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Short Communication

Understanding the stability of pyrolysis tars from biomass in a view point of free radicals

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HIGHLIGHTS

- The bio-tars contain large amounts of radicals at a level of 10^{16} spins/g.
- The bio-tars generate more radicals and coke at temperature of 573 K or higher.
- The behavior of tar radicals indicates that they are rich in weak covalent bonds.
- The coke formed in the bio-tars contain radicals.

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ABSTRACT

Fast pyrolysis of biomass has attracted increasing attention worldwide to produce bio-tars that can be upgraded into liquid fuels and chemicals. However, the bio-tars are usually poor in quality and stability and are difficult to be upgraded. To better understand the nature of the bio-tars, this work reveals radical concentration of tars derived from pyrolysis of two kinds of biomass. The tars were obtained by condensing the pyrolysis volatiles in 3 s. It shows that the tars contain large amounts of radicals, at a level of 10^{16} spins/g, and are able to generate more radicals at temperatures of 573 K or higher, reaching a level of 10^{19} spins/g at 673 K in less than 30 min. The radical generation in the tar samples is attributed to the formation of THF insoluble matters (coke), which also contain radicals. The radical concentrations of the aqueous liquids obtained in pyrolysis are also studied.

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1. Introduction

Biomass pyrolysis is commonly regarded as a simple and an effective method to produce bio-tars and consequently fuels and chemicals, and fast heating speeds up the process and results in a higher tar yield (Tsai et al., 2007; Heo et al., 2010; Kader et al., 2013; Duman et al., 2011). Many fast pyrolysis processes have been developed worldwide, including fluidized bed, moving bed, transported bed and rotating cone with scales up to thousands kg/h, such as Ensyn of Canada (4000 kg/h) and Dynamotive of Canada (8000 kg/h) (Bridgwater, 2012). It was found, however, that bio-tars collected in most of the processes are poor in quality (Cao et al., 2011; Ben and Ragauskas, 2013) and in stability (Bridgwater, 2012; Czernik and Bridgwater, 2004; Jahirul et al., 2012) and are difficult to be upgraded at an acceptable cost. Furthermore product lines of pyrolysis reactors were frequently found to be clogged by solid formation causing operation and safety problems (Oasmaa and Czernik, 1999; Kechagiopoulos et al., 2006). Extensive technical efforts have been made to solve these problems but the improvements were often unsatisfactory. New insight especially on the fundamental chemistry of pyrolysis is, therefore, important to tackle these problems.

Although biomass pyrolysis mechanisms proposed involve the generation of radical fragments, (Demirbas, 2000; Amen-Chen et al., 2001) limited information on the radicals can be found in the literature (Bakr et al., 1991). In principle, volatiles generated from biomass pyrolysis contain free radical fragments and coupling of the free radical fragments forms final products, such as the tar. However, it is likely that the tars still contain free radical fragments due to incomplete coupling reaction before its condensation, and this may become more significant in fast pyrolysis

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Table 1
Lignocelluloses content of the biomass and ultimate analyses of the biomass and the liquid pyrolysis products.

Raw materials	Lignocellulose content (%)			Ultimate analysis (wt.%, daf)				
	Lignin	Cellulose	Hemicellulose	C	H	N	O[a]	S
Walnut shell (WS)	31.7	13.8	16.6	53.1	3.2	1	42.3	0.4
Corncob (CC)	13.8	22.5	22.1	53.6	3.2	1	41.9	0.3
WS tar	–	–	–	54.7	7.1	0.3	37.8	<0.1
CC tar	–	–	–	53.3	7.1	0.6	38.9	<0.1
WS aqueous liquid	–	–	–	22.9	9.2	0.1	67.7	<0.1
CC aqueous liquid	–	–	–	27.5	8.7	0.3	63.4	<0.1

[a] By difference.

(Bridgwater et al., 1999; Mohan et al., 2006) due to the high heating rate of biomass and the short residence time of the volatiles. Radicals in tars are unstable and react even at the room temperature, which may lead to the poor quality and stability of the tars (Usmen and Khan, 1989; Yokono et al., 1983; Yamada et al., 1984) and clogging of the product lines.

To understand the radical behavior of biomass tars and to verify the above hypothesis, this work studies the radical concentrations of tars and aqueous liquids obtained from pyrolysis of two types of biomass, including changes in radical concentration of them at temperatures similar to that of the pyrolysis reactor, the high temperature product lines and the high temperature vapor-dust removal units.

2. Methods

2.1. Sample preparation

The biomass used is walnut shell (WS in short) and corncob (CC in short). They were ground to sizes less than 0.3 mm and dried at 383 K in a vacuum for 4 h. The compositions and ultimate analyses of the biomass are shown in Table 1. As expected, WS contains more lignin than CC does.

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out in a quartz tube reactor that contains a quartz crucible loaded with 7 g biomass sample. The experiment started by inserting the quartz tube into a furnace preheated to 873 K and ended when the temperature of the biomass reaches 813 K. The volatiles generated from the pyrolysis were purged by a flow of N_2 at a rate of 200 mL/min, which allows the volatiles been condensed at the cold end of the quartz tube in about 3 s. The condensed volatiles, the tar and the aqueous liquids, were sampled by capillaries of 1 mm in diameter separately and weighed. The sample-loaded capillaries were then sealed and stored in liquid nitrogen. The ultimate analyses of the tars and the aqueous liquids are also shown in Table 1.

2.3. ESR measurements

The Electron Spin Resonance (ESR) spectrometer used is JES FA 200 (JEOL, Japan) operated at 9.5 GHz and 0.998 mW. The central magnetic field is 337 mT, the sweep width is 7.5 mT, the sweep time is 1 min, and the time constant is 0.03 s. The samples were measured at 298 K and the results were calibrated by DPPH. The sample capillaries showed little influence on the samples' ESR results.

2.4. Treatments of the liquid samples

To simulate the high temperature environment the volatiles would experience in large pyrolysis reactors, such as the void space in the reactor, the product lines, and the dust removal units, the tars (sealed in the capillaries) were kept at temperatures of 293, 373, 473, 573, 623, 673, and 723 K and their radical concentrations were measured during a 4 h period. The use of the long treatment time is to better reveal the kinetic behavior of the radical reaction. Due to the high vapor pressure of water at high temperatures, the aqueous products were kept only at 573 K to avoid rupture of the capillary. The tar and the aqueous liquid samples treated at these temperatures for different time were extracted by tetrahydrofuran (THF) for 12 h to remove the THF soluble matters. The THF insoluble matters were dried at 353 K in a vacuum for 4 h and weighed, and their radical concentrations were determined.

3. Results and discussion

Table 2 shows the radical concentrations of the raw biomass and the condensed pyrolysis volatiles, as well as those kept at the ambient temperature for 2 weeks. The radical concentrations of the two biomass are similar, about 6×10^{16} spins/g. The radical concentration of the WS tar is twice as much as that of the CC tar, at the level of 10^{16} spins/g, due probably to WS's high lignin content. The radical concentration of the tars doubled in 2 weeks, and the color of the tars changed from brown to dark brown while the radical concentration of the biomass changed little in the period. This difference may be ascribed to the difference in mobility of the radicals, mobile in the tars but immobile in the biomass. The increase in radical concentration in the tars may be resulted from reactions of the tars with oxygen that may have been trapped in the tars during the sampling. The reaction was reported in the literatures for coal tars (Usmen and Khan, 1989). These data indicate that the poor stability of the tars may be attributed, at least partly, to their high radical concentrations as reported (Usmen and Khan, 1989; Yokono et al., 1983; Yamada et al., 1984) and evidenced by the fact that the stable commercial fuels such as diesel and gasoline contain no radical and do not generate radicals at the ambient temperature. The aqueous liquids contain few radicals and do not generate radicals at the ambient temperature in 2 weeks due probably to their low organic contents, which are mainly oxygenates.

Table 2
Radical concentration of the biomass and the pyrolysis liquids.

	Sample	Radical concentration ($\times 10^{16}$ spins/g)	
		WS	CC
Fresh	Biomass	6.1	5.8
	Tar	3.2	1.3
	Aqueous phase	0	0
After 2 weeks at the ambient temperature	Biomass	6.1	5.9
	Tar	5.8	2.7
	Aqueous phase	0	0

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