Fuel Processing Technology 143 (2016) 118–129

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Effect of fast pyrolysis conditions on biomass solid residues at high temperatures

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ARTICLE INFO

Article history:
Received 29 August 2015
Received in revised form 28 October 2015
Accepted 10 November 2015
Available online 3 December 2015

Keywords:
Fast pyrolysis
Drop tube furnace
Wire mesh reactor
Soot
CAMSIZER XT

ABSTRACT

Fast pyrolysis of wood and straw was conducted in a drop tube furnace (DTF) and compared with corresponding data from a wire mesh reactor (WMR) to study the influence of temperature (1000–1400)°C, biomass origin (pinewood, beechwood, wheat straw, alfalfa straw), and heating rate (10^3 °C/s, 10^4 °C/s) on the char yield and morphology. Scanning electron microscopy (SEM), elemental analysis, and ash compositional analysis were applied to characterize the effect of operational conditions on the solid residues (char, soot) and gaseous products. The char yield from fast pyrolysis in the DTF setup was 3 to 7% (daf) points lower than in the WMR. During fast pyrolysis pinewood underwent drastic morphological transformations, whereas beechwood and straw samples retained the original porous structure of the parental fuel with slight melting on the surface. The particle size of Danish wheat straw char decreased in its half-width with respect to the parental fuel, whereas the alfalfa straw char particle size remained unaltered at higher temperatures. Soot particles in a range from 60 to 300 nm were obtained during fast pyrolysis. The soot yield from herbaceous fuels was lower than from wood samples, possibly due to differences in the content of lignin and resin acids.

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. Unlike coal, biomass is difficult to mill to <100 μm due to its fibrous structure, resulting in higher energy consumption for the comminution process. The shape and size distribution of ground biomass particles consists of a larger fraction of flake- and cylinder-like particles with a particle size >300 μm. In biomass suspension firing, it is a challenge to achieve high fuel conversion at the short residence time while minimizing the input for milling. This is further challenged by application of a broad biofuel range to obtain high operational flexibility at power plants. Thus an increased energy input into the biomass comminution process affects the total efficiency of a power plant, and large particle sizes may cause problems with flame stability and burnout.

In suspension firing, biomass particles are heated rapidly to high temperatures of 1000–1400 °C, leading to volatile release and formation of solid residues (char and soot) during devolatilization. The solid residue yield and its properties, including particle size and shape, composition, reactivity and burnout, depend strongly on the operational conditions of fast devolatilization [1–4]. A number of studies [5–11] have investigated structural changes of different biomass types and their plant cell components during fast pyrolysis. Sharma et al. [5–7,12] reported structural changes of lignin and tobacco char at temperatures up to 750 °C with rapid heating rates, accompanied by softening and melting of a solid phase. The effect of char plasticization was observed mostly at high heating rate of pyrolysis (>10^3 °C/s) [8,9,13–15]. 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. [16,17]. They pointed out that the char fluidity is influenced by small differences in the cross-linking rate with oxygen, affecting cross-linking and preventing char fluidity [18].

Previous investigations of biomass pyrolysis [9,15,19,20] ascribed the char structural transformations and changes in reactivity to the catalytic effect of minerals (K, Ca, Mg and Si). Wornat et al. [19] reported migration of alkali and alkaline earth metals to the particle surface for high oxygen content fuels, with the formation of beads on the char shell, accompanied by a highly cross-linked carbon structure that hindered crystallite mobility and graphitization during combustion. Dall'Ora et al. [9] studied fast pyrolysis of beechwood in an entrained-flow reactor, and concluded that calcium and potassium catalyze cross-linking, resulting in a higher char yield and less severe char morphological changes.

In the present study the relation between different types of biomass and their solid residue (char, soot) properties was investigated. Char

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http://dx.doi.org/10.1016/j.fuproc.2015.11.002
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and soot yields were obtained from fast pyrolysis in a drop tube furnace (DTF). The char yields from the DTF were compared with results from a wire mesh reactor (WMR) [21] at temperatures >1000 °C to study the simultaneous effect of temperature, heating rate, and biomass origin on the char yield. The influence of extractives on the structural changes, on which available literature is not extensive, was also studied using char from the DTF. This work also attempted to fill a gap about the effect of biomass origin on the soot formation during fast pyrolysis. The influence of ash composition, particularly of K and Ca elements, on the char morphological changes under fast heating was characterized by SEM and TEM microscopy.

2. Materials and methods

2.1. Original biomass characterization

Pinewood, beechwood, Danish wheat straw, and alfalfa straw were selected for the fast pyrolysis study in the DTF and WMR. 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 [21]. The leached wheat straw was selected to study the influence of alkali on the char and soot yields.

The proximate and ultimate analyses of fuels are shown in Table 1. The fuels were milled on a Retsch rotor mill RZ200 and sieved to a particle size fraction of 0.2–0.425 mm. The wood and herbaceous fuels were selected for the present study, based on the differences in organic and inorganic matter. The compositional analysis of 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], and shown in Table 2.

The water-ethanol extraction was performed on wheat straw and alfalfa straw which contain a high level of hydrophilic and lipophilic extractable compounds as described by Thammasouk et al. [25]. Extraction with acetone on pinewood and beechwood was done for the quantitative estimation of extractives in the original biomass, and to remove resin and fatty acids, waxes, and phytosterols for the investigation of char structural changes under fast heating as described in the supplemental material.

2.2. Experimental apparatus and procedure

2.2.1. Drop tube furnace

The Drop Tube Furnace (DTF) used in the present study is shown in Fig. 1. The cylindrical reactor tube was made of alumina ceramic (grade C799) with an inner diameter of 54 mm. The reactor tube was heated by tube furnace modules using SiC rods as heating elements (Elite Thermal Systems Ltd.) with a maximum temperature of 1500 °C. Supply of primary gas was led through the biomass feeder, and secondary gas was led to the top of the reactor through a packed bed of ceramic balls that distributed the gas flow equally in the radial direction. Inlet gas flows of O_2, N_2, H_2, CO and CO_2 were controlled by mass flow controllers (EL-FLOW® Select, Bronkhorst High-Tech B.V.), while the flow rate of H_2O was controlled by a syringe pump (Legato 100, KD Scientific Inc.). A syringe pump type biomass feeder was used to supply biomass at low feeding rates [26]. The feeding probe was water-cooled at 20 °C to ensure a high heating rate of the biomass when it entered the reactor. The Reynolds number of the gas flow inside the reactor was 60–100, dependent on the reaction temperature.

Biomass was rapidly heated and reacted while it fell down through the reactor. Reaction products were separated into coarse particles (mainly char and fly ashes), fine particles (mainly soot and precipitated ash vapor), and permanent gases. Soot particles passing the cyclone (cut size 2.5 μm) were captured from the product gas flow by a grade QM-A quartz filter with a diameter of 50 mm (Whatman, GE Healthcare Life Science). The larger particles (e.g. char) could either fall down to a char bin or a stainless steel cyclone with cut size of 2.5 μm (URG-2000-30ENS-1, URG Corporation). After an activated carbon filter (VACU-GUARD 150, GE Healthcare Life Science), the gas composition was measured by a micro gas chromatograph (Model 490, Agilent Technologies). The μGC was equipped with two columns (CP-MolSieve 5 A for H_2, O_2, N_2, CH_4 and CO; and PoraPlot U for CO_2, C_2H_4, C_2H_6, C_2H_2, and C_3H_6/C_3H_8) and thermal conductivity detectors. The temperature of the char bin and product gas was controlled by heating controllers (HTC-5500, Hemi Heating AB) with thermo-tapes (S-type, Hemi Heating AB) and kept at 200 °C to avoid tar condensation.

Table 1
Proximate, ultimate and ash analyses of fuels.

Fuel	Pinewood	Beechwood	Wheat straw	Alfalfa straw	Leached wheat straw	Pinewood*	Beechwood*
Proximate analysis							
Moisture, (wt.% ar)	5.1	4.5	5.5	5.2	4.3	5.1	5.1
Ash (550 °C), (wt.% db)	0.3	1.4	4.1	7.4	2	0.3	1.5
Volatiles, (wt.% db)	86.6	79.4	77.5	75.9	84.2	84.9	79.3
HHV, (MJ/kg)	21.6	20.2	18.8	19.7	18.7	20.3	20.3
LHV, (MJ/kg)	20.2	19	17.5	16.9	17.4	19	19
Ultimate analysis, (wt.% db)							
C	53.1	50.7	46.6	42.5	45.7	50.1	50
H	6.5	5.9	6.1	6.7	6.6	6	5.8
O	40	41.9	42.5	43.1	45.4	43.5	42.6
N	0.06	0.13	0.6	0.3	0.3	0.05	0.08
S	<0.01	0.02	0.1	0.03	0.02	0.008	0.019
Ash compositional analysis, (mg/kg, db)							
Cl	0.01	0.02	0.1	0.5	0.01	0.005	0.02
Al	10	10	150	600	100	8.3	15.9
Ca	600	2000	2500	12,900	1300	620	2090
Fe	20	10	200	–	350	8	10
K	200	3600	11,000	28,000	1300	250	3700
Mg	100	600	750	1400	350	120	610
Na	30	100	150	1000	50	60	150
P	6	150	550	1900	80	25	120
Si	50	200	8500	2000	6200	33	200
Ti	2	8	10	30	10	1	4

* After extraction.