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

Anna Trubetskaya⁹, Avery Brown⁷, Geoffrey A. Tompsett⁷, Michael T. Timko⁶, Jens Kling⁵, Markus Broström⁸, Mogens Larsen Andersen⁴, Kentaro Umeki⁶

⁹ Thermochemical Energy Conversion Laboratory, Umeå University, 90187 Umeå, Sweden
⁷ Chemical Engineering Department, Worcester Polytechnic Institute, 01609 Worcester, MA, USA
⁵ Center for Nanoscopy, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
⁴ Department of Food Science, University of Copenhagen, Rolighedsvej 26, 1958 Copenhagen, Denmark
⁶ 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 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.

https://doi.org/10.1016/j.apenergy.2017.12.068
Received 28 September 2017; Received in revised form 30 November 2017; Accepted 10 December 2017
0306-2619/ © 2017 Elsevier Ltd. All rights reserved.
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 polylyne intermediates. The importance of C\(_2\H\)\(_2\) 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 phenolic 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 oriented crystals 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 microscopy 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 stoves 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 absorbs 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 displaced 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 experiment, ≈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. Course 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).
دریافت فوری متن کامل مقاله

<table>
<thead>
<tr>
<th>ISI Articles</th>
<th>مرجع مقالات تخصصی ایران</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ امکان دانلود نسخه تمام متن مقالات انگلیسی</td>
<td></td>
</tr>
<tr>
<td>✓ امکان دانلود نسخه ترجمه شده مقالات</td>
<td></td>
</tr>
<tr>
<td>✓ پذیرش سفارش ترجمه تخصصی</td>
<td></td>
</tr>
<tr>
<td>✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله</td>
<td></td>
</tr>
<tr>
<td>✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله</td>
<td></td>
</tr>
<tr>
<td>✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب</td>
<td></td>
</tr>
<tr>
<td>✓ دانلود فوری مقاله پس از پرداخت آنلاین</td>
<td></td>
</tr>
<tr>
<td>✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات</td>
<td></td>
</tr>
</tbody>
</table>