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A comparative investigation into the formation behaviors of char, liquids and gases during pyrolysis of pinewood and lignocellulosic components

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HIGHLIGHTS

- Lignin accelerated the decomposition of cellulose.
- Complex componential interactions occurred during pine wood pyrolysis.
- Pine wood-derived char was more inhomogeneous in the constituents.
- Pine wood produced more bio-oil than xylan, cellulose and ADF.
- ADF- and pine wood-derived bio-oils were less oxygenated.

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ABSTRACT

The pyrolysis characteristics of xylan, cellulose, ADF (a mixture of cellulose and lignin extracted from pine wood) and pine wood were investigated in a fixed-bed reactor by determining the distributions of three-phase products, the elemental compositions of char products, the conversions of components and the profiles of gas release rate during pyrolysis as well as the compositions of liquid products. Interactions were found to occur between the different components. Lignin accelerated the release of CO_2 and CO from cellulose and intensified the decomposition of cellulose to smaller molecular weight liquid compounds. Pine wood exhibited the componential interactions, resulting in the broadened temperature range of mass loss, the enhanced yield of char, and the increased heterogeneity of char. Pine wood produced more bio-oil than each component sample, with the compositional formula of $CH_{1.07}O_{0.31}$. The formation of liquid compounds from pine wood was also observed to be influenced by the componential interactions.

1. Introduction

Biomass as a renewable and carbon-neutral energy resource has recently received a considerable interest over the world. Many advanced technologies are being vigorously developed to modernize the inherited and laggard patterns of biomass utilization (Mohammad et al., 2012). Pyrolysis is an important thermochemical conversion process, which is promising particularly for the conversion of lignocellulosic biomass to solid product (bio-char), liquid product (bio-oil), and gaseous product. The pyrolysis products become more energy-intensive and easier to transport and handle, and thus are more useful and more efficient in use. Moreover, the pyrolysis process is versatile to optimize three-phase products in their yields and properties for match with downstream processing to a wide range of value-added products, such as transportation fuels and fine chemicals.

On the other hand, biomass pyrolysis is a complex process involving in almost innumerable reactions of degradation, depolymerization, decomposition, recombination, isomerization, repolymerization and condensation occurring in both fixed phase (solid) and dynamic phase (gas and liquid). The pyrolysis behaviors are influenced by a multitude of conditional parameters, such as heating rate, final temperature, residence time and catalyst (Mythili et al., 2013; Pasangulapati et al., 2012; Stefanidis et al., 2014; Wang et al., 2013, 2009). The complexity is also due to the compositional diversity of biomass (Sanchez-Silva et al., 2012). In general, lignocellulosic biomass is composed of three main components (hemicellulose, cellulose and lignin), with some extractives. The different pyrolysis characteristics of individual components in company with their interactions lead to multivariable scenarios in the distributions, compositions and properties of products. To design an efficient biomass thermoconversion process toward the

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production of desired products, it is essential to understand the pyrolysis behaviors of individual components and their interactions.

Numerous researches have addressed the pyrolysis characteristics of hemicellulose, cellulose and lignin. One aspect is the thermal stability of three components (Cao et al., 2014; Lv et al., 2013; Raveendran et al., 1996; Shen and Gu, 2009; Yang et al., 2007). Hemicellulose is a polysaccharide consisting of pentose and hexose monomers (e.g., xylose, galactose, mannose, and arbinose) and their acidified forms (e.g., glucuronic acid and galacturonic acid). It is affirmed to be a labile component due to its amorphous structure unlike crystalline cellulose (Ebringerová et al., 1992; Peng and Wu, 2010). Lignin, a cross-linked polymer of aromatic alcohols, contains thermally unstable and resistant functional groups so that the decomposition covers a wide range of temperature (Lv et al., 2013; Yang et al., 2007). A more important aspect is the distributions and compositions of three-phase products from individual components. Lignin is known as a good precursor of char production, while cellulose is highly volatile (Raveendran et al., 1996; Wang et al., 2011). The release profiles and productivities of gases (H_2, CO_2, CO, CH_4, etc.) from individual components have been extensively investigated using TG–FTIR and fixed-bed reactor (Shen and Gu, 2009; Xin et al., 2013; Yang et al., 2007). Yang et al. (2007) reported that hemicellulose (xylan) had higher CO_2 yield, cellulose generated higher CO yield, and lignin owned higher H_2 and CH_4 yield. To understand the reaction pathways and mechanism of biomass pyrolysis, researchers have devoted to characterizing the compositions of bio-oils derived from individual components. Acids, furans and ketones are the typical liquid compounds formed from hemicellulose in the case of less severity of secondary pyrolysis (Shen et al., 2010). Levoglucosan is an initial product degraded from cellulose, and it can be subsequently cracked to low molecular weight volatiles (Brandbury et al., 1979; Pasangulapati et al., 2012). Guaiacols and phenols are mainly ascribed to the breakage of lignin (Stefanidis et al., 2014). However, a bio-oil produced from even a single component generally contains copious oxygenated compounds depending on pyrolysis conditions. This makes it difficult to quantitatively determine all compounds in bio-oil.

There is a rationale that the pyrolysis of a biomass holds an additive result if the interactions of components in it can be ignored. Raveendran et al. (1996) argued from the mass loss profiles and the product distributions that there was no noticeable interaction between the components during pyrolysis in both the TGA and the packed bed reactor. Stefanidis et al. (2014) observed on the TGA that the final char yields of the component mixture could be predicted from those of individual components in an additive way, but the DTG curves displayed limited heat transfer when using the mixing sample. In recent years, however, several studies have justified the interactions between different components from the yields of liquid compounds. Hosoya et al. (2007, 2009) found that lignin suppressed the polymerization of cellulose-derived levoglucosan and accelerated the gas formation; cellulose in turn reduced the char formation of lignin along with more production of lignin-derived liquids such as guaiacols. While Hosoya et al. observed weak interaction between cellulose and hemicellulose, some studies indicated the inhibitory effect of hemicellulose on the formation of altrose and levoglucosan from cellulose and the cellulose-promoted formation of hemicellulose-derived acetic acid and furfural (Liu et al., 2011; Wang et al., 2011).

In this work, a special effort is made to quantify the yields and compositions of all three-phase products in a unified experiment, for a better understanding of the relationships between the formations of three-phase products and the elemental partitions to three-phase products. Since the commercial reagent of lignin is commonly alkalized or acidified, which is likely to be much different in nature with lignin in pine wood, a specific sample of cellulose and lignin mixture (ADF) isolated gently from pine wood is used in the study. Comparison has therefore been made between biomass components and pine wood to correlate their pyrolysis characteristics and to reveal the interactions between different components. Moreover, the conversions of different components during pyrolysis are examined by an extraction method.

2. Experimental

2.1. Materials

The pine wood sample was the sawdust waste collected from a local wood processing factory in Shanghai, China. The pine wood sample was sieved to the particle size of about 0.15–0.45 mm. The pine wood sample used in all experiments was dried at 105 °C to a constant weight. The samples of cellulose and xylan were purchased from Aladdin Ind. Co. The cellulose sample was a white powder with the particles size of around 0.19 mm. The xylan sample was a white powder with the particle size of less than 0.15 mm. From the sample instruction, the xylan sample was separated from birch wood. The sample of a mixture of cellulose and lignin (ADF) was obtained by complete removal of extractives and hemicellulose from the pine wood sample used. The extraction method is described in the next section. The proximate and ultimate analyses of the four samples (pine wood, cellulose, xylan, and ADF) are shown in Table 1. The contents of main components in the four samples are shown in Table 2. It should be pointed out that xylan, although generally a representative sample of hemicellulose, behaves unlike hemicellulose in the solubility. The xylan sample is entirely soluble in an aqueous solution of sodium lauryl sulfate like a neutral detergent solute (NDS), whereas hemicellulose inherent in biomass is classified to be insoluble in this solution.

2.2. Determination of fiber components

A national standard method of China (GBT-20805-2006) was used to determine the main components in the four samples used in this study. This method is widely applied to determine the fiber constituents in various vegetable feeds such as forages and foodstuffs. In this method, a biomass is divided into four main components, neutral detergent solute (NDS), hemicellulose, cellulose, lignin, with residual ash (silicate). The main procedures are described elsewhere (Shi et al., 2012) and outlined as follows.

A segment of biomass sample is used to extract out NDS by refluxing in a neutral detergent (3% sodium lauryl sulfate). The extractive (NDS) is typically composed of saccharide, starch, fat and various nutrients (protein, terpene, etc.). The insoluble remainder obtained after removal of NDS is termed neutral detergent fiber

Table 1
Properties of biomass samples.

	Xylan	Cellulose	ADF	Pine wood
Proximate analysis (wt.%, dry basis)				
Volatile	93.6	93.9	78.5	87.2
Fixed carbon[a]	6.3	6.1	21.1	12.3
Ash	0.1	–	0.4	0.5
Ultimate analysis (wt.%, daf. basis)				
C	43.9	44.3	52.5	51.8
H	6.4	6.2	6.4	6.3
O[a]	49.5	49.5	40.8	41.7
N	–	–	0.3	0.3
S	0.2	–	–	–

[a] By difference.