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Hydrothermal liquefaction of cornstalk: 7-Lump distribution and characterization of products

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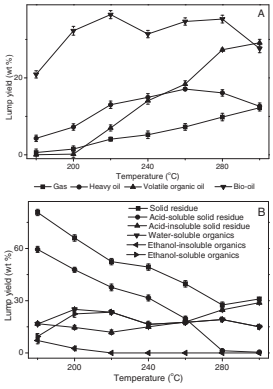
HIGHLIGHTS

- During Hydrothermal liquefaction of cornstalk, the polymerization reaction is mainly present at lower temperatures.
- The higher heating value of the solid residue obtained after treatment at 300 °C was 24.2 MJ/kg.
- Ethanol-insoluble organics originated from the decomposition of hemicelluloses.

GRAPHICAL ABSTRACT



Effect of temperature on product yields of (A) gas, heavy oil, volatile organic compounds, and bio-oil; (B) solid residue, acid-soluble solid residue, acid-insoluble solid residue, water-soluble organics, ethanol-insoluble organics, and ethanol-soluble organics (conditions: reaction time of 0 min, 10 g of cornstalk, 100 ml of water).

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ABSTRACT

Hydrothermal liquefaction of cornstalk at 180–300 °C at ratios of water to cornstalk of 6–14 was conducted, and the reaction products were lumped into gas, water-soluble organics (ethanol-insoluble and ethanol-soluble organics), heavy oil, volatile organic compounds, and acid-soluble and acid-insoluble solid residues. Low temperature, high ratio of water to cornstalk, and short reaction time favored the formation of bio-oil (ethanol-insoluble organics, ethanol-soluble organics, and heavy oil) but inhibited the formation of acid-insoluble solid residue. Increasing temperature and reaction time increased the yields of gas and volatile organic compounds, whereas decreased the yield of acid-soluble solid residue. Bio-oil yields increased first and then decreased at a ratio of water to cornstalk higher than 10. Overall, the studied reaction parameters influenced the conversion among the lumps and product properties. This study suggests that lump analysis provides a promising approach to describe the product distributions in biomass liquefaction.

1. Introduction

Thermo-chemical conversion processes (pyrolysis and liquefaction) are effective methods to convert biomass such as wood, forestry residues, and agricultural residues into products which are

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potential intermediates for the production of biofuels or chemicals (Zhang et al., 2007a).

During pyrolysis, the usually dry biomass feedstock is heated under low-oxygen or oxygen-free conditions (Zhang et al., 2007b), whereas, during hydrothermal liquefaction, wet biomass is used. The products of pyrolysis and hydrothermal liquefaction are a complex mixture of compounds, and it is difficult to describe the chemical reactions occurring during these processes since the major components of biomass (cellulose, hemicelluloses, and lignin) form a complex structure, resulting in heterogeneous processes proceeding inside and, in particular, on the surface of biomass particles (Kruse and Gawlik, 2003). The method of lump analysis has been used to investigate the complexity of the reaction processes by lumping the large number of chemical compounds into groups of pseudo-components, according to their boiling points as well as molecular characteristics. An 8-lump model of cornstalk liquefaction in sub- and super-critical ethanol has been established, and the lumps were defined as gas, water-soluble organics, heavy oil, volatile organic compounds, and solid residue (carbon, hydrogen, oxygen, and nitrogen) based on the characteristics of the material and products (Liu et al., 2011, 2012b). There was a reversible reaction between the heavy oil and volatile organic compounds, and the decrease in the water-soluble organics yield was mainly attributed to the conversion of water-soluble organics to gas in the sub- and super-critical ethanol. Therefore, lump analysis was effective for the study of biomass liquefaction.

In the present study, cornstalk was liquefied in hot-compressed water, and the reaction products were segregated into gas (GA), water-soluble organics (WSO), heavy oil (HO), volatile organic compounds (VO), acid-soluble solid residue (ASSR), and acid-insoluble solid residue (AISR). In addition, the water-soluble organics were further divided into ethanol-insoluble organics (EIO) and ethanol-soluble organics (ESO). The effects of temperature, reaction time, and the ratio of water to cornstalk on product yields and major compounds of the liquid products were identified by Fourier transform infrared spectrometer (FT-IR) and gas chromatography-mass spectrometry (GC–MS). The EIO was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The solid residue (SR) was characterized to investigate the mechanism of the hydrothermal liquefaction process by FT-IR, X-ray diffraction, and element analysis.

2. Methods

2.1. Materials

Cornstalk was collected in Guangzhou, Guangdong Province China. The samples were air-dried, ground in a universal high-speed smashing machine and sieved to give fractions with particle sizes less than 0.45 mm. The cornstalk flour was extracted with distilled water and ethanol to remove water-soluble organics and polar organics, dried at 105 °C for 24 h, and stored in a desiccator at room temperature. The ash of cornstalk was determined by burning at 650 °C for 6 h. The chemical components of cornstalk were determined according to Liu et al. (2012a). The cornstalk contained 39.2% cellulose, 35.1% hemicelluloses, 20.2% lignin, and 5.5% ash (on a dry basis). Acetone (analytical grade) and filter paper (ASTME832-81) were purchased from Beijing Chemical Reagent Limited Company.

2.2. Liquefaction

The reaction was carried out in a 1000-ml stainless-steel autoclave (Parr, USA) with a magnetic stirrer. The autoclave was heated with an external electrical furnace, and the temperature was measured with a type-J thermocouple. In a typical liquefaction experiment, 10 g of cornstalk and 100 ml de-ionized water were fed into the autoclave and the reactor was purged three times with nitrogen. Agitation was set at 150 rpm and kept constant for all experiments. The reactor was heated to the desired temperature at a heating rate of about 4 °C/min. The autoclave was cooled to room temperature by means of cooling coils inside the reactor. The density of the gas was estimated according to Liu et al. (2012a) after measuring the volume of the gas sample by expelling water from a measuring cylinder.

The bio-oil was separated from the autoclave as described previously (Liu et al., 2012a). The reaction mixtures were separated by filtration though filter paper under vacuum, and 200 ml of de-ionized water was used for washing the solid products. After removal of the water from the wash solution under reduced pressure in a rotary evaporator, the solid were weighed and designated as water-soluble organics (WSO). The WSOs obtained at 180 and 200 °C were further divided into ethanol-insoluble organics and ethanol-soluble organics by washing with 75% ethanol. The water-insoluble fractions were treated with acetone in an extraction apparatus until the solvent in the thimble became colorless. After removal of the acetone, this fraction was weighed and designated as heavy oil (HO). The acetone-insoluble fraction was dried at 105 °C for 24 h, weighed, and designated as solid residue (SR). To further evaluate the effect of reaction conditions on the SR, the SRs were further divided into acid-soluble solid residue (ASSR) and acid-insoluble solid residue (AISR) after treatment with 3% H_2SO_4 for 4 h at 100 °C. The amount of volatile organic compounds phase was calculated from the material balance. All the product yields were calculated on a dry-ash-free basis. Each experiment was conducted in duplicate and the differences between the results of two tests were below 4% of the values.

2.3. Product analysis

Fourier transform infrared spectrometry (FT-IR) experiments were conducted with a Nicolet iN10 FT-IR spectrophotometer (USA). The instrument was performed with a MCT detector and the spectra were recorded in the region of 4000–650 cm^{-1} at a resolution of 4 cm^{-1}.

To examine changes in the crystalline forms of cellulose in the cornstalk during liquefaction process, X-ray diffraction (XRD) was carried out using a Cu-Kα radiation source ($\lambda = 0.154$) at 40 kV and 30 mA. Samples were scanned at a speed of 2°/min, ranging from $2\theta = 5$–40° and a step size of 0.02° at room temperature. The crystallinity index (*CrI*) was calculated from XRD data and determined based on the formula by Segal et al. (1959) as follows,

$$CrI = [(I_{002} - I_{am})/I_{002}] \times 100 \quad (1)$$

In which I_{002} is the intensity for the crystalline portion of biomass (i.e., cellulose) at about $2\theta = 22.0$ and I_{am} is the peak for the amorphous portion (i.e., cellulose, hemicelluloses, and lignin) at about $2\theta = 15.8$.

The elemental composition of the solid residue was analyzed by a CHNO Elemental Analyzer Vario EL (ELEMENTAR, Germany). The amount of oxygen (O) was estimated by difference. The higher heating value (HHV) of the sample was calculated based on the Dulong's formula.

$$HHV(MJ/kg) = 0.3383 \times C + 1.442 \times (H - O/8) \quad (2)$$

In which C, H, and O represent the weight percentages of carbon, hydrogen, and oxygen, respectively.

Compounds in bio-oil were identified by GC/MS (Agilent 7890A/5978, USA) using a 30 m × 0.25 mm × 0.25 μm capillary column (HP-5). Gas chromatography was carried out at 40 °C for 2 min before the temperature was increased at 5 °C/min to 300 °C. The injection size was 0.1 μl and the injector temperature was