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Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor

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HIGHLIGHTS

- Pretreated eucalyptus wood gave higher bio-oil yield than original eucalyptus wood.
- Contents of ketones and acids in bio-oil were lowered by hydrothermal pretreatment.
- Hydrothermal pretreatment significantly enhanced levoglucosan content in bio-oil.
- Hydrothermal pretreatment improved fuel quality of bio-oil.

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ABSTRACT

Eucalyptus wood powder was first subjected to hydrothermal pretreatment in a high-pressure reactor at 160–190 °C, and subsequently fast pyrolyzed in a fluidized bed reactor at 500 °C to obtain high quality bio-oil. This study focused on investigating effect of hydrothermal pretreatment on bio-oil properties. Hemicellulose and some metals were effectively removed from eucalyptus wood, while cellulose content was enhanced. No significant charring and carbonization of constituents was observed during hydrothermal pretreatment. Thus pretreated eucalyptus wood gave higher bio-oil yield than original eucalyptus wood. Chemical composition of bio-oil was examined by GC/MS and ^{13}C NMR analyses. Bio-oil produced from pretreated eucalyptus wood exhibited lower contents of ketones and acids, while much higher levoglucosan content than bio-oil produced from original eucalyptus wood, which would help to improve thermal stability of bio-oil and extract levoglucosan from bio-oil. Hydrothermal pretreatment also improved bio-oil fuel quality through lowering water content and enhancing heating value.

1. Introduction

The growing concern with depletion of fossil fuels and global climate change provides impetus to the use of renewable biomass resources, and great efforts are placed on the production of chemicals and liquid fuels from biomass through a variety of possible conversion approaches (McKendry, 2002; Maniatis and Millich, 1998). Fast pyrolysis as a thermochemical procedure has become a candidate pathway for producing chemicals and fuels from biomass. By this process up to 70–80% of the dry biomass can be directly converted into a liquid fuel called bio-oil that is readily stored and transported (Bridgwater and Peacocke, 2000; Uzun et al., 2006). In general, this process is conducted in the absence of oxygen at the carefully controlled temperature of around 500 °C with very high heating rates (>100 °C/s), short hot vapours residence times inside the reactor (typically less than 2 s) and rapid cooling of vapour (Bridgwater, 2012). The resulting bio-oil is a dark brown liquid that can be taken as a supplement for conventional petroleum oils. However, the chemical composition of biomass-derived oil is quite different from that of petroleum-derived oils. High contents of water and oxygenated organic compounds in bio-oil are mainly responsible for the poor fuel quality of bio-oil (Oasmaa and Czernik, 1999). The complexity of chemical composition makes fractional distillation of bio-oil to extract high added-value chemicals difficult (Mohan et al., 2006). Interaction of lightweight reactive compounds in bio-oil to form larger molecular results in the thermal unstability and phase separation of bio-oil during storage and transportation (Diebold and Czernik, 1997). Moreover, the significant corrosion of thermal devices during the application of bio-oil may be caused by the organic acids in bio-oil. Therefore, the quality improvement of bio-oil will be desired for more effective application.

Most compounds in bio-oil are essentially derived from the depolymerization of hemicellulose, cellulose and lignin in biomass during fast pyrolysis, and the physical and chemical properties of bio-oil are obviously feedstock dependent. Thus pretreatment to modify the chemical composition of biomass will affect the bio-oil properties. Recently, biomass torrefaction as a thermal

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pretreatment for fast pyrolysis has received an increasing interest (Liawa et al., 2013; Meng et al., 2012). Torrefaction is also called as mild pyrolysis and conducted in the temperatures range of 200–300 °C (Chen et al., 2011). By this process, most of hemicellulose in biomass can be removed from biomass, and plenty of water and some lightweight organic compounds consisting of ketones, aldehydes, alcohols, and acids are produced from degradation of main constitutes in biomass (Prins et al., 2006; Wannapeera et al., 2011). Consequently, water and other lightweight compounds are less formed in the subsequent fast pyrolysis of torrefied biomass with less hemicellulose. Thus more stable bio-oil with lower water content is obtained from fast pyrolysis of torrefied biomass. The torrefaction-aid fast pyrolysis is considered as a step-wise pyrolysis, in which major biomass constituents with different thermal stability are desired to be selectively converted into target products with less complexity. The main purpose of torrefaction treatment prior to fast pyrolysis is to degrade selectively hemicellulose in biomass. However, the charring and cross-linking of other biomass constituents occur during torrefaction. Thus the selective pyrolysis for major chemical components can not be achieved effectively. Bio-oil yields in fast pyrolysis of torrefied biomass are significantly reduced with torrefaction severity owing to detrimental effect of torrefaction on chemical structure of biomass constituents, although obvious quality improvement of bio-oil can be achieved by torrefaction treatment (Zheng et al., 2012, 2013). Seeking more effective pretreatment methods for removing hemicellulose from biomass is desired to obtain higher quality bio-oil with less yield penalties.

Hydrothermal pretreatment which is also referred to as wet torrefaction is an effective method for fractionating biomass in hot compressed liquid water (Allen et al., 1996). The process generally is carried out under the saturated vapor pressure at temperatures varying from 150 to 260 °C. During hydrothermal pretreatment, hemicellulose in biomass can be completely solubilized into aqueous compounds, the lignin seal is broken, and cellulose is almost entirely preserved in the solid product (Laser et al., 2002; Sasaki et al., 2002). The process significantly increases the accessibility of cellulose to enzyme and is mainly used as a pretreatment method for subsequent enzymatic hydrolysis of cellulose. In view of effective removal of reactive hemicellulose from biomass, hydrothermal pretreatment will also be a potential pretreatment method prior to fast pyrolysis to improve quality of bio-oil through decreasing the formation of water, acids, and other reactive compounds in fast pyrolysis. Particularly, severe charring and cross-linking of biomass constitutes may be avoided in hydrothermal pretreatment owing to relatively mild reaction condition, which will help to reduce bio-oil yield penalties in fast pyrolysis. In addition, the ash may be removed from biomass during hydrothermal pretreatment, which will be also helpful to fast pyrolysis. However, hydrothermal pretreatment as a pretreatment method for fast pyrolysis has been less considered in previous literatures.

Eucalyptus is one of most important fast-growing trees, and approximately 3.5 million hectares of eucalyptus plantation with the productivities of 15–30 m^3/ha/a have been established in South China (Zhou and Wingfield, 2011). Currently, eucalyptus is mainly utilized for pulp production and furniture making, where plenty of wood residue is produced and has not been utilized effectively. Therefore, eucalyptus wood was selected as biomass feedstock in the present study. The samples were first subjected to hydrothermal pretreatment in a high-pressure batch reactor in the temperature range of 160–190 °C for 5 min. Subsequently, the fast pyrolysis of pretreated eucalyptus wood was conducted in a fluidized bed reactor to acquired higher quality bio-oil. The main aim was to investigate the effects of hydrothermal pretreatment on physical and chemical properties of bio-oil.

Table 1
Mass yield and chemical component analysis of pretreated eucalyptus wood (on dry basis).

Samples	Mass yield (wt%)	Chemical component[a] (wt%)		
		Hemicellulose	Cellulose	Acid insoluble fibers
Eucalyptus wood		24.02	44.08	28.25
PE-160	96.45	21.85 (87.75)	45.28 (99.07)	27.74 (94.69)
PE-170	90.82	18.02 (68.14)	47.90 (98.68)	28.07 (90.23)
PE-180	81.51	8.82 (29.93)	50.39 (93.16)	30.60 (88.27)
PE-190	73.29	3.47 (10.58)	52.59 (87.44)	31.86 (82.65)

[a] Values in the parentheses are the recovery rate of chemical components in pretreated eucalyptus wood.

2. Methods

2.1. Material preparation

Eucalyptus wood used in this study was acquired from a local wood processing factory in Guangzhou, China. Prior to hydrothermal pretreatment, the samples were ground to small particle size and subsequently sieved to a mean particle size of 0.25–0.42 mm. Then these selected particles were oven-dried to around 6% moisture content. The results of chemical component analysis of the samples were listed in Table 1.

2.2. Hydrothermal pretreatment of eucalyptus wood

Hydrothermal pretreatment of eucalyptus wood was carried out in a high-pressure batch reactor at 160, 170, 180, and 190 °C for 5 min. Severe degradation of cellulose in eucalyptus wood could be avoided at such relatively low temperatures and short retention

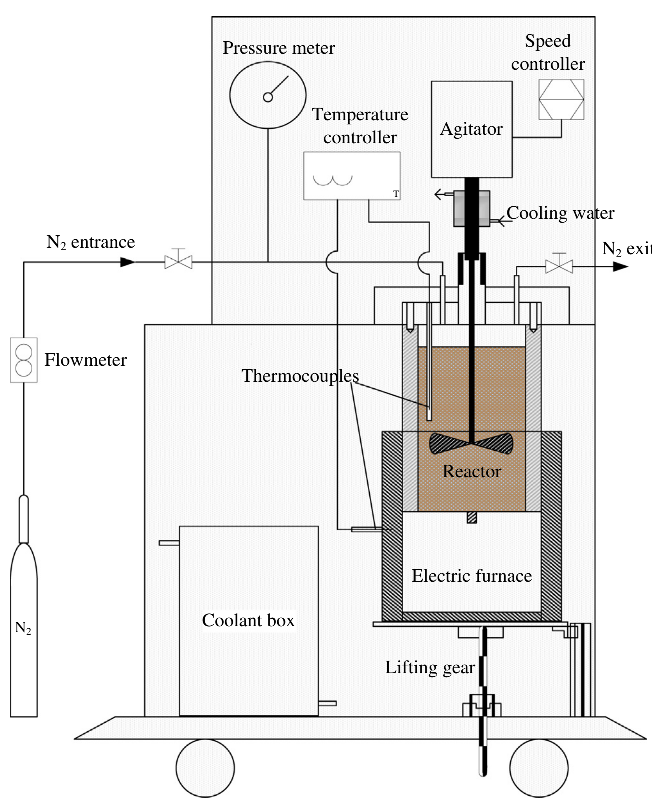

Fig. 1. Schematic diagram of the high-pressure batch reactor for hydrothermal pretreatment.