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Alkaline pretreatment and the synergic effect of water and tetralin enhances the liquefaction efficiency of bagasse

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HIGHLIGHTS

- Sugarcane bagasse was liquefied in a water/tetralin mixed solvent.
- The mixed solvent showed significantly synergic effect on bagasse liquefaction.
- The compositions of heavy oil obtained in different solvents are quite different.
- Alkaline pretreatment enhanced bagasse liquefaction in water-containing solution.

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ABSTRACT

Bagasse liquefaction (BL) in water, tetralin, and water/tetralin mixed solvents (WTMS) was investigated, and effects of tetralin content in WTMS, temperature, and alkaline pretreatment of bagasse on liquefaction efficiency were studied. At 300 °C, bagasse conversion in WTMS with tetralin content higher than 50 wt% was 86–87 wt%, whereas bagasse conversion in water or tetralin was 67 wt% or 84 wt%, respectively. Because the solid conversion from liquefaction in WTMS with tetralin content higher than 50 wt% was always higher than that in water or tetralin at temperatures between 250 and 300 °C, a synergic effect between water and tetralin is suggested. Alkaline pretreatment of bagasse resulted in significantly higher conversion and heavy oil yield from BL in water or WTMS. The effect of deoxygenation by the present liquefaction method is demonstrated by lower oxygen contents (16.01–19.59 wt%) and higher heating values (31.9–34.8 MJ/kg) in the produced oils.

1. Introduction

Recently, biomass-derived liquid fuels, including bio-oil, bio-ethanol, and biodiesel, have attracted attention as potential renewable energy sources (Mazaheri et al., 2010; Yang et al., 2014). In the past decades, technologies using food crops such as corn and soybean to produce bio-ethanol and biodiesel have received considerable attention. However, fuel production from these food crops faces increasing competition with direct use of these crops as food and animal feed, which has an impact on both the availability and the price of these crops (Wu et al., 2011; Wang et al., 2011). Instead, thermochemical processes such as pyrolysis, gasification, and direct liquefaction allow the production of bio-oil from abundantly available and inexpensive non-food biomass materials such as agricultural residues and forestry wastes (Rezzoug and Capart, 2003; Yaman, 2004). While both pyrolysis and gasification require high operating temperatures, direct liquefaction requires less energy and can be consequently carried out at relatively low temperatures.

Usually, direct liquefaction is carried out under specific temperature and pressure conditions in the presence of solvents and/or catalysts. Since water is environmentally benign and inexpensive, it is one of the most studied solvents, mainly used as supercritical water. However, due to harsh operating conditions such as high temperature and pressure, most studies on this process have been carried out as lab- or bench-scale experiments (Toor et al., 2011; Qian et al., 2007). Several recent studies reported that liquefaction

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Abbreviations: BL, bagasse liquefaction; DTG, differential thermogravimetric; E_a, activation energy; HHV, high heating value; HO, heavy oil; SR, solid residue; Tb, burnout temperature; TG, thermogravimetric; TL, tetralin liquefaction; Tp, temperature corresponding to the peak height; WL, water liquefaction; WTMS, water/tetralin mixed solvents.

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of pinewood in the presence of various organic solvents, such as acetone and ethanol, improved the bio-oil yield and solid conversion (Liu and Zhang, 2008; Wang et al., 2013). However, due to their high volatility, utilization of these low molecular weight solvents likely increases the reaction pressure. In contrast, tetralin, a hydrogen donor solvent with high boiling point (207 °C), has been widely used as a solvent for coal liquefaction. Interestingly, liquefaction of pure cellulose by using tetralin resulted in a high solid conversion of 90 wt% (Demirbas, 2000). It is suggested that tetralin is able to dissolve, disperse, and stabilize the free radicals produced in the liquefaction process while preventing the repolymerization of intermediate products (Ogi and Yokoyama, 1993). Recently, biomass liquefaction in mixed solvents, especially organic solvent-water mixtures, has received much attention (Cheng et al., 2010; Chen et al., 2014; Zhao et al., 2013). These studies demonstrated that methanol/water mixed solvents were better than a single solvent in enhancing the total bio-oil yield and conversion of woody biomass (Zhao et al., 2013; Cheng et al., 2010). However, to the best of our knowledge, biomass liquefaction in a water/tetralin mixed solvent (WTMS) has not been reported. Since water and tetralin are insoluble, the interplay between them is rather physical than chemical. WTMS as a solvent has the potential to combine the excellent decomposing ability of subcritical water with the ability of tetralin to act as a hydrogen donor solvent; this improves the liquefaction efficiency to its maximum.

In addition, pretreatment of biomaterials plays an essential role in increasing the yield of liquid products and improving the operational conditions of biomass liquefaction. Chen et al. (2014) reported that compared to untreated samples, physical pretreatment, including centrifugation and ultrasonication, of wastewater algae decreased the activation energy (E_a) of the thermal decomposition from 50.2 kJ/mol to 35.9 kJ/mol while increasing the biocrude oil yield from 30 wt% to 55 wt%. The studies of Liu et al. (2011) on the behavior of acid–chlorite pretreatment and hydrothermal liquefaction of cornstalk, indicate that acid–chlorite pretreatment, especially in hot-compressed water liquefaction at 200–240 °C increased the water-soluble bio-oil yield. Later, Liu et al. (2014) demonstrated that compared to untreated cypress liquefaction, alkaline pretreatment prior to hydrothermal liquefaction markedly increased the bio-oil yield from 27.5 wt% to 48.4 wt% at 300 °C, while suppressing repolymerization reactions and the formation of solid residues. However, as far as we know, only few attempts were made using alkaline pretreatment methods for biomass liquefaction using tetralin or WTMS as the liquefaction medium.

In the present study, sugarcane bagasse was used as a biomass sample. To understand the synergic effect of water and tetralin on biomass liquefaction, bagasse liquefaction (BL) was carried out in subcritical water, tetralin, and WTMS. Moreover, the influence of alkaline pretreatment on liquefaction efficiency and product distribution was investigated. Our results might help in understanding the mechanism of biomass liquefaction in mixed solvents, while being useful to develop efficient biomass utilization processes.

2. Methods

2.1. Materials

Sugarcane bagasse was obtained from Pumiao Paper Factory in the city of Nanning, located in southern China. After sugar production, it was piled for one more year after which the air-dried bagasse was crushed and screened. The fraction with particle size between 20 and 80 mesh was collected and used in all the experiments. The ground bagasse was dried at 110 °C for 24 h and kept in desiccators at room temperature. All chemicals were analytical reagent grade and used as received. The chemical composition was determined according to the corresponding Chinese Standards as follows: lignin, GB/T 2677.8-1994; holocellulose, GB/T 2677.10-1995; extractives, GB2677.6-1994; ash, GB/T 2677.3-1993. Cellulose content was determined by the nitric acid–ethanol method (Wang and Cheng, 2011). The content of hemicellulose was calculated by the difference between holocellulose and cellulose contents. All data were based on dry raw material. The elemental analysis of bagasse was conducted with a CHNS/O analyzer (CHNS 932). The results show that bagasse contains 48.63 wt% cellulose, 32.20 wt% hemicellulose, 19.51 wt% lignin, 2.40 wt% extractives, and 0.90 wt% ash. The content of carbon, hydrogen, oxygen, nitrogen, and sulfur in bagasse are 47.58 wt%, 6.29 wt%, 46.03 wt%, 0.08 wt%, and 0.02 wt%, respectively.

2.2. Alkaline pretreatment

Alkaline pretreatment of bagasse was performed as follows: 30 g of bagasse (20–80 mesh, dry basis), 0.03–3.6 g of NaOH (the dosage was 0.1–12 wt% of bagasse), and 120 g of distilled water were weighed. NaOH was dissolved in the preweighed water, and the preweighed bagasse and NaOH solution were mixed in a polythene bag. The bag was sealed and kept for 23 h at room temperature. After that, the treated bagasse and the NaOH solution were used together in the subsequent liquefaction reaction.

2.3. Liquefaction procedure and product separation

All the liquefaction experiments were conducted in a 1000-ml stainless steel autoclave, with a magnetic stirrer (CFR-1, Yantai Jianbang Chemical Mechanical Co., Ltd., Yantai, China). The bagasse/solvent mass ratio was maintained at 1:8. In a typical liquefaction reaction, 30 g of bagasse and 240 g of solvent (water, tetralin, or a WTMS) were loaded in the autoclave. To liquefy NaOH-pretreated bagasse with water or WTMS as the solvent, 30 g of pretreated bagasse in wet state was loaded in the autoclave together with the alkaline solution and 120 g of solvent (water or tetralin). To liquefy NaOH-pretreated bagasse with pure tetralin as the solvent, the water content of 30 g of pretreated bagasse was removed by drying at 105 °C, after which it was loaded in the autoclave together with 240 g of tetralin.

After the reactants were mixed well, the reactor was sealed and purged three times with hydrogen to remove the air/oxygen in the reactor airspace. Agitation was set at 300 rpm and maintained for the duration of the experiment. The reactor was heated to the desired temperature (200–320 °C) at a rate of 5 °C/min by an external electric furnace and held for 60 min. It was then cooled to room temperature in a water bath. Once the reactor was cooled to room temperature, the reactor pressure was noted by a pressure gauge installed on the reactor head, and the gas produced was vented without being analyzed further. The liquid and solid products were collected from the bottom of the reactor. The mixture was filtered under reduced pressure through a preweighed filter paper to separate the insoluble material. The insoluble material and the reactor were further washed with dichloromethane and acetone successively until the washing solution became colorless. The collected washing solution was heated to 30 °C in a rotary evaporator to evaporate dichloromethane and acetone and then heated to 70 °C to evaporate water and residual solvents. After removal of the solvents, the obtained fraction was weighed and designated as heavy oil (HO). The insoluble material was rinsed with water and dried at 110 °C for 24 h; it was weighed and designated as solid residue (SR).

In addition, to study the effect of the solvent ratio on BL, the experiments were carried out with 30 g of untreated bagasse at 300 °C for 60 min. The bagasse/WTMS mass ratio was maintained at 1:8. The mass ratio of water/tetralin in WTMS was set at 1:0,