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Alkaline pretreatment and hydrothermal liquefaction of cypress for high yield bio-oil production

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ABSTRACT

The aim of this study is to investigate the feasibility and reaction mechanism of hydrothermal liquefaction of cypress via alkaline pretreatment to increase the bio-oil yield. The solid/liquid products were divided into ethanol insoluble organics, ethanol soluble organics, diethyl ether insoluble oil, diethyl ether soluble oil, acid soluble solid residue, and acid insoluble solid residue. The results showed that alkaline pretreatment could markedly enhance the bio-oil yield from 27.5% to 48.4% at 300 °C and was more helpful for suppression the re-polymerization reactions to form acid insoluble solid residue as compare to the un-pretreated cypress liquefaction runs. The optimum temperature of pretreated cypress liquefaction in hot-compressed water for ethanol soluble organics and diethyl ether soluble oil was raised from 280 to 300 °C. Alkaline pretreatment enhanced the decomposition temperature of cellulose and led to an increase in the crystal structure in cypress.

1. Introduction

Biomass, as a potentially renewable and environmentally friendly source of energy and chemicals, is one of the largest resources in the world because of its advantages, such as reproducibility, low pollution, and wide spread [1]. The main biomass conversion technologies used for obtaining biofuels are thermochemical and bio-chemical processes, which include fermentation, gasification, pyrolysis, and liquefaction in different solvents [2]. Among these various technologies, hydrothermal liquefaction is an environmentally friendly technology based on the thermochemical conversion of biomass in the presence of water. It does not require a drying pretreatment step for biomass, which is often necessary in other conversion technologies, such as pyrolysis and gasification [3,4].

Lignocellulosic materials comprise cellulose, hemicelluloses, and lignin. The three biopolymers components form an insoluble three-dimensional network with a very complex structure, which makes the lignocellulosic biomass more difficult to convert [5]. Moreover, the biopolymer of lignin is more obstinate and difficult to degrade in hot-compressed water [6]. Therefore, wood biomass is one of the most difficult biomass types to liquefy in hot-compressed without any catalysts because of a large amount of lignin in wood. Although hydrothermal liquefaction of biomass has been investigated extensively in recent decades, the commercial application of hydrothermal liquefaction still suffers from many challenges such as low yield of bio-oil and conversion of biomass. Recently, many studies have been developed pretreatment and liquefaction of biomass technologies which can increase the yield of bio-oil and decrease the reaction temperature [6–8]. Liu et al. [9] reported the behavior of acid-chlorite pretreatment and hydrothermal liquefaction of cornstalk. The results showed that acid-chlorite pretreatment could increase the water-soluble oil yield at 200–260 °C, and decrease the heavy oil yield at 260–320 °C because of a small amount of lignin in pretreated cornstalk. Alkaline pretreatment can break down lignocellulose and it is one of the most popular chemical agents because it is relatively inexpensive. To the best of our knowledge, there are no studies carried out using alkaline pretreatment method for enhancing bio-oil yield in hydrothermal liquefaction of wood biomass process. Thus, it is necessary to develop an alkaline pretreatment and hydrothermal liquefaction of wood biomass approach to improve the bio-oil yield.

The method of lump analysis has been used to investigate the complexity of biomass liquefaction and the bio-oil was defined as water-soluble organics (ethanol soluble and ethanol insoluble organics) and heavy oil based on the characteristics of bio-oil [10,11]. The results showed that lump analysis was effective for the investigation of biomass liquefaction. Previous study on the structural characteristics of solid residues from cypress hydrothermal liquefaction in different water amounts were investigated which help understand the mechanisms of the liquefaction process and the solid residues have been divided into acid-soluble and

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Table 1
Elemental analysis and compositions of untreated and pretreated cypresses.

Samples	Elemental components (wt %)				Cellulose	Hemicelluloses	Lignin
	C	H	N	O			
Cypress	48.9	6.0	0.3	44.8	43.6	27.6	28.8
0.5 h	47.7	5.8	<0.3	46.2	46.7	28.5	24.8
1 h	46.6	6.0	<0.3	47.1	53.4	24.6	22.0
2 h	45.3	6.1	<0.3	48.3	48.5	37.2	14.3

acid-insoluble solid residues [12]. To further investigate the behavior of alkaline pretreatment and hydrothermal liquefaction of wood biomass, in this study, the bio-oil and solid residue were segregated into water-soluble organics (ethanol soluble and ethanol insoluble organics), heavy oil (ethyl ether soluble oil and ethyl ether insoluble oil), acid soluble solid residue, and acid insoluble solid residue. The objective of this study is to investigate the feasibility of hydrothermal liquefaction of wood biomass by alkaline pretreatment to improve the bio-oil yield. The effects of pretreatment time and liquefaction temperature on the product lumps distribution and characteristics of solid residue are explored, respectively.

2. Experimental

2.1. Feedstock and pretreatment

The wood biomass used in this study was cypress, which collected from Henan Province in China. It was milled to pass through 40-mesh and dried at 105 °C for 24 h before used. The chemicals used were analytical reagent grade. For the alkaline pretreatment, cypress (150.0 g) was incubated with 5% (w/v) aqueous sodium hydroxide solution at a solid-to-liquid ratio of 1:6 (w/v) at 90 °C for 0.5, 1 and 2 h. The pretreated materials were washed to pH 7 with water and then dried at 105 °C for 24 h before used. Table 1 presents the elemental analysis and compositions of untreated and pretreated cypresses [13].

2.2. Liquefaction procedure

Hydrothermal liquefaction experiments have been carried out in a batch stainless steel autoclave reactor (Parr, USA) equipped with a magnetic stirrer. The typical run was described previously [14]. The procedure for the separation of liquefaction products is shown in Fig. 1. As shown, the resulting solid/liquid mixture was divided into six different lump products after the hydrothermal liquefaction process: ethanol insoluble organics (EIO), ethanol soluble organics (ESO), diethyl ether insoluble oil (DEIO), diethyl ether soluble oil (DESO), acid soluble solid residue (ASSR), and acid insoluble solid residue (AISR). The reaction mixtures were separated by filtration though filter paper (pore size: 15–20 μm; brand: Xinxing, China) under vacuum, and 200 ml of de-ionized water was used for washing the solid products. The water soluble organics (WSO) obtained by removing the water under reduced pressure in a rotary evaporator. The WSO was further divided into EIO and ESO by washing with 75% ethanol. The water insoluble fractions were washed with acetone until the solvent became colorless. After removal of the acetone, the acetone soluble oil was designated as heavy oil (HO). The HO was further divided into DEIO and DESO by washing with the diethyl ether/dichloromethane mixtures (90:10, v/v). The acetone insoluble fraction was further divided into ASSR and AISR after treatment with 3% H_2SO_4 for 4 h at 100 °C. All the lump yields were calculated on a dry-ash-free basis of feedstock. Each experiment was repeated two times under nominally identical conditions to ensure the repeatability of the results. The maximum standard deviations for lump yields were less than 3%.

2.3. Characterization

Fourier transform infrared spectroscopic analysis (FT-IR) was carried out on a Nicolet iN10 FT-IR Spectrophotometer (Madison, WI, USA) equipped with a liquid nitrogen-cooled MCT detector to determine the functional groups in the solid residue. The crystallinities of the solid residue were measured on an X-ray diffractometer (Shimadzu XRD-6000, Tokyo, Japan). The samples were irradiated at 5–35° with a scan rate of 4°/min. The crystallinity index (*CrI*) was calculated on the basis of formula as reported previously [15]. The neutral sugar composition of solid residue was determined by hydrolysis with 3% H_2SO_4 for 2.5 h at 105 °C [16]. The liberated neutral sugars were analyzed by high performance anion exchange chromatography (Dionex ICS-3000, Sunnyvale, CA, USA) and a Carbopac PA-1 ion exchange column (4 nm × 250 nm). The contents of cellulose and hemicelluloses were calculated basis on the neutral sugar analysis.

3. Results and discussion

3.1. Effect of alkaline pretreatment on product yields

The biomass components are main carbohydrates and lignin. Water serves as both reaction medium and reactant in hydrothermal liquefaction of biomass process [17]. The hydrothermal liquefaction mechanism can be described as: (1) depolymerization of carbohydrates and lignin resulting in macromolecular fragments and (2) thermal–chemical decomposition of the monomers to smaller molecules [13,18,19]. The bio-oil is the targeted products in biomass liquefaction. Many studies have divided the bio-oil into WSO and HO. The WSO and HO are primarily formed from the conversion of carbohydrates and lignin, respectively [20]. However, in

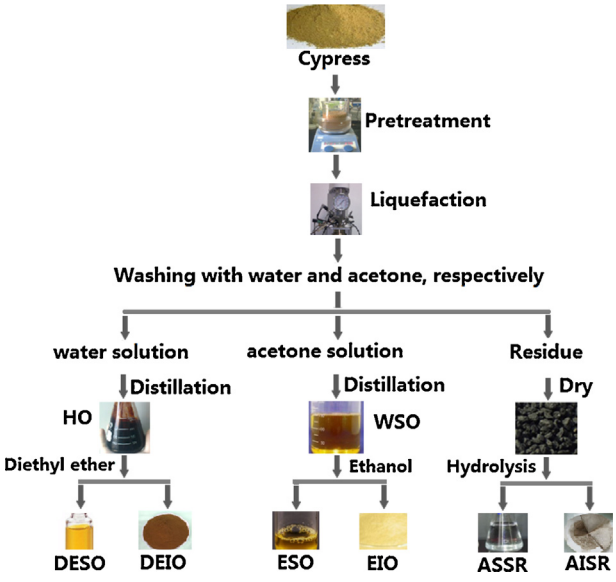

Fig. 1. Procedure for separation of liquefaction products.