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,*

aDepartment of Mechanical & Manufacturing Engineering, Centre for Environmental Engineering Research & Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4
bDepartment of Chemical & Petroleum Engineering, Centre for Environmental Engineering Research & Education (CEERE), Schulich School of Engineering, University of Calgary, Calgary, Alberta, Canada T2N 1N4

A R T I C L E   I N F O

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

A B S T R A C T

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.

© 2011 Elsevier Ltd. All rights reserved.

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 precautionary 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).

Moreover, 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) is usually relevant to the initial alkalinity of reaction medium, initial alkalinity could be an important operating factor that influences the reaction pathway change.
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 (Na₂CO₃), which are used widely in alkaline-HTC studies. The pH of the NaOH and Na₂CO₃ solutions ranged from 8 to 14 and from 8 to 11, respectively. The highest pH level of the Na₂CO₃ solution used in this study was 11 because the pH of the saturated Na₂CO₃ 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 ºC 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 ºC 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 ºC, the highest alkaline-HTC bio-oil yields were usually obtained at 300 ºC (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 ºC 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 ºC. The temperature inside the tubular reactor was monitored continuously using a K-type thermocouple. Once the temperature inside the reactor reached 300 ºC, 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 (CH₂Cl₂) 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 (BU-CHI, RE-121 Rotavapor, with BUCHI, 461 water bath) at 40 ºC to remove the CH₂Cl₂. 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 ºC, oven temperatures from 30 to 230 ºC with a heating rate of 10 ºC/min, and final temperature of 230 ºC 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 Na₂CO₃ 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 Na₂CO₃ 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 ºC, 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 Na₂CO₃ solution is stronger than that of a NaOH solution at the same initial pH level, the final pH values of the Na₂CO₃ solutions
were always higher than those of the NaOH solutions, as shown in Fig. 3A.

3.2. Bio-oil compositions

Figs. 2B and 3B show that the bio-oils had different compositions when produced in weak and strong alkaline solutions, i.e. HMF and carboxylic acids, respectively. The molar ratio of HMF to carboxylic acids of the bio-oils decreased with increasing alkalinities of the solutions. For the NaOH and Na2CO3 solutions with the same pH of 8, the molar ratios of HMF to carboxylic acids of the bio-oils were 9 and 8, respectively. However, when the strong alkaline solutions of NaOH with a pH of 14 and Na2CO3 with a pH...
were used, the corresponding HMF-to-carboxylic-acid ratios decreased to only 0.1 and 0.2, respectively.

The change of the main bio-oil components with the initial alkalinities was in accordance with the reaction pathways of alkaline-HTC of cellulose illustrated in Fig. 1. HMF is one of the main products of the acid-HTC of cellulose. In this study, when the final pH values of weak NaOH and Na2CO3 solutions were less than 7, HMF was the main bio-oil component.

As the initial alkalinity increased and the final pH became greater than 7, carboxylic acids gradually became the dominant bio-oil components (Figs. 2B and 3B), which are also the main products of HTC of biomass by following the alkaline pathway (Fig. 1). Hence, the reaction pathways were greatly influenced by the final pH levels. Furthermore, the final pH levels were dependent on the initial pH values of the HTC processes (as shown in Figs. 2A and 3B) leading to the conclusion that the initial alkalinity of the alkaline solutions had an important impact on the reaction pathways of alkaline-HTC of biomass to bio-oil.

The effects of alkalinity on the compositions of alkaline-HTC bio-oils also partly explain why the alkaline-HTC bio-oils reported in the literature varied significantly. There has been a wide range of alkali concentrations used in the experimental studies reported in literature and, consequently, the impacts of alkaline on the reaction pathways in these studies differ from each other.

Moreover, the inconsistency in the studies documented in literature made it difficult to develop a standard to define the composition of alkaline-HTC bio-oil. As such, to compare alkaline-HTC bio-oils properly in the future, it is recommended to further classify the alkaline-HTC processes into: (1) those only involving alkaline pathway, and (2) those involving both acidic and alkaline pathways. This classification is intended to allow for a better understanding of alkaline-HTC of biomass to bio-oil and, in the meantime, may contribute to the development of a standard definition of alkaline-HTC bio-oil.

### 3.3. Bio-oil yields

The effects of alkalinity on the bio-oil yields are presented in Figs. 2C and 3C. It is noted that the yields of the alkaline-HTC bio-oils decreased with increasing the alkalinities of the NaOH and Na2CO3 solutions. For the NaOH and Na2CO3 solutions with a pH of 8, the alkaline-HTC bio-oil yields from cellulose were 4.8 wt.% and 7.8 wt.%, respectively. However, when the pH value of the NaOH solution was increased to 14 and Na2CO3 solution to 11, their bio-oil yields decreased to 3.2% and 5.2%, respectively.

Since alkaline-HTC bio-oil was extracted from the conversion liquid products, the bio-oil yield was largely determined by the solubility of the liquid products in the bio-oil extraction solvents (CH2Cl2 in this study). Because the polarity of HMF is weaker than those of carboxylic acids (Palma and Taylor, 2001), HMF can be more easily extracted as bio-oil.

Under weak alkaline conditions, the main conversion product was HMF rather than carboxylic acids leading to relatively high bio-oil yields (by mass). However, with an increase in the solution alkalinity, the main liquid products gradually became polar carboxylic acids resulting in decreased bio-oil yields. This observation was consistent with some experimental findings reported in literature.
Yokoyama et al. (1987) studied alkaline-HTC of sewage to bio-oil using Na₂CO₃ solutions and also found that the bio-oil yields decreased with increasing alkalinity of the Na₂CO₃ solutions. A maximum bio-oil yield of approximately 50% was obtained when the Na₂CO₃ load was 5.0 wt.% of the input biomass and the final pH was 5.4. However, the bio-oil yield decreased to only 25% as the Na₂CO₃ load increased to 20 wt.% and the final pH became 8.6.

On the other hand, it has also been reported that alkaline-HTC bio-oil yields increased with an increase in alkalinity (Bhaskar et al., 2008; Karagöz et al., 2006). These contradicting literature results may be attributed to the differences in compositions between lignin-rich biomass and cellulose-rich biomass. For lignin-rich biomasses, the main components of alkaline-HTC bio-oils were produced from the degradation of lignin. Since it is well known in the pulp industry that alkaline treatment can greatly promote the degradation and removal of lignin content from biomass, it is sensible that the alkaline-HTC bio-oil yields from lignin-rich biomass increased with strong alkaline solutions.

Unlike lignin-rich biomass, cellulose-rich biomass mainly degrades to polar carboxylic acids under strong alkaline conditions. As mentioned above, the solubilities of these acids in non-polar extraction solvents are lower than that of HMF, thus resulting in the decrease of bio-oil yields with increasing the alkalities of alkaline solutions.

3.4. Reaction pathway change

Based on the results and analyses above, the influence of alkalinity on the reaction pathway change of alkaline-HTC of cellulose to bio-oil was proposed and is illustrated in Fig. 4. In strong alkaline solutions (Fig. 4), hydrolysis of cellulose to glucose was first promoted by alkaline. Glucose was then mainly converted to carboxylic acids. Due to the high initial concentrations of alkaline, the final pH of the reaction solutions still remained higher than 7. As a result, carboxylic acids were the main bio-oil components under these conditions.

In weak alkaline solutions (Fig. 4), carboxylic acids were first formed from cellulose via the alkaline pathway and then neutralized/acidified the alkaline solutions. After the pH of the reaction media was reduced to less than 7, the acidic HTC pathway came into action, and the main bio-oil component gradually became HMF. For medium alkaline solutions, alkali- and acid-catalyzed HTC reactions both occurred to comparable extents (Fig. 4) and as a result, the corresponding bio-oils contained both carboxylic acids and HMF.

The proposed pathways in Fig. 4, in fact, were consistent with literature (Aida et al., 2007; Srokol et al., 2004). Srokol et al. studied hydrothermal conversion of glucose under neutral, acidic and alkaline conditions, and they also found that compared with neutral conditions, acidic conditions mainly formed HMF, while alkaline conditions mainly carboxylic acids such as lactic acids and acetic acids.

But, the proposed pathways in Fig. 4 further showed that during hydrothermal conversion, acidic, neutral and alkaline pathways were not totally independent from each other. Under weak alkaline conditions, the reaction can gradually change from the alkaline pathway to the acidic pathway due to the pH decrease caused by the formation of carboxylic acids under initial alkaline conditions.

This change of reaction pathways partly explained the complicated chemical compositions of the bio-oil from alkaline hydrothermal conversion of biomass. Also, it helped to explain why literature reported different trends of bio-oil yields against conversion parameters (such as temperature and pressure) during alkaline hydrothermal conversion. The results of this paper further indicated that pH could be a simple but key parameter of controlling the reaction pathways to help produce more bio-oils or desired chemicals.

4. Conclusions

Although alkaline hydrothermal conversion has been widely used in literature for the hydrothermal conversion of biomass in alkaline solutions, alkaline hydrothermal conversion can, in fact, involve not only alkaline, but also acidic pathways depending on the initial alkalinity. Furthermore, the change of the reaction pathways partly explained the inconsistent literature results on the bio-oil yields and compositions from alkaline hydrothermal conversion of biomass. To better apply and control this conversion process, it is suggested to further classify alkaline hydrothermal conversion into two sub-categories: (1) those only involving alkaline pathway, and (2) those involving both alkaline and acidic pathways.

References


