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Soot formation during biomass pyrolysis: Effects of temperature, water-leaching, and gas-phase residence time

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ABSTRACT

Soot particles from biomass incomplete combustion, as a major source of particulate matter, arouse significant concerns due to its harmful impacts on environment and human health. In this paper, the effects of pyrolysis temperature, volatile residence time and water-leaching of biomass on soot formation during biomass pyrolysis were studied in a lab-scale furnace. The physicochemical characteristics of soot particles were comprehensively analyzed. Results show that soot is formed by the secondary reactions of volatiles from biomass thermal-cracking requiring a certain high temperature and long volatile residence time. With a short volatile residence time of 0.2 s, no soot is formed at 900–1200 °C. When the residence time increases to 2 s, soot is significantly formed at > 1000 °C, when onion-like shell/core structures is observed. With pyrolysis temperature increasing, the soot particle size decreases and becomes uniform, the carbon content in soot increases, and the ordered structure of carbonization is enhanced, which leads to the degradation of soot oxidation reactivity. The water-leaching pretreatment for biomass leads to the increases of soot yield, particle size, and carbon content, as well as the KCl absence in soot and significantly lowered oxidation reactivity of soot. This indicates strong catalysis of potassium on soot production and consumption. Both gas and tar analyses support soot formation mechanism: (1) H₂ yield increases due to formation of soot, but C₂H₂ yield reaches peak at 1000–1100 °C; (2) tar is dominated by PAHs, which molecules grow with the increase of temperature and residence time.

1. Introduction

Under the severe intensification of greenhouse effect and depletion of fossil fuels, biomass fuel, generally regarded as CO₂-neutral and environmentally friendly, are now receiving worldwide attentions [1]. Biomass energy is the most abundant renewable resource on earth and the world's fourth largest energy resource after coal, oil and natural gas, accounting for around 10% of the world primary energy consumption [2]. The contents of sulfur and nitrogen species in biomass fuel are generally much lower than those in common fossil fuels, which arouses the utilization of combustion of individual biomass fuel or co-combustion of biomass fuel and other solid fuels to realize low emission of SO₂ and NO_x and reduction of acid rain pollution [3–6].

However, further utilization of biomass fuel is still facing great challenges. Severe facility and environment problems including deposition, slagging, corrosion and emission of fine particulates with sizes lower than 2.5 μm in diameter (PM_{2.5}) can be induced due to the presence of high contents of chlorine and alkali and alkaline earth metals (AAEMs) in biomass [7–10]. Relatively high content of volatile matters in biomass fuel might accounts for the relatively low combustion

efficiency, and easily leads to incomplete combustion which is a dominating cause of main carbonaceous pollutants including CO, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and soot [11,12]. Zhang and Tao [13] estimated 16 main PAH species all over the world in 2004 and found that their total emission was 520 Gg per year with 56.7% of biomass as the major source, and that was 66.4% in China due to the wide use of conventional biomass stoves. PAHs are strong carcinogenic substances with pluripotentiality to cause adverse health effects to humans and animals [14,15]. Under the condition of high temperature (> 1000 °C), PAHs play the role of precursor and undergo processes of polymerization, condensation, and growing into soot particles [16]. The diameters of primary soot particles mainly distribute in the range of 10–50 nm which is fine and easy to get inhaled. It is also highly toxic due to its high sorption ability of PAHs and heavy metal species [17,18]. Cho et al. [19] compared the toxicities of common carbonaceous pollutants to human lung and proved soot to be the most hazardous kind. Soot is also of high radiation absorptivity and able to enhance the heat transfer by radiation in combustion chamber. Modeling work of Saveliev et al. [20] indicated that high concentration of soot in the flame leads to enhancement of radiant heat exchange

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reflected in the reduction of flame temperature by 10–50 K as well as the reduction of peak NO concentrations by 20–25%. Besides, soot aerosols existing in the atmosphere are the dominant absorber of visible solar radiation, and soot radiative forcing estimates range between 0.2–1.2 W m⁻², making soot second only to CO₂ in terms of global warming potential [21–23].

Plenty of studies have been carried out to investigate soot formation mechanisms and soot property characterizations during the combustion of micro-molecular hydrocarbon fuels, e.g. methane, ethylene, diesel, etc., basing on which numbers of detailed models are available to predict soot concentrations in a flame [24]. It is widely accepted that nascent soot is formed by condensed heavy PAHs at high temperature. The formation process of the initial aromatic ring plays the role of a rate limiting step, and subsequent growth of PAHs are dominated by reactions as ‘H-abstraction-C₂H₂-addition’ (HACA) and ‘ring-ring’ mechanisms [25]. However, due to the much higher complexity of physico-chemical compositions of biomass fuel, the internal reactions and chemical mechanisms happened during decomposition, thermal cracking and recombination are still not well understood. Few studies have been reported to investigate the soot formation mechanisms of biomass fuel, neither a recognized theory has been proposed to explain the formation pathway of soot from biomass fuel. Biomass materials are mainly composed of cellulose, hemicellulose, lignin, as well as track amount of inorganic mineral species [26]. When pyrolyzed, mainly saccharides, phenols, ketones and aromatics are generated after cracking of macro molecules [27]. The pathways from these species with relatively high molecular weights to nascent soot particles are much more complicated than from those small molecules (methane, ethylene, etc.). Besides, mineral species represented by potassium are also influential to biomass pyrolysis volatiles in their yields and compositions (especially PAHs and C₂H₂ that greatly affect formation of soot particles). Hence, temperature and water-leaching might be possible factors that are able to influence the process of soot formation. In addition, certain amount of fine particulates born in combustion of biomass fuel consist of inorganic mineral compounds, among which the part of PM_{1.0} was observed to mainly consists of alkalis as well as of chlorine, where high amount of phosphorus and sulfur also existed, and vaporization followed by condensation was proved dominant mechanism of submicrometer particles formation [28]. Most of current studies, however, merely consider the two processes, that is vaporization-condensation of mineral species and soot formation, isolated during particulate formation, and the potential hybridization and catalysis processes during particulates’ formation, growth and oxidation are generally neglected.

Therefore, this study was carried out to further understand the effects of temperature, volatile residence time and biomass water-leaching on the formation and characteristics of soot during biomass pyrolysis, and to indicate the formation mechanism of soot particle and the interaction between soot and inorganic mineral species. Considering the much higher AAEM contents and larger amounts of straw biomass than that of woody biomass [5,10], in this work, wheat straw was chosen as raw biomass sample. The raw sample was leached by deionized water to prepare water-leached biomass sample, and pyrolysis experiments were conducted in two fixed-bed reactors at 900–1200 °C. High-resolution transmission electron microscopy (HRTEM), elemental analyzer, X-ray diffractometer (XRD) and thermogravimetric analyzer (TGA) were used to characterize the nano-morphologies, chemical compositions, crystal structures and oxidation kinetics of soot products. Gas chromatography and mass spectrometer (GC–MS) was used to measure the composition of gas and tar products.

2. Material and methods

2.1. Materials

Wheat straw used in this study was collected from a farm around

Table 1

The ultimate and proximate analyses of the raw straw.

Ultimate analysis (wt.%)					Proximate analysis (wt.%)		
<i>C_{ad}</i>	<i>H_{ad}</i>	<i>O_{ad}</i>	<i>N_{ad}</i>	<i>S_{ad}</i>	<i>V_{ad}</i>	<i>FC_{ad}</i>	<i>A_{ad}</i>
41.1	5.5	51.6	1.2	0.6	69.2	17.7	13.1

(*V_{ad}*: volatile matter as air dried basis; *FC_{ad}*: fixed carbon as air dried basis; *A_{ad}*: ash as air dried basis).

Xi’an, Shaanxi Province, China. The ultimate and proximate analyses are shown in Table 1. Wheat straw was milled and sieved to the diameter of < 150 μm. To prepare water-leached biomass samples, deionized water was used to leach wheat straw, heated in water bath of 80 °C for 24 h, and the ratio of water to straw was controlled 50 ml : 1 g. After leaching, straw samples were collected, dried at 105 °C for 24 h, and milled and sieved again to the diameter of < 150 μm to prepare water-leached biomass samples. Both samples were dried again before use. As shown in Table 1, the ash content decreased from 13.1% to 8.95%, 31.7% of ash content removed by water-leaching. Ash composition analyses of both raw and water-leached biomass samples were shown in Table 2. As shown in Table 2, the contents of K, Cl, S and P in ash decreased. Contents of K₂O and Cl decreased from 26.8% to 10.3% and from 5.6% to 0.8%, respectively, 74% of K content and 90% of Cl content removed by water-leaching.

2.2. Fixed-bed reactor system

In this study, pyrolysis experiments were conducted in two fixed-bed reactors where difference in volatile residence times can be realized. The whole system is shown in Fig. 1, and from left to right are the nitrogen control unit, the temperature control unit, the quartz reactor unit, the soot collecting unit, the tar condensation unit, the gas filter and dryer unit, and the metering and analyzing unit. A long quartz tube with a constant-temperature region of 800 mm is set in a large furnace to realize a long volatile residence time of about 2 s (1.716–2.155 s, depending on temperature), while a small one with length of 80 mm in a small furnace is of a short volatile residence time of about 0.2 s (0.172–0.216 s, depending on temperature). The internal diameter of both quartz tubes is 30 mm. Nitrogen with high purity (N₂ content > 99.9%) is adopted to realize inert atmosphere, and gas flow rates in both reactors are 4 l min⁻¹. The details about how to calculate the residence time of the volatiles in the reactor is provided in Table S1.

The reactor was heated to target temperatures (900–1200 °C) at a constant heating rate of 20 °C min⁻¹ at first. 1 ± 0.005 g samples contained in a corundum boat were placed in the lower temperature region on the reactor left, and N₂ flow of 4 l min⁻¹ was kept 10 min before sampling began. When a constant temperature and purely inert atmosphere were obtained, the corundum boat was rapidly pushed into the constant-temperature reaction zone and pyrolyzed. The pyrolysis process of each sample lasted for 10 min which is an appropriate time that has proven to ensure the completion of total gas release [29]. After that the corundum boat was pulled back to the lower temperature region, cooled to room temperature in the N₂ atmosphere, and the solid residues were collected.

Soot particles were collected by a metal filter membrane supported in a porous metal cone frame. The soot collecting unit was heated to 250 °C which was 50 °C higher than that in the work of Trubetskaya et al. [30] to avoid the significant condensation of tar products, and the collected soot was preserved for further characterization. There is a tiny amount of carbon deposit on the reactor wall. Compared to the volume of soot collected in the filter, the volume of carbon deposit on the reactor wall is negligible. The outlet of reactor is covered with heat insulation materials to avoid overcooling of tar vapors, and the tar condensation unit containing dichloromethane is cooled in the iced water to collect the condensable bio-oil for GC–MS analysis. The volume of

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