



## Research article

# Aggravated fine particulate matter emissions from heating-upgraded biomass and biochar combustion: The effect of pretreatment temperature



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## ABSTRACT

Heat pretreatment is a promising method for biomass upgrading. However, PM formation from the combustion of such pretreated biomass has not been fully evaluated. In this work, the effect of pretreatment temperature on PM emission of the upgraded biomass and biochar combustion was studied in an entrained flow reactor. The physical and chemical properties of upgraded biomass, biochar and PMs at varied pretreatment temperatures were obtained to illustrate the PM formation mechanism. Results show that pretreatment temperature significantly affects the concentration and particle size distribution of PM emissions, through changing the char yield and K/Cl contents in char. With increase in pretreatment temperature, the PM<sub>1.0</sub> emission of upgraded biomass and biochar combustion first increases, reaches maximum at 500 °C, and then decreases. A linear relationship between the PM<sub>1.0</sub> emission and Cl content in upgraded biomass and biochar was found. This result indicates that the combustion of upgraded biomass and biochar produced at moderate temperatures of 250–500 °C result in aggravated fouling and PM emissions.

## 1. Introduction

Utilization of more sustainable and environmentally-friendly sources of energy can help to abate the effect of greenhouse gas emissions. Biomass is an alternative source that is carbon-neutral with a potential to reduce CO<sub>2</sub> and SOx/NOx emissions [1,2]. As a big agricultural country, China has an abundant biomass energy resource, and its direct combustion is of great potential to reduce fossil fuel utilization and ensure energy-supply security. However, utilization of raw biomass for commercial power generation still faces several drawbacks to its implementation [3,4]. These drawbacks include low bulk density, low energy density, high moisture content, high logistic cost and poor grindability [5,6]. Therefore, for industrial use, many technologies have been proposed to upgrade biomass materials, overcome these drawbacks and improve the efficiency of biomass utilization. Heat pretreatments, including torrefaction and pyrolysis, are simple, promising and effective methods for biomass upgrading [7,8].

Torrefaction is a mild thermolysis process at relative low temperatures of 200–300 °C, mainly to improve the thermo-chemical properties of biomass [9,10]. In contrast, pyrolysis results in the deep decomposition of biomass materials at relatively higher temperatures, mainly converted into bio-fuels with high energy density, such as liquid (bio-oil), gas and solid sample (biochar) [11]. The solid products from both

torrefaction and pyrolysis share significant improvement on fuel properties, with high energy density and good grindability, and are suitable for the utilization as alternative and supplementary fuels for power generation [12,13].

Due to the high chlorine and alkali metal contents in biomass, direct combustion or co-firing with coal contributes significantly to PM<sub>1.0</sub> (particulate matter with aerodynamic diameter < 1.0 μm) emission [14,15], inducing ash deposition, fouling, and slagging [16,17]. The heat pretreatment of biomass results in complex transformation to biochar and the release of a considerable amount of alkali and chlorine into the flue gas [18,19]. However, the residual biochar pretreated at moderate temperatures still contains abundant species of alkali and chlorine, which may result in significant PM<sub>1.0</sub> emission. Extensive studies on the characteristics of PM from raw biomass combustion [20,21] or its co-firing with coal [22,23] have been reported. Few studies were conducted on the PM emission from biochar combustion. Yani et al. [19] adopted a drop-tube furnace to investigate the behavior of PM<sub>1.0</sub> emission from the combustion of biochar obtained through torrefaction at 220–280 °C. They observed bimodal mass-based particle size distribution (PSD) from biochar combustion, which is similar to that from raw biomass combustion. Nonetheless, when the biomass pretreatment temperature was further increased to 400–550 °C, a unimodal PSD was observed for the PM<sub>1.0</sub> emission, and the PM<sub>1.0</sub>

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(particulate matter with diameter  $< 1.0 \mu\text{m}$ ) emission is negligible [24]. The biomass feedstocks used in these two works on biochar combustion contain low chlorine contents ( $< 0.2\%$ ). However, straw, which is the most part of biomass energy resource with a share of 72% in China [25], has a relatively high chlorine. The chlorine content in straw [26–29] can be up to three times or higher than that in biomass used in previous studies [19,24]. The chlorine species in biomass have been widely reported to be the main cause for the formation of fine particles during biomass combustion [14,30]. These significant differences in the chlorine content of biomass may result in different characteristics of  $\text{PM}_{1.0}$  emission during biochar combustion. In addition, the effect of pretreatment temperature within a wide range on the PM emission from upgraded biomass and biochar combustion has not been fully explored. Therefore, a deep and systematic understanding on the fine particle emission from upgraded biomass and biochar combustion, is important for the high-efficient and environment-friendly utilization of biomass in China.

In this study, the behaviors of PM emission from the combustion of upgraded biomass and biochar prepared in a wide temperature range of 250–1000 °C, were carried out in a laboratory-scale entrained flow reactor at 1200 °C. The biomass pretreated below 300 °C is called “upgraded biomass”, while the biomass pretreated above 350 °C is called “biochar”. The fine particles were collected by a Dekati low pressure impactor (DLPI). Morphologies and chemical composition of the fine particles were analyzed by a scanning electron microscopy equipped with energy dispersive X-ray spectrometry (SEM-EDS). Based on the experimental results, the PM formation mechanism during upgraded biomass and biochar combustion is illustrated.

## 2. Materials and methods

### 2.1. Fuel properties

The biomass used in the present study is the typical wheat straw from Baoji city of Shaanxi province. The proximate and ultimate analyses, and ash compositions are presented in Tables 1 and 2, respectively. As seen from Table 2, the chlorine and potassium contents are high, 6.15% and 27.68%, respectively. The straw samples were ground, sieved into diameter  $< 100 \mu\text{m}$ , and then put into sealing bag for use. The fuel samples were dried in an oven at 105 °C for 2 h before the preparation of upgraded biomass and biochar and combustion tests in entrained flow reactor.

### 2.2. Experimental setup

#### 2.2.1. Fixed-bed pyrolysis reactor

The preparation of upgraded biomass and biochar was performed in a fixed-bed pyrolysis system as shown in Fig. 1. The quartz tube reactor is 40 mm in internal diameter and 2000 mm in length. The temperature was measured by a K-type thermocouple ( $\pm 1 \text{ }^\circ\text{C}$ ). A corundum crucible with 1.0 g straw was placed into the reactor and exposed to nitrogen with gas flow of 1 L/min for 30 min. Then, the samples were heated to and maintained at the desired temperature for 120 min to ensure complete pyrolysis. Thereafter, the residual char was cooled to ambient temperature and weighed by an electronic balance ( $\pm 0.0001 \text{ g}$ , AEL-200, Shimadzu, Japan) to obtain the char yield. Each test was repeated 5 times. The upgraded biomass and biochar was

**Table 1**  
Properties of wheat straw used in this study.

Proximate analysis (wt%, ad)				Ultimate analysis (wt%, ad)					
$M_{\text{ad}}$	$A_{\text{ad}}$	$V_{\text{ad}}$	$FC_{\text{ad}}$	$C_{\text{ad}}$	$H_{\text{ad}}$	$O_{\text{ad}}$	$N_{\text{ad}}$	$S_{\text{ad}}$	$Cl_{\text{ad}}$
3.25	14.24	70.02	17.31	42.5	5.98	49.11	1.58	0.60	1.03

**Table 2**  
The composition of wheat straw ash.

Component	MgO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{SO}_3$	Cl	$\text{K}_2\text{O}$	CaO
Straw (wt%)	2.42	2.83	42.77	3.55	4.52	6.15	27.68	10.08

ground and sieved into diameter below 100  $\mu\text{m}$ . X-Ray fluorescence (XRF, S4-Pioneer, Bruker Co., Germany) was employed to directly determine the potassium and chlorine contents, and X-ray diffraction (XRD, X'pert MPD Pro, PANalytical, Netherlands) was used to analyze the mineral phases in the upgraded biomass and biochar at different pretreatment temperatures. The solid products were dried in oven for 6 h before XRF characterization, therefore, the presented elemental content in this paper is in dry basis.

#### 2.2.2. Entrained flow reactor system

The behavior of PM emission from upgraded biomass and biochar combustion was studied in an entrained flow reactor system as shown in Fig. 2. The corundum tube reactor is heated by silicon carbide of three zones. The temperature was measured by a B-type thermocouple ( $\pm 1 \text{ }^\circ\text{C}$ ), generating an isothermal region of  $\sim 500 \text{ mm}$ . The reactor is 1200 mm in height with an internal diameter of 50 mm. The fuel samples are fed by a micro-scale fluidized feeder, where the particles were entrained by the nitrogen of 1 L/min. Before each test, the feeding rate of 90–150 mg/min was determined first, and then the fuel particles were fed into the reactor via a water-cooled feeding probe. The experiments were operated at 1200 °C and at a total gas flow of 4 L/min with a  $\text{N}_2\text{:O}_2$  ratio of 1:4. The residence time of fuel particles in the isothermal zone was  $\sim 3.5 \text{ s}$  to ensure the complete combustion and avoid the carbonaceous particles.

The fine particles in the flue gas were sampled by a water-cooled probe, where another  $\text{N}_2$  flow was introduced to quench and dilute the flue gas. The diluted particle-containing flue gas first passed the  $\text{PM}_{10}$  cyclone to separate the coarse particles with diameters  $> 10 \mu\text{m}$ , and then was introduced to DLPI (Dekati low pressure impactor, Finland) for size classification and collection. The sampling devices and related pipelines were heated up to  $150 \pm 5 \text{ }^\circ\text{C}$ , in order to avoid and prevent acid gas condensation. The mass of deposits on the substrates was analyzed by a high precision electronic micro-balance ( $\pm 0.001 \text{ mg}$ , Sartorius M2P, Germany), to obtain the mass PSD of  $\text{PM}_{10}$ . In each case, the sampling was repeated three times to ensure reproducibility. The particles collected on the substrates were analyzed by SEM-EDS (JEM-7800F, JEOL, Japan) for morphologies and elemental compositions.

## 3. Results and discussion

### 3.1. The yield of char and the evolution of K/Cl during straw pyrolysis

The yield of char as a function of temperature during the process of heat pretreatment is presented in Fig. 3(a). With the increasing in the pretreatment temperature from 250 °C to 350 °C, the char yield decreases from 55.5% at to 42.7%, and further decreases to 32% at 1000 °C. This trend of the temperature-dependent char yield is similar to previous research [7], while these yields are somewhat different. It might be due to the difference of fuel properties. Biomass mainly consists of cellulose, hemicellulose and lignin. The thermal decomposition of cellulose starts at  $< 150 \text{ }^\circ\text{C}$ , generating the more stable anhydrocellulose [31]. This process is the dominant below 300 °C, thereby resulting in a higher char yield as shown in Fig. 3(a). With increase in temperature, the cellulose depolymerizes and produces volatiles [32], leading to a decrease of char yield at 350 °C. Lower char yield with increase in temperature may be caused by the enhanced volatile-release through promotion of primary decomposition or secondary decomposition at higher temperatures [33,34].

It is well known that during biomass combustion, K and Cl in

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