



Comparative study on lignocellulose liquefaction in water, ethanol, and water/ethanol mixture: Roles of ethanol and water

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ARTICLE INFO

Article history:

Received 11 January 2018

Received in revised form

23 April 2018

Accepted 3 May 2018

Available online 8 May 2018

Keywords:

Water/ethanol mixture

Lignocellulosic biomass liquefaction

Bio-crude

Solid residue

ABSTRACT

This study aimed to investigate the roles of ethanol and water in the water/ethanol mixed solvent in liquefaction of lignocellulose biomass. To this end, an organosolv lignin, cellulose, cellulose/lignin (50:50, w/w) mixture and an acetone extracted white birch bark (EWBB) were comparatively liquefied in pure water, water/ethanol mixture (50:50, v/v) and pure ethanol at fixed condition (300 °C and 15 min). It was demonstrated that biomass liquefaction efficiency in three reaction media with respect to the bi-crude yield followed the order of water/ethanol mixed solvent > pure water > pure ethanol regardless of the feedstocks. Cellulose derived bio-crudes mainly contained esters, furfurals and furfurals derivatives, and carboxylic acid substantially existed in the bio-crude from cellulose liquefaction in water, while lignin derived bio-crude mainly contained aromatics, as expected. It was found that hot-compress water accelerated biomass depolymerization by hydrolyzing cellulose/hemi-cellulose, while on the other hand ethanol promoted lignin degradation by dissolving the de-polymerized lignin products and hence prevented the repolymerization of the reaction intermediates. In addition, the mixed ethanol-water solvent increased the permeation of the solvent into the lignocellulose biomass structure, and increased the solubility of liquefaction intermediates, hence contributing to a higher bio-crude yield in liquefaction of lignocellulose biomass.

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1. Introduction

Direct liquefaction of biomass at mild temperatures has been widely reported since 1970s and is considered as a promising pathway for thermochemical conversion of lignocellulosic biomass into bio-chemicals and liquid bio-fuels. Liquefaction media have an important impact on products (gas, oil and char) distribution and chemical composition of the liquid products, and hence the final applications of the liquid products [1]. For instance, catalytic liquefaction of lignocellulosic biomass in phenol at relatively low temperatures (120–180 °C) has been realized, and the target product containing phenolated products and free phenol show great potential for phenol formaldehyde (PF) resin synthesis [2–4]. While bio-oil obtained from acid catalyzed liquefaction of lignocellulosic biomass in polyhydric alcohols consists of bio-polyols,

which is mainly applied in polyurethane material production [5].

Hot compressed organic solvents such as monohydric alcohols are also applied for biomass liquefaction. Solvents, temperature and residence time exert great effects on the bio-crude/bio-oil yield [6–8]. In the study of Yamazaki et al. [9], woody biomass liquefaction in supercritical methanol was found to strongly depend on feedstocks and temperature: beech wood can be liquefied to a greater extent than cedar wood at 270 °C, while at 350 °C, both beech and cedar wood were liquefied extensively. As for the effects of monohydric alcohol type (methanol, ethanol, 1-propanol, 1-butanol, 1-octanol, 1-decanol) on Japanese beech liquefaction at 270 °C and 350 °C under supercritical pressure, solid residue yield from liquefaction at 270 °C for 10 min did not change too much as a result of the increased alcohol alkyl chain length. But when the residence time was over 10 min, the solid residue yield decreased with the increased alcohol alkyl chain length. Besides, cellulose was much more resistant than hemicellulose and lignin to liquefaction in alcohols at 270 °C. However, when the temperature was 350 °C, cellulose, hemicellulose and lignin were all readily liquefied. Even though alcohols of longer alkyl chains tended to liquefy wood faster

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at 350 °C, 90% of wood can be eventually liquefied regardless of the alcohol type.

In addition to alcohol, water has been widely applied in biomass liquefaction. To use water instead of organic solvents as the liquefaction reagent is advantageous from the environmental and economic points [7]. However, liquefaction in pure water generally yielded bio-oil with a low yield (less than 40%), high oxygen content, low HHVs [10–13]. Using water/alcohol mixture as liquefaction media instead could significantly enhance bio-oil yield and quality [14–16]. Water/alcohol mixtures favor biomass liquefaction by reducing the formation of high boiling-point intermediates or solid residue. Density and dielectric constant of water/alcohol mixture have great effects on dissolving lignin and cellulose derivatives. It was found that Alcell lignin solubility in aqueous ethanol varies with ethanol concentration: it increases strongly as ethanol concentration increases up to 50%, then increases slowly at the ethanol concentration over 50%, and reaches a maximum solubility when ethanol concentration is 70% [17]. For D-glucose, sucrose, sorbitol, maltose monohydrate, their solubility in aqueous ethanol decreases slowly with the increasing ethanol concentration from 0 to 50%, but further ethanol concentration increase over 50% decreases the solubility sharply [18]. Besides, a higher temperature led to a higher solubility of D-glucose in aqueous ethanol [19]. Wang et al. [20] hydrolyzed cellulose in water/alcohol (methanol, ethanol or isopropanol) mixture with various volume ratios at 200–280 °C and found that water/alcohol mixture favored to yield more reducing sugar than pure water. As a result of temperature elevation, reducing sugar yield increased first, then decreased regardless of the alcohol type in the water/alcohol mixture. Based on these, it is thus considered that aqueous ethanol at the concentration of 50% is optimal for dissolving biomass or intermediate that contains both lignin and cellulose derivatives, and it is has been confirmed that water/ethanol mixture with a volume ratio of 50:50 demonstrated to be optimal for biomass liquefaction, yielding bio-oil that contained phenolic compounds, long-chain alkanes, ketones and esters [16,21–26].

Currently, most of the published works are mainly on process optimization and products distribution analysis as well as bio-crude characterizations, including a previous work by the authors [27], where we found that the use of water-ethanol mixed solvent (50:50, v/v) showed synergistic effects for biomass liquefaction, resulting in very high bio-crude yields at 300 °C for 15 min. However, the mechanism of the synergistic effects of mixed solvents of water-alcohol and the role of alcohol component in the mixed solvents in lignocellulose biomass liquefaction are yet to be elucidated. This present work aimed to investigate the role of alcohol in lignocellulose biomass liquefaction by comparing the liquefaction of lignin, cellulose, and cellulose/lignin (50:50, w/w) mixture as well as a lignocellulosic biomass (acetone extracted white birch bark (EWBB)) in pure water, water/ethanol mixture (50:50, v/v), and pure ethanol at fixed reaction temperature and time (300 °C, 15 min).

2. Materials and methods

2.1. Materials

White birch bark was provided by a local sawmill in Thunder Bay, Ontario, Canada. The obtained bark was firstly air-dried, then ground into particles of 20 mesh. According to our previous results [27], white birch bark contains 11.18% extractives and these extractives flow together with lignin/cellulose/hemicellulose derivatives into bio-crude product after bark liquefaction. Thus, white birch bark was extracted to minimize the effect of extractives on the final bio-crude yield. As for the extraction, ground air dried white

birch bark was extracted through lixiviation in 70 vol% aqueous acetone at a solid/solvent ratio of 1:20 g/mL at room temperature for 180 min. The extracted white birch bark was then oven-dried at 105 °C for 24 h, designated as extracted white birch bark (EWBB). Organosolv lignin was supplied by a mill in British Columbia, Canada. Cellulose powder was purchased from Sigma-Aldrich, Canada. Both organosolv lignin and cellulose powder were vacuum dried at 50 °C and stored in a sealable plastic bag for use. Primary analyses on white birch bark and organosolv lignin are as shown in Table 1. Chemicals such as anhydrous ethyl alcohol (ethanol) and acetone ($\geq 99.5\%$) were purchased from Caledon Laboratory Canada and were used as received without any pre-treatments.

2.2. Liquefaction process

Liquefaction of various feedstocks was carried out in a 100 mL Parr 4590 Micro Bench-top reactor. In a typical liquefaction run, ~5.0 g feedstock (cellulose, cellulose/lignin (50:50, w/w) designed as C/L, lignin, or EWBB) and ~50.0 mL liquefaction reagent (pure water, water/ethanol (50:50, v/v) mixture, or pure ethanol) were charged into the reactor. Residual air in the reactor was removed through alternate vacuuming-N₂ purge for three times, the reactor was then pressurized to 2.0 MPa with N₂, and heated under the stirring (175 rpm) to 300 °C in 30 min (pressure at 300 °C with pure water, water/ethanol (50:50, v/v) mixture and pure ethanol was around 8.0 MPa, 12.0 MPa, and 16.0 MPa, respectively), and hold at 300 °C for 15 min. Liquefaction was then stopped through quenching the reactor in a water/ice bath.

After the reactor was cooled down to room temperature, gas in the reactor was collected into a 1.0 L gas bag for GC-TCD (Agilent Micro-GC 3000) analysis using 100 mL atmospheric air as the internal standard. The reactor was then opened and rinsed with acetone, the slurry and rinsing acetone were collected and filtered, solid residue (SR) was rinsed with acetone till the falling filtrate became colourless. The SR was then oven-dried together with filter paper at 105 °C to constant weight. Acetone, ethanol and water in the filtrate was respectively removed at 45 °C, 60 °C and 75 °C through rotary evaporation under reduced pressure, the left black viscous product was weighed and designated as bio-crude. Liquefaction of each feedstock under identical condition was repeated for at least three times to demonstrate acceptable reproducibility. Products from liquefaction here are grouped into three lumped fractions: Gas + water + volatiles (GWV), bio-crude and SR. Biomass liquefaction has been known to yield water through dehydration or condensation. Also, low boiling point chemicals are produced. Both water and low boiling point chemicals are removed during recovery of bio-crude through rotary evaporation under reduced pressure. Thus, water, low boiling point chemicals are lumped into GWV with gas. Yields of SR, bio-crude and GWV were calculated as the following equations:

$$SR_{yield} = \frac{W_{SR}}{W_f} \times 100\% \quad (1)$$

$$Bio - crude_{yield} = \frac{W_{bio-crude}}{W_f} \times 100\% \quad (2)$$

$$GWV_{yield} = 100\% - SR_{yield} - Bio - crude_{yield} \quad (3)$$

where W_f is the oven-dried weight of feedstock (g), W_{SR} is the oven-dried weight of SR (g), and $W_{bio-crude}$ is the weight of bio-crude (g).

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