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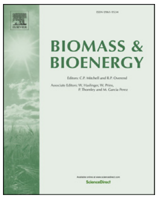

Research paper

Comparison of high temperature chars of wheat straw and rice husk with respect to chemistry, morphology and reactivity

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ABSTRACT

Fast pyrolysis of wheat straw and rice husk was carried out in an entrained flow reactor at high-temperatures (1000–1500) °C. The collected char was analyzed using X-ray diffractometry, N_2-adsorption, scanning electron microscopy, particle size analysis with CAMSIZER XT, ^{29}Si and ^{13}C solid-state nuclear magnetic resonance spectroscopy and thermogravimetric analysis to investigate the effect of inorganic matter on the char morphology and oxygen reactivity. The silicon compounds were dispersed throughout the turbostratic structure of rice husk char in an amorphous phase with a low melting temperature (≈ 730 °C), which led to the formation of a glassy char shell, resulting in a preserved particle size and shape of chars. The high alkali content in the wheat straw resulted in higher char reactivity, whereas the lower silicon content caused variations in the char shape from cylindrical to near-spherical char particles. The reactivities of pinewood and rice husk chars were similar with respect to oxidation, indicating less influence of silicon oxides on the char reactivity.

1. Introduction

The use of combustion units entirely based on renewable energy is an important step in the reduction of greenhouse gas emissions. However, the chemical and physical properties of biomass are different from those of coal and vary significantly between wood and herbaceous species. This introduces a range of major technical challenges, related to the operation of the power plants. Irregular fibrous biomass particles increase the required energy input into the milling compared to coal, affecting the biomass burnout and creating additional challenges with the flame stability [1,2].

The biomass utilization at Danish power plants focuses on wood pellets, but introduction of new solid biomass materials such as waste products from agriculture and energy crops, will demand an increased operational flexibility. The quality of agricultural wastes is lower than that of wood due to a higher ash content that leads to deposition and corrosion of the boiler units. Moreover, in pulverized biomass combustion only a short residence time is available for biomass conversion, and the lignocellulosic material reactivity is affected by the biomass composition, namely organic matter and minerals [3–5].

Little is known about the structural transformation of pulverized biomass during high heating rate and high temperature pyrolysis. The majority of investigations on the biomass potential of agricultural waste is focused on wheat straw and rice husk chars, pyrolyzed under slow heating rate (1–50 K min^{-1}) and long holding time (1–4 h) [6–11]. The rice husk contains high concentrations of silicon that is present as silicon oxides with small amounts of alkalis and other trace elements. Lanning [12] concluded that silicon occurs in rice husk in a hydrated amorphous form (opal or silica gel), located mainly in the outer epidermis and filling the inner channels in the spiral structure of the epidermal cells. In addition, Liu et al. [13] and Sharma et al. [14] proposed that the silica in the rice husk is combined with carbohydrates. This hypothesis was examined and verified by ^{29}Si NMR by Freitas et al. [9]. Guerrero et al. [15] reported no major morphological changes of rice husk under fast heating, and ascribed this observation to a high thermal resistance of rice husk ash, containing mostly silicon compounds. Pottmaier et al. [11] concluded that rice husk is less reactive than wheat straw,

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prepared at temperatures (300–1300 °C) under slow and fast heating, and related differences in reactivity to the higher contents of lignin and silicon in the rice husk. The investigation of Freitas et al. [9] on slowly pyrolyzed rice husk at high temperatures (1000–1400 °C) and long holding time (1–2 h) indicated an increased formation of crystalline silicon carbides at the expense of amorphous silicon oxides with increasing temperature. Nehdi et al. [16] stated that silicon oxides in rice husk can remain in amorphous form at combustion temperatures of up to 900 °C if the combustion time is less than one hour, whereas crystalline silicon oxides are produced at 1000 °C with combustion time greater than 5 min.

Several different methods have been used to characterize silicates from biomass pyrolysis and combustion. Nair et al. [17] showed that ^{1}H -^{29}Si CP/MAS solid-state NMR spectroscopy is more accurate than X-ray diffraction for the detection and quantification of the amorphous and crystalline Si bearing compounds. Hamdan et al. [18] studied rice husk ash, oxidized above 700 °C, and observed a broad Q^4 resonance without any silanol groups. The Q^n notation refers to the number of bridging oxygens on a particular tetrahedral silicon site [19]. Abreu and Schneider [20] analyzed by rice husk oxidation in a fluidized bed furnace at temperatures up to 890 °C and observed the presence of Q^3 and Q^2 sites in the amorphous fraction and a small amount of crystalline material assigned to cristobalite. Bardet et al. [10] pointed out that the origin of biomass does not affect the char structure under slow heating at temperatures up to 700 °C due to the transformation of lignocellulosic materials (wood, fescue, wheat straw) to larger saturated polyaromatic domains [21], and the remaining inorganic matter is not intercalated inside the polycyclic structures.

The present work was focused on the fast pyrolysis of rice husk and wheat straw at high temperatures (1000–1500 °C) performed in an entrained flow reactor at heating rates up to 10^4 K s^{-1} to study the properties of chars derived from herbaceous biomass. The structural transformations of rice husk and wheat straw chars were characterized by N_2-adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), ^{13}C and ^{29}Si solid-state nuclear magnetic resonance spectroscopy (NMR). The reactivity and burnout of herbaceous chars were studied using a thermogravimetric (TG) analyzer.

2. Materials and methods

2.1. Raw samples

For this study, wheat straw and rice husk were selected, based on the large difference in ash composition together with a similar distribution among the three major biomass constituents (cellulose, hemicellulose, lignin) as it is shown by the compositional analysis in Table 1. The rice husk contains a larger fraction of Si (9.8 wt.% of the dry material) and significantly less alkali in comparison to wheat straw, which is rich in alkali (K: 1.1 wt.% of the dry material; Ca: 0.24 wt.% of the dry material) but contains substantially lower Si (0.84 wt.% of the dry material). The raw rice husk (Oryza sativa L.) and wheat straw (*Triticum aestivum* L.) originate from North Vietnam (Sapa plantage) and Denmark (Aabenraa plantage). The rice husk and wheat straw were dried at 30 °C for several days in an oven desiccator without any ventilation. The moisture content decreased from 12 to 15 wt.% (as received biomass) to less than 5 wt.% (dry basis biomass) which ensured continuous biomass feeding in the entrained flow reactor.

Prior to the pyrolysis experiments, both rice husk and wheat straw were comminuted on a hammer mill (Andritz manufacturer) with an operating speed of 60 Hz. The wheat straw stems (20–40 mm) with leaves were grinded in two steps on a hammer mill down to 1 mm and thereafter down to 0.15 mm. In addition, wheat straw and rice husk were sieved to a particle size fraction of 0.09–0.18 mm to exclude particles with a characteristic length exceeding 0.5 mm, which could create challenges during the biomass feeding in the entrained flow reactor.

Table 1
Proximate, ultimate and compositional analyses of lignocellulosic materials. The abbreviations ar, db, wt stay for as received, dry basis and weight percentage. The proximate, ultimate and compositional analyses were conducted on wheat straw and rice husk particles sieved to 0.09–0.18 mm.

Fuel	Wheat straw	Rice husk
Proximate analysis		
Moisture, (wt.% ar)	5.5	4.5
Ash (550 °C), (wt.% db)	4.1	21.7
Volatiles, (wt.% db)	77.5	64.3
HHV, (MJ kg^{-1})	18.8	15.5
LHV, (MJ kg^{-1})	17.5	14.5
Ultimate analysis, (wt.% db)		
C	46.6	37.8
H	6.1	4.7
N	0.6	0.3
O	42.5	35.5
S	0.1	0.03
Cl	0.1	0.05
Ash compositional analysis, (mg kg^{-1} db)		
Al	150	70
Ca	2500	750
Fe	200	80
K	11,000	2500
Mg	750	400
Na	150	70
P	500	600
Si	8500	98,500
Ti	10	5
Structural analysis of biomass, (wt.% db)		
Cellulose	35.9	36.7
Hemicellulose	18	17.7
Lignin (acid insoluble)	19.2	21.6
Lignin (acid soluble)	6.5	1.2
Extractives	10.1	1
Protein	6.3	0.6

The compositional analysis of the biomass (cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, protein and extractives) was conducted according to NREL technical reports [22–24] and Thammasouk et al. [25]. The water-ethanol extraction was performed on wheat straw and rice husk which contained a high level of hydrophilic and lipophilic extractable compounds, according to the procedure described in the Supplemental material [25].

This work was performed on substrates of unknown provenance, for which the chain of custody is not known. The species cultivars cannot be specified, while the authors believe that this work exemplifies the difference between wheat straw and rice husk – there is a reasonable concern that there may be substrate factors that influence the results obtained if the work was performed with different cultivars, grown under different conditions.

2.2. Experimental procedure

2.2.1. Entrained flow reactor

The entrained flow study was carried out with the Baby High Temperature Entrained Flow Reactor (BabiTER) at TU Munich. The layout of the reactor is shown in Fig. 1 [26,27]. The BabiTER can be operated at atmospheric pressure and at a maximal temperature of 1600 °C. The particle residence time for the investigation in this work is below 1 s, calculated from the average gas residence time, and considering the effects of particle free fall velocity, velocity profile and biomass particle properties.

A defined gas mixture (2) is preheated (4) before entering the