



# Effects of several types of biomass fuels on the yield, nanostructure and reactivity of soot from fast pyrolysis at high temperatures



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## HIGHLIGHTS

- Biomass soot samples were generated at fast pyrolysis conditions in a drop tube reactor at 1250 and 1400 °C.
- The reactivity of soot was determined in 5 vol.% O<sub>2</sub> and 5 vol.% CO<sub>2</sub> gasification by thermogravimetric analysis.
- The reactivity of soot, generated at 1400 °C was higher than that at 1250 °C for all biomass types.
- Pinewood was less reactive than other soot samples with respect to oxidation and CO<sub>2</sub> gasification.
- Potassium content played a more important role on the soot reactivity than the particle size and nanostructure.

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## ABSTRACT

This study presents the effect of biomass origin on the yield, nanostructure and reactivity of soot. Soot was produced from wood and herbaceous biomass pyrolysis at high heating rates and at temperatures of 1250 and 1400 °C in a drop tube furnace. The structure of solid residues was characterized by electron microscopy techniques, X-ray diffraction and N<sub>2</sub> adsorption. The reactivity of soot was investigated by thermogravimetric analysis. Results showed that soot generated at 1400 °C was more reactive than soot generated at 1250 °C for all biomass types. Pinewood, beechwood and wheat straw soot demonstrated differences in alkali content, particle size and nanostructure. Potassium was incorporated in the soot matrix and significantly influenced soot reactivity. Pinewood soot particles produced at 1250 °C had a broader particle size range (27.2–263 nm) compared to beechwood soot (33.2–102 nm) and wheat straw soot (11.5–165.3 nm), and contained mainly multi-core structures.

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## 1. Introduction

Suspension firing of biomass is widely used for power generation and has been considered as an important step in reduction of greenhouse gas emissions. Biomass gasification offers high conversion efficiency and the possibility to handle different lignocellulosic materials to a wide variety of applications such as heat, electricity, chemicals and transport fuels [1]. Fast pyrolysis at high temperatures and at high heating rates is the initial step of the suspension biomass firing or biomass gasification depending on the reaction atmosphere. During pulverized biomass firing, particles first undergo rapid drying and devolatilization, leading to the

formation of char and volatiles. At temperatures below 1000 °C, secondary reactions of volatiles produce mainly tars and small amounts of soot; at higher temperatures (1350–1400 °C) these reactions produce soot and almost no tars [2,3].

In order to reduce aerosol emissions and improve radiative heat transfer during combustion, it is necessary to understand how soot particle properties are correlated with fuel composition and operating conditions [4]. Understanding soot characteristics is also an important step for the optimization of gasification processes because the complete conversion of soot is desirable to increase syngas yields [5]. In suspension firing, soot can act as a radiating agent which promotes heat transfer in large flames [6]. Soot particles absorb heat and re-emit it as disperse radiation. Chen [7] reported that the production of both thermal and fuel NO<sub>x</sub> in coal combustion depends on the reaction temperature, and thus,

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## Nomenclature

$\beta$	reflection broadening ( $2\theta$ )	$d_{sep}$	distance between graphene layers (nm)
$\kappa$	heating rate ( $^{\circ}\text{C min}^{-1}$ )	$E_a$	activation energy ( $\text{kJ mol}^{-1}$ )
$\lambda$	wavelength (nm)	$K_{Sc}$	Scherrer constant
$\mu_g$	geometric mean of $A_i$	$L_a$	lateral extension ( $\text{\AA}$ )
$\pi^*$	$\pi$ bonds	$L_c$	stacking height ( $\text{\AA}$ )
$\sigma^*$	$\sigma$ bonds	$m$	multiple cores
$\sigma_g$	geometric standard deviation	$N$	number of layers
$\theta$	Bragg angle ( $^{\circ}$ )	$n$	number of experiments
$A$	pre-exponential factor ( $\text{s}^{-1}$ )	$R$	gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$A_i$	set of numbers	$r$	ratio of relative areas
$A_{Cr}$	area of TG crucible (mm)	$r_{diff}$	diffusion controlled rate ( $\% \text{ min}^{-1}$ )
$A_{G,\pi^*}$	relative area of $\pi^*$ peak	$r_{max}$	maximal reaction rate ( $\% \text{ min}^{-1}$ )
$A_{G,\sigma^*}$	relative area of $\sigma^*$ peak	$s$	single core
$d_p$	particle diameter (nm)	$T$	heat treatment temperature ( $^{\circ}\text{C}$ )
$d_{002}$	interlayer distance ( $\text{\AA}$ )	$X$	conversion

presence of the soot in a coal flame. Soot formation reduces  $\text{NO}_x$  levels by enhancing heat transfer [8]. Emissions of atmospheric aerosols, including soot, are associated with hazardous health effects, because they can contain polycyclic aromatic hydrocarbons (PAH), many of which are highly toxic and carcinogenic [9].

Studies of the physicochemical properties of soot derived from coal and hydrocarbon feedstocks [10–13] have identified a number of factors influencing reactivity: synthesis conditions, alkali content, particle size, and nanostructure [3,5,14–16]. Van Setten et al. [17] and Vander Wal et al. [11] pointed out that the feedstock of soot samples influences their properties and oxidation reactivity. Liati et al. [16] related the morphology of primary soot particles (size, shape and internal structure) to the factors which influence soot oxidation reactivity. Müller et al. [15] showed that larger graphene layer planes, larger crystallites, and concentrically orientated crystallites decrease soot reactivity. Some of the alkali metals contained in the biomass are vaporized and participate in soot formation and conversion reactions. Several studies have addressed the influence of alkali metals on the oxidation reactivity of soot from coal pyrolysis [18,19]. Alkali is known to enhance oxidation of graphite [20] and suppress soot formation [21]. Small concentrations of alkali catalyze the reactions of carbonaceous materials with oxygen, carbon dioxide, hydrogen and water vapor [22,23]. Neef et al. [24,25] investigated the effect of inorganic materials on graphite oxidation rate and soot accumulation in a diesel engine, and found that the intensity of contact between soot and alkali is a major predictor of soot oxidation rate. Potassium carbonates decompose at temperatures higher than  $280^{\circ}\text{C}$ , leading to increased reaction rates of graphite oxidation when alkali carbonates have good contact with the carbon [24]. Several studies [26,27] reported that potassium bonded by oxygen to the carbonaceous matrix of soot increases the soot oxidation reactivity. Fredenhagen [28,29] discovered alkali metal–graphite intercalates, and showed that graphite can react with alkali metals to form lamellar compounds in which the planar graphite arrangement remains largely preserved. Wen [18] suggested that potassium carbonates may catalyze the gasification of coal char and graphite to form carbon monoxides according to Eqs. (1) and (2):



Potassium carbonate reacts with carbon to produce atomic potassium. Electron donor–acceptor (EDA) complexes are formed between potassium and the carbonaceous matrix of soot. Chen and Yang [20] suggested that alkali metals formed by reaction of

$\text{K}_2\text{CO}_3$  with graphite might form C–O–K groups on the graphite surface and thereby enhance the reactivity of the carbon matrix.

Many soot reactivity studies are based on coal [13], liquid [10,11] or gaseous hydrocarbons [12], but only a few have focused on biomass soot, which is formed by different chemical pathways [30]. Compared with soot from fossil fuel combustion, biomass soot particles are higher in inherent oxygen functionality as well as adsorbed organic species such as acids, alcohols and aldehydes [31]. Wiinikka et al. [32] concluded that the concentration of ash-forming elements significantly influences both the shape and nanostructure of pinewood soot particles during the entrained flow gasification of biomass. Septien et al. [33,3] reported that initial fuel composition, particularly potassium content, influenced steam gasification rates of beechwood soot significantly. Overall, the conversion of biomass soot generated under combustion and gasification conditions remains poorly understood. In particular, the influence of biomass type (woody vs. herbaceous), reaction atmosphere (oxygen and carbon dioxide), and alkali metal impregnation/removal on the reactivity of soot prepared at high temperatures have not been previously examined. Little is known regarding the various biomass physicochemical properties that determine soot reactivity towards  $\text{O}_2$  and  $\text{CO}_2$ .

Therefore, in this study, the impacts of biomass origin, soot nanostructure, particle size and inorganic matter content on soot reactivity towards  $\text{O}_2$  and  $\text{CO}_2$  were investigated. The specific objectives of this study were to: (1) obtain knowledge about various stages in particle formation during suspension biomass combustion and high-temperature gasification, (2) determine the reaction conditions which minimize soot formation to prevent clogging of downstream components and catalyst deactivation in high-temperature gasification, and (3) optimize soot-blower operation and heat transfer during pulverized biomass combustion.

## 2. Materials and methods

Pinewood, beechwood and Danish wheat straw were chosen for the fast pyrolysis study in a drop tube reactor (DTF). Fuel selection was based on the differences in the ash composition and plant cell compounds (cellulose, hemicellulose, lignin, extractives). The wood samples are low in ash, with slightly higher potassium and calcium contents in beechwood than in pinewood. Danish wheat straw is rich in silicon and alkali (K, Ca, Na).

Biomass soot samples collected during fast pyrolysis at  $1250$  and  $1400^{\circ}\text{C}$  were further investigated under  $\text{O}_2$  and  $\text{CO}_2$  gasification conditions in a thermogravimetric analyzer. Reactivities of

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