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# Effects of Lignocellulosic Compounds on the Yield, Nanostructure and Reactivity of Soot from Fast Pyrolysis at High Temperatures

**Anna Trubetskaya<sup>1\*</sup>, Markus Broström<sup>1</sup>, Jens Kling<sup>2</sup>, Avery Brown<sup>3</sup>, Michael T. Timko, Geoffrey Tompsett<sup>3</sup>, Kentaro Umeki<sup>4</sup>**

<sup>1</sup> *Thermochemical Energy Conversion Laboratory, Umeå University, 90187 Umeå, Sweden*

<sup>2</sup> *Center for Nanoscopy, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*

<sup>3</sup> *Chemical Engineering Department, Worcester Polytechnic Institute, 01609 Worcester, MA, USA*

<sup>4</sup> *Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden*

\* *anna.trubetskaya@umu.se*

## **Abstract**

Gasification offers the utilization of biomass to a wide variety of applications such as heat, electricity, chemicals and transport fuels in an efficient and sustainable manner. High soot yields in the high-temperature entrained flow gasification lead to intensive gas cleaning and can cause a possible plant shut down. The reduction of soot formation increases the overall production system efficiency and improves the economic feasibility and reliability of the gasification plant. Soot from biomass pyrolysis contains greater inherent oxygen functionalities than hydrocarbons soot and adsorbs primary, secondary and tertiary pyrolysis products such as organic acids, aldehydes and phenolics [1]. In this study, therefore, the impacts of lignocellulosic compounds and monolignols (syringol, guaiacol, p-hydroxyphenol) on the yield and characteristics of soot were investigated at 1250°C in a drop tube reactor. The specific objectives of this study were to: (1) obtain knowledge about lignocellulosic compounds and monolignols influence on the yield, nanostructure, composition, and reactivity of soot during high-temperature gasification, (2) understand the influence of Soxhlet extraction on the soot reactivity and characteristics, and (3) determine the reaction conditions and fuel composition which minimize soot formation leading to the efficient operation of high-temperature gasification process.

## **Methodology**

The effects of lignin type, extractives (resin acids), holocelluloses and monolignols on the soot yields and composition were studied in a drop tube reactor. The lignocellulosic compounds were reacted in the drop tube reactor (DTF) at 1250°C using a 1.06 m-long reactor tube. The reactor tube was also replaced with a 2.12 m-long tube to study the influence of residence time on the free radical concentration in the lignin soot matrix. Reaction products were separated into coarse particles (mainly char and fly ashes), fine particles (mainly soot and ash aerosols), permanent gases, and tars. Soot particles passing the cyclone (cut size 2.5 μm) were captured from the product gas flow by a grade QM-A quartz filter with a diameter of 50 mm (Whatman, GE Healthcare Life Science). In the present study, Soxhlet extraction using acetone and methanol as a solvent was performed on soot samples from pyrolysis of both lignin types by loading 0.1 g in a 100 ml Soxhlet apparatus for 12 h.

The reactivity of soot in CO<sub>2</sub> 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.

## Results and Discussion

### Soot yields

The present results indicated that soot yields from pyrolysis of lignin from softwood and extractives at 1250°C with the residence time of 0.17 s were similar as shown in Figure 1.

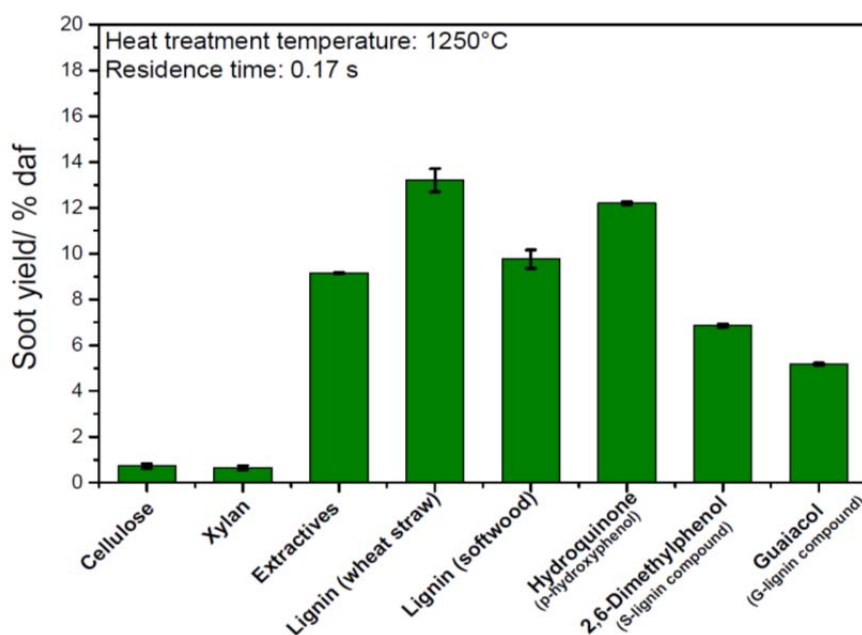


Figure 1. Soot yields (% daf) from pyrolysis at 1250°C with the residence time of 0.17 s in a drop tube reactor.

The highest soot yield was obtained from pyrolysis of wheat straw lignin and quantitatively comparable with the soot yield of hydroquinone. The presence of hydroxyl groups compared to other lignin-derived compounds representing S- and G-lignin types might enhance the soot formation. Lower soot yields were obtained from pyrolysis of cellulose and hemicellulose due to the lower presence of inherent aromatic rings [2-4]. Moreover, the soot yields from pyrolysis of potassium impregnated lignin at 1250°C with the residence time of 0.35 s were significantly lower than that of non-treated lignin samples indicating the catalytic influence of potassium inhibiting growth of polycyclic aromatic hydrocarbons, confirming the previous results of Umeki et al. [5].

### Soot reactivity

The thermogravimetric experiments demonstrated significant differences in the intrinsic reactivity of lignocellulosic compounds, monolignols and Soxhlet extracted soot samples towards CO<sub>2</sub>. The reactivity of soot samples from low ash-containing 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 extractives soot was 95 times greater than that of extracted lignin soot. 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 carbon chemistry had a strong influence on the observed differences in soot reactivity.

Higher free radical concentrations in biochars increased the oxidation reactivity [7-8]. 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. This indicates that the differences in radical concentrations had a negligible 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 large, 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 [9]. Low separation distances (close to that of graphite) and high periodicity lead to lower oxidation of soot, while the more bent graphene layers might enhance the reactivity due to more defects in the graphene structure. 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 lower than that of other soot samples. The mean separation distance of cellulose soot (0.4 nm) was significantly larger than that of other soot samples, leading to the highest reactivity. Moreover, the short graphene layers of cellulose soot (2.5 nm) could enhance the reactivity in  $CO_2$  gasification, as shown in Figure 2.

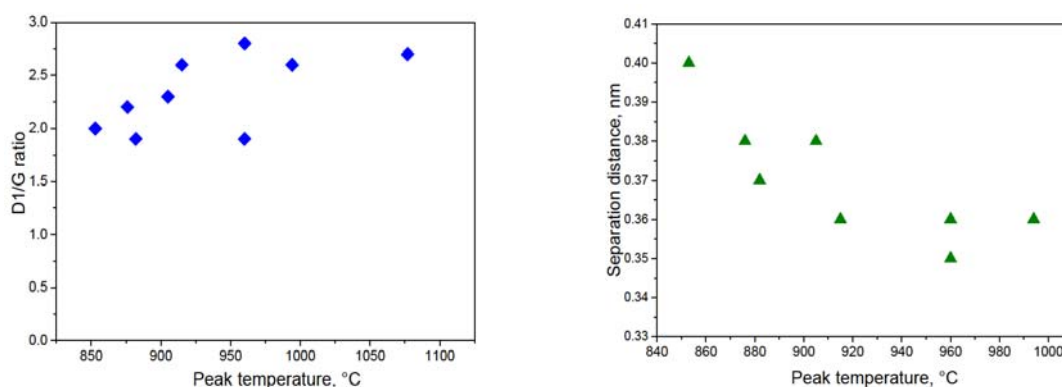


Figure 2. (a) The integrated peak area ratio ( $D1/G$ ) derived from the Raman spectroscopic data, and (b) Separation distance of graphene layers ( $d_{sep}$ ) over the relevant peak temperature are shown over the relevant peak temperature of the TG experiment in 40% volume fraction  $CO_2$ .

The DTG curves of cellulose, hemicellulose and hydroquinone soot showed a double peak in CO<sub>2</sub> gasification indicating a heterogeneous 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, whereas the more reactive carbon phase with the short and more bent graphene segments corresponds to the reactivity of carbon black, as reported by Abian et al. [10]. The compositional differences of lignocellulosic compounds also significantly affect the biomass soot reactivity in CO<sub>2</sub> gasification. Previously, the differences in soot reactivities were related to the potassium content in the original biomass. However, the observation made by Trubetskaya et al. [11] in terms of the higher wheat straw soot reactivity due to the high potassium content in the original wheat straw was extended in the present study. The high content of extractives and lignin in the pinewood and beechwood could also lead to the lower reactivity of woody soot beside 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, higher soot yields [12]. 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 from softwood lignin pyrolysis was lower 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 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 [13]. This shows that the lignocellulosic compositional differences affect both the soot yields and reactivities.

## **Conclusion**

The present results indicated that both lignin samples from softwood and wheat straw obtained higher soot yields than holocelluloses and extractives due to the higher amounts of PAHs formed during pyrolysis. The pyrolysis of p-hydroxyphenols led to the higher soot yields due to the high concentration of hydroxyl groups compared to pyrolysis of syringol and guaiacol compounds. The thermogravimetric analysis results showed that the soot reactivity towards CO<sub>2</sub> depends mainly on the soot nanostructure and less on the particle size, radical concentrations and carbon structure. 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<sub>2</sub> reactivity. The non-treated and acetone extracted softwood and wheat straw lignin soot samples showed a similar reactivity. The changes in a maximal reaction rate of both lignin soot samples were small when the residence time of soot particles was increased. The cellulose soot was more reactive than hemicellulose, extractives and lignin soot due to the more disordered structure of cellulose soot with more bent and short graphene segments. The present work emphasized a dominating role of differences in lignocellulosic composition on the soot yield and reactivity.

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