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Influence of fast pyrolysis conditions on yield and structural transformation of biomass chars

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ABSTRACT

Fast pyrolysis of biomass (wood, straw, rice husk) and its major components (cellulose, hemicellulose, lignin) was conducted in a wire mesh reactor. The aim of this study was to understand the influence of temperature (350–1400 °C), heating rate (10–3000 °C/s), particle size (0.05–2 mm) and holding time (1–4 s) on the char morphology and char yield. Scanning electron microscopy (SEM) and elemental analysis were conducted to determine the effect of operating conditions on char softening and melting during pyrolysis. The char yield decreased with heating rate for rates ≤600 °C/s; above this value a similar biomass char yield was obtained. The potassium content affected the char yield stronger than other minerals, while the distribution of the three major biomass constituents (cellulose, hemicellulose, lignin) affected the char yield only to a minor degree. Moreover, it was found that the heat treatment temperature had a larger influence on the char yield than the heating rate. Scanning electron microscopy indicated different types of biomass char plasticization influenced by the applied temperatures, heating rates, particle sizes and holding times, except for the rice husk char that formed chars with a structure similar to the parental fuel at all conditions. The less severe morphological changes of rice husk char were attributed to a high silica content.

1. Introduction

Biomass and waste combustion are significant sources of renewable electricity supply in Denmark. Currently, Danish pulverized fuel fired power plants are in a transition to 100% biomass firing to reduce the emission of greenhouse gases. The utilization of biomass leads to a range of major technical challenges for the boiler and flue gas cleaning units, due to different chemical and physical properties compared to coal, reducing reliability and efficiency of power plants and creating limits for the amount of biomass that can be supplied to the power plant.

One of the major challenges is related to the quality of agricultural residues, with a higher ash content of problematic elements that may cause slagging and fouling. Another problem is the chemical structure and morphology of woody and herbaceous biomass, which may hamper grinding to small particle size fractions (<0.5 mm). Fine biomass milling is energy-consuming, and fibrous particles with low bulk densities may cause feeding problems. Large biomass particles may create challenges with flame stability, burnout and ignition [1,2]. The challenge of achieving high fuel conversion at short residence times depends on biomass origin, morphological changes of fuel particle of different sizes, char yield, fuel reactivity, heating rate, local oxygen concentration and temperature in the boiler [3,4].

Fast pyrolysis at high temperatures and heating rates is the initial step of the pulverized biomass combustion. Similar to coal combustion, the fuel burn out is known to be influenced by the yield and reactivity of chars, produced during pyrolysis [3]. The rapid heating of small biomass particles and the short residence time at high temperatures minimize the char yield and increase char reactivity [5]. The majority of previous investigations [3,6–19] referred to low-ash containing feedstocks (softwood, hardwood). The effects of heating rate and temperature on the morphological transformations at both slow (<10 °C/s) and intermediate and fast pyrolysis environments (>100 °C/s) of the same feedstock were rarely studied. Most studies report influences of operational conditions at high heating rate on the chemical structure and morphology of chars. The effect of char plastic deformation with the occurrence of melting was emphasized at high heating rates. The char fluidity of coal and lignin during pyrolysis was described by the FG-DVC model (Functional Group - Depolymerization, Vaporization and Cross-linking model) of Solomon et al. [20,21]. They pointed out that small differences in the cross-linking rate affect drastically the fluidity of the resulting metaplast. Cetin et al. [3] recalled the occurrence of biomass plastic deformation as an effect of a high heating rate and rated this phenomena in terms of char ability to melt (softwood > hardwood > bagasse).

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In the current fast pyrolysis study, the effects of temperature, heating rate, particle size, residence time, inorganic matter and major organic components of biomass on the char yield and morphology are investigated at high temperature conditions in a wire mesh reactor (WMR). The structural char transformations, particularly char fluidity, are characterized by scanning-electron microscope (SEM).

2. Materials and methods

2.1. Raw samples

Pinewood, beechwood, Danish wheat straw, leached Danish wheat straw, alfalfa straw and rice husk were used in this work to represent softwood, hardwood and agricultural residues. The low-ash containing wood (pinewood, beechwood) of syringyl (S) or guaiacyl–syringyl (GS) lignin types and grass (wheat straw, alfalfa straw, rice husk) of hydroxy phenol–guaiacyl–syringyl (HGS) lignin type, which are rich in K, Ca and Si elements, were selected to investigate the effect of differences in ash composition and organic matter (cellulose, hemicellulose, lignin) on the char yield and structural transformations. The fuels were milled on a Retsch rotor mill RZ200 and sieved to particle size fractions of 0.05–0.2 mm, 0.25–0.355 mm, 0.355–0.425 mm, 0.425–0.6 mm, 0.425–0.6 mm, 0.6–0.85 mm and 0.85–1 mm. 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 additionally improved from 90% to 96.6% by a three step procedure involving a strong alkali treatment, bleaching and acetylation. The proximate and ultimate analyses of the fuels are shown in Table 1.

The wheat straw was leached in deionized water (room temperature) by continuous stirring for 12 h, followed by drying at 30 °C in an oven desiccator without any ventilation. The mineral content after biomass leaching was determined by ash analysis. Due to the wheat straw leaching, the metal content was reduced to ≈ 60% of the original value and the Cl, S, K, Na and P contents were strongly reduced.

2.2. Biomass compositional analysis

The compositional analysis of biomasses (cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, protein and extractives) was conducted according to NREL technical reports [22–27] and Thammasouk et al. [28], and shown in Table 2.

Two different extractions were performed on the fuels using acetone or ethanol–water as a solvent (room temperature). The detailed procedure of extraction with acetone and ethanol-water is described in the supplemental material.

2.3. Experimental procedures

2.3.1. Wire mesh reactor

The effects of the particle size and holding time on the biomass char yield were studied on the wire mesh reactor at TU Munich [29]. A reconstructed version of the reactor was used to study the influence of the temperature and the heating rate on the char yield and the structural transformation of biomasses as shown in Fig. 1. The reconstructed wire mesh reactor could be operated at temperatures up to 1700 °C, heating rates up to 5000 °C/s, and pressures up to 50 bar, whereas the original WMR could be operated at temperatures up to 1400 °C, heating rates up to 3000 °C/s. The reconstructed wire mesh reactor encloses a tar collection filter at the top of the casing. The optical ports of the original wire mesh reactor were replaced with a cylindrical chamber to ensure a better sealing.

The cylindrical reactor chamber was enclosed into a stainless steel casing by six bolts. The welded stainless steel mesh (316 L, TWP Inc., mesh width of 0.042 mm) was bended in two equal-length parts, forming a small bag with a surface area of 20 mm × 20 mm. The bended mesh served as a sample holder and resistance heater. The sample temperature was monitored in dependency on the experimental heat treatment temperature by either a thermocouple type K (max. 1000 °C), type S (max. 1450 °C) or type B (max. 1700 °C) with a diameter of 0.051 mm. The two wires of a thermocouple (type K/S/B) were directly welded into the middle of the upper mesh side to determine the mesh temperature based on the Seebeck effect. The control system

Table 1
Proximate and ultimate analysis of fuels (on %dry basis) and ash analysis (on mg/kg dry basis).

Fuel	Pinewood	Beechwood	Wheat straw	Leached wheat straw	Alfalfa straw	Rice husk	Lignin wheat straw	Lignin softwood
Proximate and ultimate analysis (% db)								
Moisture[a]	5.1	4.5	5.5	4.3	5.2	4.5	4.4	6.1
Ash (550 °C)	0.3	1.4	4.1	2	7.4	21.7	3.6	1.3
Volatiles	86.6	79.4	77.5	84.2	75.9	64.3	66.3	67.3
HHV[b]	21.6	20.2	18.8	18.7	19.7	15.5	26.7	26.4
LHV[b]	20.2	19	17.5	17.4	16.9	14.5	25.5	25.2
C	50.5	46.7	42.4	45.7	42.5	35.5	61.8	64.6
H	6.8	6.3	6.3	6.6	6.1	5.5	3.8	5.3
N	0.1	0.3	1	0.3	3.3	0.1	1.4	0.8
Ash compositional analysis (mg/kg db)								
S	<0.01	0.02	0.1	0.02	0.03	0.03	0.8	0.1
Cl	0.01	0.02	0.1	0.01	0.5	0.05	0.03	0.5
Al	10	10	150	100	600	70	300	100
Ca	600	2000	2500	1300	12,900	750	200	250
Fe	20	10	200	350	–	80	1400	600
K	200	3600	11,000	1300	28,000	2500	270	80
Mg	100	600	750	350	1400	400	40	<30
Na	30	100	150	50	1000	70	6800	4100
P	6	150	550	80	1900	600	30	30
Si	50	200	8500	6200	2000	98,500	4000	900
Ti	2	<8	10	10	30	5	100	50

[a] wt.% (ar).
[b] In MJ/kg.