyne, which subsequently reacts in a retro-Diels–Alder fashion to acetylene and diacetylene, and initiates soot formation [43].

3.3. Raman spectroscopy

Raman spectroscopy was carried out to examine primary differences in the carbon structure of soot samples. First-order Raman spectra (800 – 2000 cm^{-1}) of soot obtained by laser excitation wavelength ($\lambda_0 = 532 \text{ nm}$) are shown in the supplemental material (Figs. S-11 and S-12). All soot samples showed common features in their Raman spectra, including the G and D1 bands, which are located in the range of 1578 – 1587 cm^{-1} and 1330 – 1343 cm^{-1} ; however, some differences were observed. The width of the G bands of both lignin soot samples narrowed after solvent extraction, indicating an increase in structural order and a decrease in soot chemical heterogeneity. This finding parallels the reactivity changes previously mentioned for extracted lignin samples and may pertain to differences in organic content of the fuel. The percentage area of D1 band in guaiacol and non-treated lignin soot samples was smaller than in soot from holocelluloses and syringol, implying a lack of symmetry in soot polyaromatic structure [47]. Moreover, the D1 band in soot from monolignols, non-treated lignin and extracted lignin soot was broader than soot obtained from other feedstocks ($\text{HWHM} = 74$ – 82 cm^{-1}), showing that the crystalline size was smaller than in other soot samples. The calculated integrated peak area ratio ($A_{\text{D1}}/A_{\text{G}}$) in the supplemental material (Table S-5) showed

that the wheat straw lignin soot contained the lowest amount of carboxylates (0.3) compared to other soot samples.

Aside from these notable differences, the Raman spectra indicate minor differences in the carbon structure of soot obtained from gasification of lignocellulosic compounds and monolignols. Based on the estimated A_{D1}/A_G ratios, all samples exhibited a common structure of amorphous carbon and nano-crystalline graphite, as discussed by Ferrari and Robertson [48]. The average extension of graphene layers (L_a) in the lignocellulosic compounds and monolignol soot (1.6–2.2 nm) was less than those in the biomass soot (2.1–2.6 nm). The size of one aromatic ring is 0.25 nm [49], and therefore, the size of PAHs in the lignocellulosic compound and monolignol soot is equivalent to approximately 6–9 aromatic rings. Moreover, the average extension of graphene stacks (L_c) in all soot samples was quantitatively similar to that of commercial carbon black (Printex XE2: 2.5 nm; Vulcan XC72: 2 nm; Printex L: 1.4 nm) and less than typical of graphite (5.6 nm) [50]. These results therefore clearly establish that the soot obtained from biomass high-temperature pyrolysis is irregular and only partially crystalline, an important result for understanding reactivity.

3.4. Particle size analysis

Fig. 3 contains plots of the size distributions of primary soot particles plotted as fractions of the number of particles in each size range. The calculated geometric mean diameters varied from 34.6 to 49.3 nm, and were similar to the values reported for biomass smoke (30–50 nm) [51,52] and for the soot obtained from pyrolysis of wood and wheat straw (30.8–77.7 nm) [26]. The differences in particle size of soot samples were noticeable. The geometric mean particle diameters of both lignin soot samples were similar to one another, whereas the particle size of guaiacol and cellulose soot was significantly less in comparison to other soot samples. This indicates an influence of feedstock on soot formation, confirming the previous results of Arora et al. [53]. They reported that under smoldering conditions, the nature of lignocellulosic materials (wood, cow dung, mustard stalks) influenced the formation of soot particles, leading to various particle size distributions. Soxhlet extraction did not influence the soot particle size. No large differences in the particle clustering were determined among soot samples, suggesting that soot clustering is determined primarily by flow and mixing considerations, rather than primary chemistry.

The exceptions to the observation of spherical soot particles were hemicellulose and guaiacol soot samples, as shown in the [supplemental material](#) (Fig. S-8). TEM images of hemicellulose and guaiacol soot showed clustering of individual particles without clearly defined boundaries. The particle size of hemicellulose soot was not possible to determine due to their non-spherical shape. The hemicellulose soot particles appeared to be densely fused together with more irregular edges compared to other soot samples. Although guaiacol soot particles were less spherical than other soot samples, the particle size was possible to determine using a fraction of spherical particles.

3.5. Nanostructure

The nanostructure of the soot from lignocellulosic compounds and monolignols was studied by TEM, as shown in Figs. 4 and 5. In all cases, the soot particles appear as agglomerates. All primary soot particles exhibited a core-shell structure, with both single and multiple cores. The primary particles in cellulose and monolignol soot consisted of mainly single core particles with a large core, whereas hemicellulose and extractives soot contained a mixture of single and multi-core structures. The primary particles in softwood and wheat straw lignin soot exhibit primarily multiple core structures. Compared to the cores of lignin soot, the multiple cores of hemicellulose and extractives soot particles were located closer to each other, possibly due to particle coalescence at an earlier stage. Liati et al. [22] related the multi-core

structure to early phase soot formation consisting of nuclei coalescence and further development as a single particle.

The multi-core structure of softwood and wheat straw lignin soot reflects formation by coalescence of several smaller particles, with the particle concentration governing the rate of the coalescence process [54]. The observation of multi-core structures in soot derived from lignin is therefore consistent with the greater soot yield obtained from this feed compared to the others included in this study. The shell nanostructure of smaller and larger particles seems to be similar to one another, as shown in Figs. 4 and 5 and in the [supplemental material](#) (Figs. S-9 and S-10). TEM analysis indicates that both the fine and large primary soot particles consisted of graphene sections, which grow circumferentially from the particle core. The graphitic shell provides a clear fringe contrast from the stacking of the graphene layers, which is less obvious for larger particles due to their thickness ([supplementary Fig. S-10\(b\)](#)). This limitation also applied to the core of the larger particles for which characterization was not possible.

Figs. 4 and 5 show that the particle cores consist mainly of randomly oriented and curved graphene layers. Su et al. [55] investigated the oxidation reactivity of soot formed in diesel-engine exhaust, and suggested that the soot core is a highly reactive area due to the presence of defects on the surface being further-functionalized with volatile groups. They hypothesized that non-6-membered rings may produce highly localized olefinic structures in the soot core that are prone to oxidation. As seen in Fig. 4(f)–(e), the core size of soot particles decreased by 2–3 times and the lattice fringes became more visible in the soot shell due to the Soxhlet extraction. Extraction impacts the nanostructure of lignin soot. The wheat lignin soot particles produced after Soxhlet extraction with methanol formed a mixture of single and multi-core structures. The cores of extracted wheat straw lignin soot particles are located so close to each other that no clear transition between the cores can be observed. The number of multiple cores decreased after methanol extraction.

All soot samples exhibited a well-ordered graphitic structure except the cellulose and hemicellulose soot. Two different carbon structures were observed in cellulose, hemicellulose, and hydroquinone soot. The straight graphene layers of the neighboring particles appear to be merged, forming a continuous surface with a large number of crystallites, as shown in Figs. 4 and 5. Another type of carbon structure with more curved graphene layers was indicated on the outer shells of soot particles in Fig. 5(c) and [supplementary Fig. S-10\(d\)](#).

The particle size analysis of hemicellulose soot could be not carried out because the outer particle shells were covered by a carbon structure that made the particle edges irregularly-shaped. Therefore, hemicellulose soot particles could not be assumed spherical. The graphene segments of the extractives, lignin, methanol extracted lignin and monolignol soot samples were well ordered and flat with the smaller curvature of an average particle size (0.9–0.98; flat graphene ≈ 1 [56]). Table 2 summarizes the characteristics of different soot samples with regards to single or/and multiple cores, curvature and separation distance of graphene layers. The mean separation distance of cellulose soot graphene segments (0.4 nm) was significantly greater than that of graphite (0.335 nm), indicating the lowest degree of crystallinity [22]. The mean separation distance of methanol extracted wheat straw lignin soot was similar to that of pinewood soot (0.33 nm) [26]. In addition, the methanol extracted wheat straw lignin soot consisted of the longest graphene segments (4.5 nm) indicating the formation of structure that is more similar to graphite. The previous study showed that the Soxhlet extraction using benzene as a solvent led to the smaller separation distance of graphene layers and larger stacking height (L_c) of crystallites with the increasing heat treatment temperature, probably due to the Orlov type reactions, involving hydrogenolysis of aromatic rings [57].

3.6. Electron spin resonance spectroscopy

Free radicals present on biomass soot may influence soot activity;

Fig. 3. Particle size distributions of soot from cellulose, extractives, softwood lignin, wheat straw lignin, hydroquinone, 2,6-dimethylphenol, guaiacol, and methanol extracted soot from wheat straw lignin.

Fig. 4. TEM images of soot generated from lignocellulosic compounds. In Figures (a) and (f) the distance between graphene layers was measured in the enlarged image (red rectangle). In all Figures the arrows indicate the soot particle cores. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accordingly, ESR was used to probe the presence of free radicals in the soot samples. Fig. 6(a) shows that the ESR spectra of all soot samples generated at 1250 °C gave ESR spectra with g -values = 2.0035–2.0039. This indicates the formation of carbon-centered radicals containing oxygen. Radicals with similar g -values (2.0035–2.0037) have been observed in soot samples from wood combustion [58]. The experimental ESR-spectra were analyzed by fitting to simulated spectra to identify the individual radical species. A model based on a mixture of two radical species was found to adequately fit the experimental ESR spectra [40].

The ESR signals were symmetric without hyperfine structure and with nearly Lorentzian line-shapes, as shown in the supplemental material (Figs. S-13–S-15). The fitted ESR spectra of the soot samples had line widths (LW) in the range 2.5–4.3 G and g -values in the range 2.0031–2.0040. Atiku et al. [59] identified the composition of free radicals deposited on soot particles generated in a multi-fuel stove by selective-ion monitoring mass spectrometry. These radicals were 1–4 ring PAHs substituted with (mainly methyl) short-chain alkyl groups and carbon-centered radicals with an oxygen atom, which may also be formed in the present study based on the similar g -values and line

Fig. 5. TEM images of soot generated from monolignols (guaiacol, hydroquinone, 2,6-dimethylphenol). In Figures (a)/(c), the distance between graphene layers is enlarged using the red rectangle. In Figures (a)–(b)/(d), the arrows show the number of soot particle cores. In Figure (c) the bridging of two hydroquinone soot particles is enlarged using the red rectangle (the image was transformed into the binary form). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Summary of soot characteristics (fiber length, core, curvature, separation distance) prepared from cellulose, hemicellulose, extractives, softwood lignin, wheat straw lignin, methanol extracted wheat straw lignin, guaiacol hydroquinone, and 2,6-dimethylphenol.

Soot	Fiber length	Curvature ^b	$d_{sep}^{a,b}$	Core ^{c,d}
	nm		nm	
Cellulose	2.5 ± 1.8	0.9 ± 0.01	0.4 ± 0.02	mostly s
Hemicellulose	2.3 ± 0.9	0.9 ± 0.13	0.36 ± 0.01	m & s
Extractives	3.7 ± 2.6	0.96 ± 0.03	0.38 ± 0.03	m & s
Softwood lignin	3.1 ± 1.4	0.97 ± 0.02	0.38 ± 0.02	mostly m
Wheat straw lignin	3.8 ± 1.6	0.97 ± 0.04	0.37 ± 0.02	mostly m
Extracted wheat straw lignin	4.5 ± 3.5	0.95 ± 0.04	0.34 ± 0.01	m & s
Guaiacol	3.7 ± 2.6	0.98 ± 0.02	0.36 ± 0.01	mostly s
Hydroquinone	2.5 ± 1.2	0.91 ± 0.05	0.35 ± 0.01	mostly s
2,6-dimethylphenol	3.6 ± 1.8	0.93 ± 0.05	0.36 ± 0.02	mostly s

^{c,d} s – single core and m – multiple cores.

^a Separation distance.

^b Calculation of mean curvature and d_{sep} of graphene layers measured only on crystallites.

widths in the range 1.5–2.5 G. However, similar g-values and line widths have also been observed by grafting gallic acid onto graphene oxide, which led to the formation of highly stable phenoxyl radicals with g-value equal to 2.0040 and $LW = 3.5$ G [60], which suggest the radicals could also be phenolic derived *o*- and *p*-semiquinone structures.

Fig. 6(b) shows that the radical concentrations in soot from lignin, extractives, and monolignols were greater than the radical concentrations in soot from holocelluloses; this observation may be consistent

with the aromatic components present in lignin promoting formation of PAH precursors and a greater mixture of free radicals [59]. The homolytic cleavage of aryl-ether linkages in lignin is a major reaction to form carbon-centered and oxygen-centered polyaromatic radicals which are trapped in the polyaromatic matrix of soot and char, and stabilized by the delocalized unpaired electrons at the decay stage [61,62]. In comparison with lignin and monolignol pyrolysis, the radical concentrations in soot from cellulose and hemicellulose were low.

Fig. 6. (a) g-values, and (b) ESR radical concentration (spins $\times 10^{19} \text{ g}^{-1}$) of soot generated from lignocellulosic compounds and monolignols.

The major products from cellulose pyrolysis such as levoglucosan and other light oxygenates do not have unpaired electrons, whereas the high levels of unpaired electrons were detected over the polyaromatic ring structure of original lignin and its chars formed in pyrolysis [63,64].

The spin concentrations of soot samples range between $1.8 \cdot 10^{19}$ and $7 \cdot 10^{19}$ spins g^{-1} , as shown in Fig. 6(b). Soot produced by pyrolysis of softwood lignin contained less radicals than wheat straw lignin soot. Interestingly, the radical concentration in soot from guaiacol, which is a major unit in softwood lignin, was also less than the radical concentration in soot from hydroquinone that represents a major p-hydroxyphenyl unit in wheat straw lignin. Thus, the higher alkali content in the wheat straw lignin was probably less important for determining radical concentration than differences in lignin linkages, consistent with the soot yield data reported here and confirming previous results of Bährle et al. [64].

As seen in the supplemental material (Fig. S-14), methanol and acetone Soxhlet extraction of both lignin soot samples decreased the radical concentration of the obtained soot, indicating that soluble organic fractions play a role in radical formation. An additional ESR resonance centered at 322.5 mT with the g-value (2.07) was detected for both extracted lignin soot samples. The relative intensities of ESR signal varied significantly among extracted lignin soot samples. The broad and asymmetric signal was attributed to strongly interacting electrons, which are delocalized over the conducting domains of soot carbonaceous matrix [65]. The asymmetry of the resonance line indicates high electrical conductivity of soot particles [66]. The g-value of soot samples (2.07) was greater than that of graphite (2.05) [67], but it was comparable with the value typically found for carbon nanomaterials [68]. All biomass derived soot samples showed a broad ESR signal with the g-value (2.07) similarly to soot samples from lignocellulosic compounds, as shown in the supplemental material (Fig. S-16). The carbon-centered radicals with an oxygen atom ($g = 2.0026\text{--}2.0037$) were not observed in biomass derived soot.

4. Discussion

Thermogravimetric experiments demonstrated significant differences in the intrinsic reactivity of lignocellulosic compounds, monolignols and Soxhlet extracted soot samples towards CO_2 . In principle, the reactivity of soot from lignocellulosic compounds and monolignols can be affected by differences in particle size, presence of free radicals, carbon chemistry, and soot nanostructures. The particle size of extractives soot (38 nm) was less than that of extracted wheat straw lignin soot (40.9 nm), whereas the reaction rate of the native soot was 95

times greater than that of extracted lignin soot, as shown in supplementary Table S-4. The particle size of extracted wheat straw lignin soot was similar to that of hydroquinone soot and 7.9 nm greater than the particle size of guaiacol soot, whereas the reactivity of extracted wheat straw lignin soot was 11 times greater than the reactivity of both guaiacol and hydroquinone soot samples. Raman spectroscopy results showed that all soot samples exhibited a structure resembling carbon black based on the A_{D1}/A_G ratios (2–2.4). This indicates that neither particle size nor general features of carbon chemistry had a strong influence on the observed differences in soot reactivity.

Previous work has shown that increasing free radical concentrations increases biochar oxidation reactivity [69,70]. In the present study, the radical concentrations in soot from extractives and lignin were greater than the radical concentrations in soot from cellulose and hemicellulose, whereas the reactivity of extractives and both lignin samples was lower than that of holocelluloses soot. Methanol and acetone extraction decreased the radical concentrations in both lignin soot samples. Thus, based on radical concentration alone it might be expected that the high radical concentration in non-treated lignin soot led to higher reactivity than in the extracted soot samples. However, the reactivities of non-treated and acetone extracted lignin soot were similar, whereas the methanol extracted lignin soot was 30 times less reactive than other two samples. This indicates that the differences in radical concentrations had at most a secondary influence on the soot reactivity.

The nanostructure of soot from pyrolysis of lignocellulosic compounds and monolignols was the main factor influencing the reactivity during CO_2 gasification. The differences in nanostructure of soot samples were significant, consistent with the previous results of soot prepared by pyrolysis of acetylene and benzene, where the formation conditions have significant influence on the soot nanostructure [31]. Because the soot samples produced in the present study were formed at consistent conditions, the differences in nanostructure can instead be attributed to feedstock differences. The TEM analysis showed that the mean separation distance of extracted lignin soot graphene segments (0.34 nm) was similar to graphite (0.335 nm), whereas the reactivity of extracted wheat straw lignin soot was significantly less than that of other soot samples. The mean separation distance of cellulose soot (0.4 nm) was significantly greater than that of other soot samples, leading to the highest reactivity. Moreover, the small graphene layers of cellulose soot (2.5 nm) could enhance CO_2 gasification reactivity, as shown in Fig. 7. In conclusion, the length and separation distance of soot graphene segments were dominant structural characteristics influencing soot reactivity.

The DTG curves of cellulose, hemicellulose and hydroquinone soot showed a double peak in CO_2 gasification indicating a heterogeneous

Fig. 7. (a) The integrated peak area ratio (D1/G) derived from the Raman spectroscopic data. The outlier point (960 °C, D1/G = 1.9) characterizes the integrated peak area ratio of guaiacol soot, and (b) separation distance of graphene layers (d_{sep}) are shown over the relevant peak temperature of the TG experiment in 40% volume fraction CO_2 .

soot mixture. The TEM analysis of cellulose, hemicellulose, and hydroquinone soot indicated the formation of two carbon structures. The less reactive carbon phase with the long and flat graphene segments approached the reactivity of graphite, as shown in the supplemental material (Fig. S-4), whereas the more reactive carbon phase with the short and highly curved graphene segments behaves similarly to carbon black, as reported by Abian et al. [42]. The present results show that the high content of extractives and lignin in pinewood and beechwood could also lead to the lower reactivity of woody soot, despite the fact that the original wood is a low-ash containing biomass.

Previous results showed that increasing the concentration of lignin and extractives in the wood increases the formation of PAH precursors and thus, increases soot yields [13]. In the present study, lower soot yields were obtained from pyrolysis of cellulose and hemicellulose, indicating a major influence of lignin and extractives on the soot yield. The soot yield obtained from softwood lignin pyrolysis was less than that of wheat straw lignin which emphasized the importance of lignin composition on the soot yield. The high concentration of hydroxy groups in wheat straw lignin enhanced soot formation during high-temperature pyrolysis. The soot yields obtained from pyrolysis of lignin and extractives were greater than the soot yields from pyrolysis of woody and herbaceous biomass probably due to the presence of inorganic compounds in original biomass which tend to decrease the soot yields [71]. This shows that the lignocellulosic compositional differences affect both the soot yield and reactivity.

5. Conclusion

This work presents yield and reactivity data for soot produced in a drop-tube furnace operating at consistent conditions and using a range of biomass feeds and model compounds. The present results indicate that both lignin samples from softwood and wheat straw provide greater soot yields than holocelluloses and extractives, consistent with the aromatic content of lignin. Moreover, soot reactivity decreases with increasing feedstock lignin content. Tests with representative monolignols suggest that hydroquinone – rather than 2,6-dimethylphenol and guaiacol – plays an especially important role in soot formation.

Thermogravimetric analysis results showed that the soot reactivity towards CO_2 depends mainly on the soot nanostructure, as determined by TEM and Raman spectroscopy, and less on the particle size and radical concentrations. The effect of residual alkali was less important than the effect of lignin content. In particular, cellulose and hemicellulose soot consisted of graphene sheets spaced at approximately 0.4 nm, whereas the methanol extracted lignin-derived soot was approximately 0.34 nm. The methanol extracted soot particles with a smaller separation distances and flat graphene segments formed a

graphitic structure which is significantly less reactive than the other soot samples emphasizing the role of methanol Soxhlet extraction on the soot nanostructure and CO_2 reactivity. The non-treated and acetone extracted softwood and wheat straw lignin soot samples showed a similar reactivity. Moreover, Raman spectroscopy showed a trend between the measured D1/G ratio and reactivity, again suggestive of the importance of graphene layer spacing and size. Similarly, qualitative differences in the reactivity of some soot samples – for example the observation of multiple reaction regimes for cellulose, hemicellulose, and hydroquinone soot – was correlated with qualitative differences in their nanostructures.

These results provide a clear basis for understanding the effects of feedstock on soot formation, showing that increasing the lignin content of the feedstock increases the soot yield while decreasing the soot reactivity – both potentially negatively impacting gasifier operation and emissions. Differences in reactivity can be ascribed in part to differences in soot nanostructure. Based on this work, selection of gasification feedstocks should emphasize biomass with low lignin content.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science Foundation (Grant EEC-1605916), Kempe Foundation, the Swedish Energy Agency, the Swedish strategic research program Bio4Energy, Carl-Fredrik von Horns, Björn Wahlströms, and Jernkontoret Stiftelsen. The A.P. Møller and Chastine Mc-Kinney Møller Foundation is acknowledged for their contribution toward the establishment of the Center for Electron Nanoscopy in the Technical University of Denmark. Gerrit Surup from University of Agder is acknowledged for assisting with the ultimate and proximate analysis.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2017.12.068>.

References

- [1] Mhilu CF. Modeling Performance of High-Temperature Biomass Gasification Process. *Chem Eng J* 2012;2012:1–13.
- [2] Zhang Y, Kajitani S, Ashizawa M, Oki Y. Tar destruction and coke formation during rapid pyrolysis and gasification of biomass in a drop-tube furnace. *Fuel* 2010;89:302–9.
- [3] Svensson H, Tunå P, Hultberg C, Brandin J. Modeling of soot formation during partial oxidation of producer gas. *Fuel* 2013;106:271–8.
- [4] Septien S, Valin S, Peyrot M, Dupont C, Salvador S. Characterization of char and soot from millimetric wood particles pyrolysis in a drop tube reactor between 800 °C and 1400 °C. *Fuel* 2014;121:216–24.

- [5] Göktepe B, Umeki K, Gebart R. Does distance among biomass particles affect soot formation in an entrained flow gasification process? *Fuel Process Tech* 2016;141:99–105.
- [6] Warnatz J, Maas U, Dibble RW. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation. Springer; 2006.
- [7] Berthelot MBE. Theorie des corps pyrogenes. *Ann Chim Phys* 1866;9:469–80.
- [8] Lewes VB. The action of heat upon ethylene. *Proc Roy Soc* 1894;55:90–108.
- [9] Keller A, Kovacs R, Homann KH. Large molecules, radicals, ions, and small soot particles in fuel-rich hydrocarbon flames. Part IV: Large polycyclic aromatic hydrocarbons and their radicals in a fuel-rich benzene-oxygen flame. *Phys Chem Chem Phys* 2000;2:1667–75.
- [10] Ross AB, Junyapoon S, Jones JM, Williams A, Bartle KD. A study of different soots using pyrolysis-GC-MS and comparison with solvent extractable material. *J Anal Appl Pyrol* 2005;74:494–501.
- [11] Nowakowska M, Herbinet O, Dufour A, Glaude PA. Detailed kinetic study of anisole pyrolysis and oxidation to understand tar formation during biomass combustion and gasification. *Combust Flame* 2014;161:1474–88.
- [12] Williams A, Jones JM, Ma L, Pourkashanian M. Pollutants from the combustion of solid biomass fuels. *Prog Energy Combust Sci* 2012;38:113–37.
- [13] Trubetskaya A, Jensen PA, Jensen JD, Llamas Garcia AD, Umeki K, Glarborg P. Effect of fast pyrolysis conditions on biomass solid residues at high temperatures. *Fuel Process Technol* 2016;143:118–29.
- [14] Boerjan W, Ralph J, Baucher M. Lignin biosynthesis. *Ann Rev Plant Biol* 2003;54:519–46.
- [15] Ragauskas AJ, Beckman GT, Biddy MJ, Chandra R, Chen F, Davis MF, et al. Lignin valorization: improving lignin processing in the biorefinery. *Science* 2014;344(6185):709–20.
- [16] Xu C, Arancon RAD, Labidi J, Luque R. Lignin depolymerisation strategies: towards valuable chemicals and fuels. *Chem Soc Rev* 2014;43:7485–500.
- [17] Shin EJ, Nimlos MR, Evans RJ. The formation of aromatics from the gas-phase pyrolysis of stigmaterol: kinetics. *Fuel* 2001;80(12):1681–7.
- [18] Vasilou AK, Kim JH, Ormond TK, Piech KM, Urness KN, Scheer AM, et al. Biomass pyrolysis: Thermal decomposition mechanisms of furfural and benzaldehyde. *J Chem Phys* 2013;139(10):1–10.
- [19] Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MP, et al. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos Environ* 1999;33:173–82.
- [20] Rogge WF, Mazurek MA, Hildemann LM, Cass GR, Simoneit BRT. Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. *Atmos Environ* 1993;27(A):1309–30.
- [21] Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of Emissions from Air Pollution Sources. 3. C₁-C₂₉ Organic Compounds from Fireplace Combustion of Wood. *Environ Sci Technol* 2001;35:1716–28.
- [22] Liati A, Eggenschwiler PD, Schreiber D, Zelenay V, Ammann M. Variations in diesel soot reactivity along the exhaust after-treatment system, based on the morphology and nanostructure of primary soot particles. *Combust Flame* 2013;160(3):671–81.
- [23] Chhiti Y, Peyrot M, Salvador S. Soot formation and oxidation during bio-oil gasification: experiments and modeling. *J Energy Chem* 2013;22:701–9.
- [24] Müller JO, Frank B, Jentoft RE, Schlögl R, Su DS. The oxidation of soot particulate in the presence of NO₂. *Catal Today* 2012;191(1):106–11.
- [25] Knauer M, Schuster ME, Su D, Schlögl R, Niessner R, Ivleva NP. Soot Structure and Reactivity Analysis by Raman Microspectroscopy, Temperature-Programmed Oxidation, and High-Resolution Transmission Electron Microscopy. *J Phys Chem A* 2009;113:13871–80.
- [26] Trubetskaya A, Jensen PA, Jensen AD, Garcia Llamas AD, Umeki K, Gardini D, et al. Effects of several types of biomass fuels on the yield, nanostructure and reactivity of soot from fast pyrolysis at high temperatures. *Appl Energy* 2016;171:468–82.
- [27] Choi KH, Korai Y, Mochida I. Combustion properties of particulate matter in diesel engine exhaust. *Combust Flame* 2004;137:255–60.
- [28] Wiinikka H. High temperature aerosol formation and emission minimisation during combustion of wood pellets PhD thesis Luleå University of Technology; 2005.
- [29] Le Manquais K, Snape C, Barker J, McRobbie I. TGA and Drop Tube Furnace Investigation of Alkali and Alkaline Earth Metal Compounds as Coal Combustion Additives. *Energy Fuels* 2012;26(3):1531–9.
- [30] Vander Wal RL, Tomasek AJ. Soot oxidation: dependence upon initial nanostructure. *Combust Flame* 2003;134(1–2):1–9.
- [31] Vander Wal RL, Tomasek AJ. Soot nanostructure: dependence upon synthesis conditions. *Combust Flame* 2004;136(1–2):129–40.
- [32] Roth K. Soot formation during the production of syngas from the partial oxidation of diesel fuel PhD thesis Ruhr University of Bochum; 2006.
- [33] Fitzpatrick EM, Ross AB, Bates J, Andrews G, Jones JM, Phylaktou H, et al. Emission of Oxygenated Species from the Combustion of Pinewood and its Relation to Soot Formation. *ICHEME* 2007;85(B5):430–40.
- [34] Bach-Oller A, Kirtania K, Furusjö E, Umeki K. Co-gasification of black liquor and pyrolysis oil at high temperature: Part 1. Fate of alkali elements. *Fuel* 2017;202:46–55.
- [35] Umeki K, Kirtania K, Chen L, Bhattacharya S. Fuel Particle Conversion of Pulverized Biomass during Pyrolysis in an Entrained Flow Reactor. *Ind Eng Chem Res* 2012;51:13973–9.
- [36] Rasband WS. Image J. Bethesda (MD): U.S. National Institutes of Health. <<http://imagej.nih.gov/ij/>>.
- [37] Cenker E, Bruneaux G, Dreier T, Schulz C. Determination of small soot particles in the presence of large ones from time-resolved laser-induced incandescence. *Appl Phys B* 2015;118:169–83.
- [38] Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U. Raman spectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. *Carbon* 2005;43:1731–42.
- [39] Matthews MJ, Pimenta MA, Dresselhaus G. Origin of dispersive effects of the Raman D band in carbon materials. *Phys Rev B* 1999;59(10):R6585–8.
- [40] Trubetskaya A, Jensen PA, Jensen AD, Glarborg P, Larsen F, Hofmann, Andersen M, Larsen. Characterization of free radicals by electron spin resonance spectroscopy in biochars from pyrolysis at high heating rates and at high temperatures. *Biomass Bioenergy* 2016;94:117–29.
- [41] Russell NV, Beeley TJ, Man CK, Gibbins JR, Williamson J. Development of TG measurements of intrinsic char combustion reactivity for industrial and research purposes. *Fuel Process Tech* 1998;57(2):113–30.
- [42] Abian M, Jensen AD, Glarborg P, Alzueta MU. Soot Reactivity in Conventional Combustion and Oxy-fuel Combustion Environments. *Energy Fuels* 2012;26(8):5337–44.
- [43] Hemberger P, da Silva G, Trevitt AJ, Gerber T, Bodi A. Are the three hydroxyphenyl radical isomers created equal? – The role of the phenoxy radical. *Phys Chem Chem Phys* 2015;17:30076–83.
- [44] Dellinger B, Lomnicki S, Khachatryan L, Maskos Z, Hall RW, Adoukpe J, et al. Formation and stabilization of persistent free radicals. *Proc Combust Inst* 2007;31(1):521–8.
- [45] Hucknall KJ. Chemistry of hydrocarbon combustion. Chapman and Hall; 1985.
- [46] Mulholland JA, Lu M, Kim DH. Pyrolytic growth of polycyclic aromatic hydrocarbons by cyclopentadienyl moieties. *Proc Combust Inst* 2000;28:2593–9.
- [47] Smith MW, Dallmeyer I, Johnson TJ, Brauer CS, McEwen JS, Espinal JF, et al. Structural analysis of char by Raman spectroscopy: Improving band assignments through computational calculations from first principles. *Carbon* 2016;100:678–92.
- [48] Ferrari AC, Robertson J. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Phil Trans Roy Soc Lond* 2004;362:2477–512.
- [49] Hayashida K, Nagaoka S, Ishitani H. Growth and oxidation of graphitic crystallites in soot particles within a laminar diffusion flame. *Fuel* 2014;128:148–54.
- [50] Jawhari T, Roid A, Casado J. Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon* 1995;33(11):1561–5.
- [51] Chakrabarty RK, Moosmüller H, Garro MA, Arnott WP, Walker J, Susott RA, et al. Emissions from the laboratory combustion of wildland fuels: Particle morphology and size. *J Geophys Res* 2006;111(D7):1–16.
- [52] Sachdeva K, Attri AK. Morphological characterization of carbonaceous aggregates in soot and free fall aerosol samples. *Atmos Environ* 2008;42(5):1025–34.
- [53] Arora P, Jain S. Morphological characteristics of particles emitted from combustion of different fuels in improved and traditional cookstoves. *J Aerosol Sci* 2015;82:13–23.
- [54] Lee KO, Cole R, Sekar R, Kang J, Bae C, Zhu J. Detailed Characterization of Morphology and Dimensions of Diesel Particulates via Thermophoretic Sampling. *SAE Tech Pap* 2001:1–10.
- [55] Su DS, Müller JO, Jentoft RE, Rothe D, Jacob E, Schlögl R. Fullerene-like soot from EURO-IV diesel engine: consequences for catalytic automotive pollution control. *Top Catal* 2004;30(31):241–5.
- [56] Müller JO, Su DS, Wild U, Schlögl R. Bulk and surface structural investigations of diesel engine soot and carbon black. *Phys Chem Chem Phys* 2007;9:4018–25.
- [57] Kinney CR, Nunn RC, Walker PL. Carbonization of Anthracene and Graphitization of Anthracene Carbons. *Ind Eng Chem* 1957;49(5):880–4.
- [58] Lomnicki SM. EPRs Formation/Emission from Waste Burning. *Austin Environ Sci* 2017;2(2):1–5.
- [59] Atiku FA, Mitchell EJS, Lea-Langton AR, Jones JM, Williams A, Bartle KD. The Impact of Fuel Properties on the Composition of Soot Produced by the Combustion of Residential Solid Fuels in a Domestic Stove. *Fuel Process Tech* 2016;151:117–25.
- [60] Stathi P, Gournis D, Deligiannakis Y, Rudolf P. Stabilization of Phenolic Radicals on Graphene Oxide: An XPS and EPR Study. *Langmuir* 2015;31:10508–16.
- [61] Britt PF, Buchanan AC, Cooney MJ, Martineau DR. Flash Vacuum Pyrolysis of Methoxy-Substituted Lignin Model Compounds. *J Org Chem* 2000;65:1376–89.
- [62] Kawamoto H, Ryoritani M, Saka S. Different pyrolytic cleavage mechanisms of β-ether bond depending on the side-chain structure of lignin dimers. *A Anal Appl Pyrol* 2008;81:88–94.
- [63] Ponomarev AV. Radiolysis of lignin: Prospective mechanism of high-temperature decomposition. *Rad Phys Chem* 2017;141:160–7.
- [64] Bährle C, Custodis V, Jeschke G, van Bokhoven JA, Vogel F. In situ Observation of Radicals and Molecular Products During Lignin Pyrolysis. *ChemSusChem* 2014;7:2022–9.
- [65] Chipara M, Zaleski JM, Hui D, Du C, Pan N. Electron spin resonance on carbon nanotubes-polymer. *J Polym Sci Part B* 2005;43:3406–12.
- [66] Corzilius B, Dinse KP, Hata K, Haluska M, Skakalova V, Roth S. SWNT probed by multi-frequency EPR and nonresonant microwave absorption. *Phys Stat Sol* 2008;245(10):2251–4.
- [67] Matsubara K, Tsuzuku T, Sugihara K. Electron spin resonance in graphite. *Phys Rev B* 1991;44(21):845–51.
- [68] Corzilius B. Electromagnetic properties of single-walled carbon nanotubes investigated by microwave absorption PhD thesis Technical University of Darmstadt; 2008.
- [69] Brown R. Biochar production technology. In: Lehmann J, editor. Biochar for environmental management. Earthscan; 2009.
- [70] Bourke J, Manley-Harris M, Fushimi C, Dowaki K, Nunoura T, Antal MJ. Do all charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. *Ind Eng Chem Res* 2007;46(18):5954–67.
- [71] Mul G, Kapteijn F, Moulijn JA. Drift analysis of surface oxygen complexes on soot formed by metal oxides. *ACS Div Fuel Chem* 1996;41(1):230–4.