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Research paper

The influence of different chemical compositions in biomass on gasification tar formation

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ABSTRACT

To elucidate the relationship between biomass composition and tar formation, forest residue sawdust, rich in lignin, and agriculture waste cornstalks, rich in cellulose, were gasified in a spout-fluidized bed reactor from 700 °C to 900 °C. Gel permeation chromatography (GPC) coupled with a photodiode array detector (PDA) and gas chromatography – mass spectrometry (GC–MS) were used to analyze the tar character. The GPC results showed that the molecular mass distribution of the gasified tars were unchanged, only the amount of each component changed when the temperature increased during gasification. The amount of heaviest molecular mass components decreased, while the lighter components increased with temperature. Sawdust tar and cornstalks tar both showed aromatic character, while cornstalks tar contained more aliphatic compounds than sawdust tar. The tar formation mechanism has been proposed from the experimental data analysis.

1. Introduction

Tar is currently the primary bottleneck to commercialization of biomass gasification, in addition to tar fouling and eroding process equipment, tar formation also wastes 5–15% of the effective energy from biomass gasification. It contradicts the green and sustainable character of biomass [1–4]. On the other hand, tar compositions provide significant chemical information for thermochemical processes – the knowledge of different biomass tar formation could help us adjust the rate-determining step of tar deposition, so that we can control tar production. The raw material properties are important factor that affects the products distribution. Drift [5] demonstrated the water content in biomass was the most important parameter affecting carbon conversion, cold gas efficiency, and high heating value of product gas by using ten biomass raw materials. The tar content has no straightforward correlation with equivalence ratio, particle size, or H/C ratio. While, Herguido etc. [6,7] showed the porosity of particle affected the tar content based on oak tree and bagasse gasification tests. They deduced the lower porosity of the oak particles, as opposed to the bagasse ones would make the tars remain a longer time in the particles of lower porosity. More tar would thus be cracked in the particle and converted into gases. Some researchers [8–10] used pure cellulose, hemicelluloses and lignin as samples to investigate the tar formation. The conclusion is the bio-oil yield was proportional to the content of cellulose during biomass pyrolysis. Yang [11] and Hosoya [12,13] researched secondary reactions of the primary tar using pure cellulose and lignin on a molecular basis. They concluded unsaturated side-chain and phenolic aromatic rings were the primary tar fraction derived from lignin and were easily converted to condensed products. The tar components from cellulose were readily gasified into gases.

In this paper, two kinds of biomass, one rich in cellulose, the other rich in lignin, were gasified under similar conditions for investigating the tar formation mechanism. The fresh tar was quenched after it just emitted out from the spout-fluidized bed. The tar can provide enough information about the thermal process due to the short residence time in the heating area. The structure of whole molecular mass (MM) and molecular mass distribution of tar was investigated with gel permeation chromatography (GPC) coupled with photodiode array detection (PDA) and gas chromatography – mass spectrometry (GC–MS). Based on the analysis

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results, the tar formation mechanism is proposed. Information about the tar formation mechanism is beneficial for the development of tar gasification and cracking kinetics.

2. Experimental

2.1. Sample and analysis

The gasification feedstocks were a forest residue, poplar sawdust, obtained from a lumber mill, and an agricultural waste, cornstalks, collected directly from a field. The sawdust was the heartwood and sapwood of the poplar, obtained from a lumber mill and kept in a dry and well-ventilated laboratory for one and half a years. The particle size of the biomass samples was 80–124 μm in order to fit the gasifier feeder. Samples were dried at 80 °C in the oven overnight before being charged to the hopper. The properties of the samples are given in Table 1. The proximate analysis was performed following the China State Standard GB/T 212–2008, and the ultimate analysis was performed with a Vario EL (I) elemental analyzer. The Van Soest acid detergent fiber method [14] was used to analyze the fiber component. Briefly, extractions were conducted in the order of neutral detergent fiber (NDF), acid detergent fiber (ADF), and acid detergent lignin (ADL). Based on this procedure, contents of neutral detergent soluble (NDS), hemicellulose, cellulose, and lignin were calculated. Table 1 shows that the two materials had similar proximate and ultimate analyses, but the content of components was different. Lignin was the most abundant component in sawdust, while cellulose was the greatest portion in cornstalks.

2.2. Apparatus and experimental method

The schematic diagram of bench scale spout-fluidized bed reactor is shown in Fig. 1. Detailed information about the spout-fluidized bed reactor was shown in the references [15,16]. The main part of reactor consists of a 34 mm (i.d.)*500 Incoloy 800 stainless steel tube. A 26 mm (i.d.) loosely fitted quartz liner was put into the stainless steel tube. The quartz tube supporter fit well with the hole at the bottom of the quartz liner, where the sample and air/argon were introduced into the reactor. Wire mesh was put on the top of the quartz tube to prevent the small particles flying out of the reactor.

After the reactor reached the desired temperature, and the gas flow stabilized, the sample was continuously fed into the reactor by a screw feeder at a constant rate, with argon and air as fluidizing gases at the flow rate of 28 mL/S. The equivalence ratio was kept for sawdust 0.28–0.29 and corncob 0.18–0.19, separately. The gasification temperature was increased from 700 °C to 900 °C with 50 °C intervals for each respective experiment. The gas residence time in the hot area was 1.36 S–1.13 S from 700 °C to 900 °C under standard state. The tar trap, consisted of a 16 mm diameter tube packed with wire-mesh, cooling by the acetone-and-ice mixture (about −15 °C), was fixed at gas outlet to condense the biomass syngas. After each experiment, the tar trap, mesh, and tube were washed with a chloroform/methanol (1:3) solvent until the mixed solvent had not changed color. The solvent was then evaporated and the tar was weighed to calculate the tar yield. The tar resoluted in the 8 mL mixed solvent again and kept in the refrigerator. Tar components' molecular mass and molecular mass distribution were analyzed by GPC-PDA, and the analysis method can be seen in the literature [15,16]. The detailed compositions were analyzed with a HP 6890^{+} gas chromatograph equipped with a HP 5-MS capillary column (30.0 m × 250 μm, with 0.25 μm 5% phenyl methyl siloxane stationary phase film). Samples were injected splitless with the injector temperature of 230 °C. The gas chromatograph was directly connected to a HP 5973 mass spectrometer working in electron impact ionization mode at 70 ev, and scanned masses in the range of 50–500 amu. The carrier gas was helium with a flow rate of 0.5 mL min^{-1}. The temperature program was as follows: the initial temperature of 80 °C was held for 2 min, followed by a temperature ramp to 180 °C at 20 °C min^{-1}, another ramp to 250 °C at 15 °C min^{-1}, and then held for 10 min. The solvent delay was set to 3 min. For each analysis, a 0.1 μL tar sample was injected into the GC–MS. Data was acquired in a full scan mode and processed with the HP Chemstation software. The identification of the peaks was based on computer matching of the mass spectra with the NIST library. Quantization of the compounds was performed by integration of appropriate peak areas in total ion chromatograms (TIC).

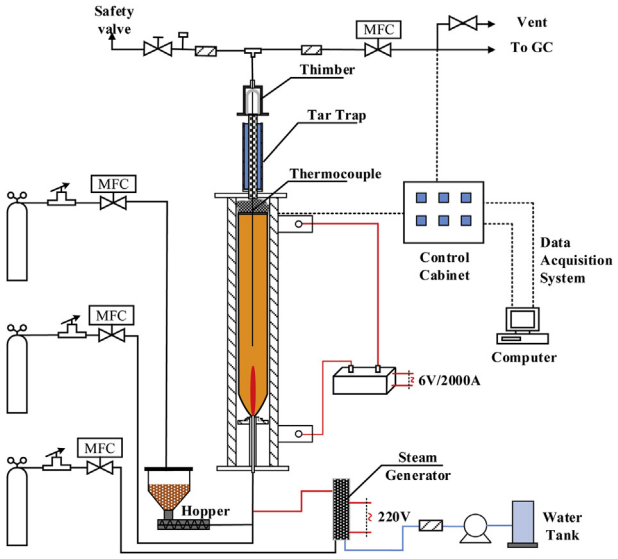

Fig. 1. Schematic diagram of the spout-fluidized bed reactor.

Table 1
Chemical Analysis of the sawdust and cornstalks.

Sample		Sawdust	Cornstalks
Proximate analysis (wt%, ar)	Moisture	3.17	7.74
	Ash	2.17	8.94
	Volatile	69.12	75.70
	Fixed carbon	25.54	7.62
Ultimate analysis (wt %, daf)	C	48.37	46.09
	H	5.75	6.58
	O[a]	45.53	44.85
	N	0.25	1.87
	S	0.10	0.61
Composition analysis (wt %, ar)	Cellulose	17.99	31.53
	Hemicellulose	12.59	25.86
	Lignin	33.88	13.99
	NDS[b]	33.29	25.52
	AIA[c]	2.25	3.10

[a] By difference.
[b] NDS (Neutral Detergent Solute) contains: fat, starch, polysaccharide, protein.
[c] AIA: Acid-Insoluble Ash.

3. Results and discussion

3.1. Tar yield

The tar yield was calculated by the dry weight of tar divided by the weight of biomass raw material (dry basis). Fig. 2 shows that the tar yield of both samples decreased with an increase in