Bioresource Technology 102 (2011) 6605–6610

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Alkaline hydrothermal conversion of cellulose to bio-oil: Influence of alkalinity on reaction pathway change

Sudong Yin [a], Anil K. Mehrotra [b], Zhongchao Tan [a,*]

[a] Department of Mechanical & Manufacturing Engineering, Centre for Environmental Engineering Research & Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4

[b] Department of Chemical & Petroleum Engineering, Centre for Environmental Engineering Research & Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4

ARTICLE INFO

Article history:
Received 17 November 2010
Received in revised form 2 February 2011
Accepted 20 March 2011
Available online 14 April 2011

Keywords:
Hydrothermal conversion
Alkalinity
Cellulose
Bio-oil
Reaction pathway

ABSTRACT

The effects of alkalinity on alkaline hydrothermal conversion (alkaline-HTC) of cellulose to bio-oil were investigated in this study. The results showed that the initial alkalinity greatly influenced the reaction pathways. Under initial strong alkaline conditions with final pH greater than 7, alkaline-HTC only followed the alkaline pathway. However, under initial weak alkaline conditions with final pH of less than 7, acidic as well as alkaline pathways were involved. The main mechanism behind this change of reaction pathways under weak alkaline conditions was that carboxylic acids were first formed from cellulose via the alkaline pathway and then neutralized/acidified the alkaline solutions. Once the pH of the alkaline solutions decreased to less than 7, the acidic instead of the alkaline reaction pathway occurred. This change of the reaction pathways with initial alkalinity partly explained the inconsistent results in the literature of alkaline-HTC bio-oil compositions and yields.

1. Introduction

Interest in alkaline hydrothermal conversion (alkaline-HTC) of biomass to bio-oil has been increasing due to the shortfall of and environmental concerns relating to crude oil. Studies have shown that this technology can convert different types of biomass to bio-oil. The feedstock tested includes, but are not limited to, wood chips, straw, animal manure, microalgae and municipal garbage (Biller and Ross, 2011; He et al., 2000; Minowa et al., 1995; Xu and Lad, 2008; Yin et al., 2010; Zhou et al., 2010).

Compared with the biological process for bio-oil production, alkaline-HTC can use inedible biomass instead of food crops as conversion feedstock. Another advantage is that alkaline-HTC can convert wet biomass to bio-oil without any pre-drying because water is used as the reaction medium. Moreover, alkaline-HTC features high conversion rates and low char yields (Akhtar et al., 2010; Mazaheri et al., 2010a,b). To date, the effects of operating parameters such as temperature, reaction residence time and the type of processing gas on alkaline-HTC of biomass have been well documented in literature (Karagöz et al., 2004; Mazaheri et al., 2010a,b; Xu and Lad, 2008; Yin et al., 2010). The same cannot be said, however, for the effects of alkalinity on alkaline-HTC of biomass. Most existing reports dealing with alkaline-HTC only did precursory studies on the process using one or two alkali concentrations. On the other hand, some recent papers indicated that alkalinity may play an important role in the composition and yield of the bio-oil as well as in the change of reaction pathways during alkaline-HTC process.

Bhaskar et al. (2008) and Karagöz et al. (2006) studied alkaline-HTC of different wood chips to bio-oil at four different initial alkali concentrations and found that the compositions of these four bio-oils differed from each other. In addition, they investigated the influence of alkalinity on the yields of alkaline-HTC bio-oil and found that alkaline-HTC bio-oil yields increased with the alkalinity of aqueous solutions. But, the opposite trend of reduced alkaline-HTC bio-oil yields with decreasing alkalinity has also been reported by other researchers (Minowa et al., 1994; Yokoyama et al., 1987).

Morever, the initial alkalinity of the reaction medium may also affect the reaction pathways. Recently, some final pH values of less than 7 after alkaline-HTC of biomass were reported. This indicated that alkaline-HTC may involve not only alkaline pathways, but also acidic pathway under certain conditions (Aida et al., 2007; Dolan et al., 2010; Eberhardt et al., 2010; Klinke et al., 2002; Weil et al., 1998; Yokoyama et al., 1987; Zhang et al., 2010). As shown in Fig. 1 (Aida et al., 2007), the acidic and alkaline HTC pathways produce totally different main final products from cellulose. Because the final pH (<7 or >7)t is usually relevant to the initial alkalinity of reaction medium, initial alkalinity could be an important operating factor that influences the reaction pathway change.

* Corresponding author. Tel.: +1 519 888 4567x38718; fax: +519 885 5862.
E-mail address: tanz@uwaterloo.ca (Z. Tan).

0960-8524/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2011.03.069

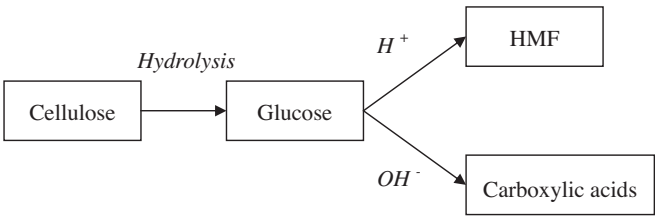

Fig. 1. Simplified acidic and alkaline pathways of hydrothermal conversion of cellulose.

In view of the above considerations, it is necessary to systematically study the impact of alkalinity on alkaline-HTC of biomass. This study aims to investigate the effects of alkalinity (pH ranging from 7 to 14) on the reaction pathway change by studying final pH, bio-oil composition and yield.

2. Methods

Cellulose (Sigma Aldrich, Cat. No. C6413) was used as a feedstock in this study. Alkaline aqueous solutions were prepared by adding sodium hydroxide (NaOH) or sodium carbonate (Na_2CO_3), which are used widely in alkaline-HTC studies. The pH of the NaOH and Na_2CO_3 solutions ranged from 8 to 14 and from 8 to 11, respectively. The highest pH level of the Na_2CO_3 solution used in this study was 11 because the pH of the saturated Na_2CO_3 solution is 11 (Knadler et al., 1986). During the preparation of the alkaline solutions, the pH of each solution was monitored by a pH meter (Oakton, Ion 5) with an accuracy of 0.01.

Reaction conditions of 300 °C and a 0-min reaction residence time were chosen for this study. The reaction residence time refers to the duration that the reactor was maintained at a desired temperature (300 °C in this study). But, it does not include preheating time (28 min in this study). Studies in literature showed that, in the temperature range of 150–380 °C, the highest alkaline-HTC bio-oil yields were usually obtained at 300 °C (Fang et al., 2004; Sugano et al., 2008; Xu and Lad, 2008; Yin et al., 2010). Additionally, alkaline-HTC bio-oil yields were more favored by short reaction times than by long reaction times (Minowa et al., 1995; Yin et al., 2010).

In this study, alkaline-HTC of cellulose to bio-oil was carried out in a tubular reactor. It mainly consisted of stainless steel tubing (2.5 cm ID and 20 cm length), a stainless steel cap at one end, and a needle valve connected to the other end (Dolan et al., 2010). Air inside the tubing reactor can be removed by a vacuum pump through the needle valve and then replaced by argon. The maximum temperature and pressure allowed in this reactor was 320 °C and 3000 psig, respectively.

In a typical test, one gram of cellulose with 30 mL of alkaline solution was loaded into the tubular reactor. After replacing the air inside the reactor with argon, the reactor was sealed and put into a preheated muffle furnace (StableTemp Muffle Furnaces, Cole-Parmer) at 300 °C. The temperature inside the tubular reactor was monitored continuously using a K-type thermocouple. Once the temperature inside the reactor reached 300 °C, the reactor was removed from the furnace and immersed into a water bath filled with tap water to quench further reactions. The gas products were released from the reactor via the needle valve. The remaining liquid in the reactor was filtered using Whatman #1 filter paper to remove the solid products.

After measuring its pH value, the filtrate was mixed with dichloromethane (CH_2Cl_2) at a volumetric ratio of 1:1 in a 150 mL separation funnel for extraction. After 30 min of extraction, the extract was collected and treated in a rotary evaporator (BUCHI, RE-121 Rotavapor, with BUCHI, 461 water bath) at 40 °C to remove the CH_2Cl_2. The remaining liquid was bio-oil (Meier et al., 1986). The bio-oil yield was defined as the mass ratio of the bio-oil to the input cellulose.

The bio-oil composition was analyzed by using gas chromatography (Varian 430) coupled with a CP7717 wax column and a flame ionization detector (FID) indictor. The gas chromatography (GC) separation program was set up as follows: an injection temperature of 230 °C, oven temperatures from 30 to 230 °C with a heating rate of 10 °C/min, and final temperature of 230 °C for 10 min. Before chemical analysis, the GC was calibrated using pure chemicals that are typical of HTC bio-oil components such as acetone, methanol, acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, *n*-valeric acid, isocaproic acid, caproic acid, heptanoic acid, dihydroxyacetone, lactic acid, levulinic acid, and 5-(Hydroxymethyl)-furfural (HMF).

Each test condition in this study was repeated at least three times until the deviation between the results was less than 10%. The mean values are reported in this paper.

3. Results and discussion

3.1. Final pH values

The final pH values after alkaline-HTC of the cellulose were plotted against the initial pH values of the NaOH and Na_2CO_3 solutions in Figs. 2A and 3A, respectively. Both figures show that the final pH values decreased, becoming lower than the initial pH values. Furthermore, as weak alkaline solutions were used, the final pH values decreased to less than 7. For example, for the NaOH solutions with initial pH between 7 and 13.5, the corresponding final pH values were all less than 7. Similarly, for the Na_2CO_3 solutions with initial pH of 8–11, the final pH values were also all less than 7. These results indicate that alkaline-HTC can involve acid-catalyzed reactions.

The decrease of pH during alkaline-HTC was mainly caused by the formation of carboxylic acids from the biomass such as lactic acid, acetic acid and formic acid (Beckman and Boocock, 1983; He et al., 2008). The produced carboxylic acids reacted with the input alkalis, decreasing the pH values of alkaline solutions.

Yan et al. (2007) studied alkaline-HTC of glucose to lactic acid by using NaOH or calcium hydroxide ($Ca(OH)_2$) solutions. They found that the lactic acid yields increased with alkali concentrations and that, with 2.5 M NaOH at 300 °C, the yield of lactic acid reached 27% (based on the starting carbon mass of glucose). They also applied alkaline-HTC to the conversion of cellulose and starch to lactic acids, obtaining similar trends and results (Yan et al., 2010).

Shen et al. (2009) also successfully converted as much as 90% of glycerin to lactic acids by alkaline-HTC. Significant acetic acid yields were also achieved by alkaline-HTC of biomass such as rice hull, sawdust, rice husk, plant seed and cellulose (Eberhardt et al., 2010; Hsieh et al., 2009; Karagöz et al., 2005).

For formic acid, a high yield of 75% was produced from biomass by alkaline-HTC in the presence of oxygen gas (Jin et al., 2008). When the amount of carboxylic acids in the products exceeded that of the input alkalis, the reaction media switched from being alkaline to acidic. Furthermore, since weak alkaline solutions contained few alkalis, it was relatively easy to decrease their pH values. Taking a weak NaOH solution with a pH of 8 as an example, its final pH was as low as 3.2.

On the other hand, the decrease in pH level was influenced by the buffer capacities of alkaline solutions. Since the buffer capacity of a Na_2CO_3 solution is stronger than that of a NaOH solution at the same initial pH level, the final pH values of the Na_2CO_3 solutions