Hydrothermal liquefaction of cellulose to bio-oil under acidic, neutral and alkaline conditions

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Abstract

Hydrothermal liquefaction (HTL) of biomass to bio-oil under alkaline or neutral conditions has been widely reported in literature. However, there has been limited data available in literature on comparing HTL of biomass to bio-oil under acidic, neutral, and alkaline in terms of chemical compositions and yields by using the same reaction conditions and reactor. Using cellulose as a feedstock we conducted the comparative studies for pH = 3, 7 and 14 at temperatures of 275–320 °C with reaction residence times of 0–30 min. Results showed that the chemical compositions of the bio-oils were different for acidic, neutral and alkaline conditions. Under acidic and neutral conditions, the main composition of HTL bio-oil was 5-(Hydroxymethyl)furfural (HMF). Under alkaline conditions, the main compounds became C2–5 carboxylic acids. For bio-oil yields, it was observed that high temperatures and long residence times had negative effects, regardless of the pH levels. However, the corresponding reaction mechanisms are different. Under acidic conditions, the decrease in the bio-oil yields was mainly caused by polymerization of 5-HMF to solids. Under neutral conditions, the bio-oil yields decreased because 5-HMF was converted to both solid and gaseous products. Under alkaline conditions, the bio-oil decomposed to gases through the formation of short chain acids and aldehydes. Therefore, although they were all referred to as HTL bio-oil in literature, they were formed by different reaction pathways and had different properties due to their different chemical compositions. Given these differences, different strategies are recommended in this study to further improve HTL of biomass to bio-oil.

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1. Introduction

Hydrothermal liquefaction (HTL) is one of the promising biofuel production technologies, which can convert inedible biomass to bio-oil [1,2]. Because HTL uses hot-compressed water as reaction medium, wet biomass can be directly converted without pre-drying processes. To date, HTL has been tested using various biomass feedstocks including sewage [3], livestock manure [4,5], algae [6,7], agriculture waste [8,9] and domestic garbage [10]. In a typical HTL process, biomass is first liquefied to produce liquid products. Bio-oil is then extracted from the liquid products by organic solvents. Since extraction step usually does not involve chemical reactions, the yields and compositions of HTL bio-oil are essentially determined by HTL reaction step. Accordingly, the effects of reaction parameters such as temperature, pressure, processing gas, residence time and biomass particle size on HTL have been widely investigated to improve HTL bio-oil yields [3,5,8,11,12].

Most of the data in HTL literature, however, was obtained at either alkaline or neutral conditions. Limited data were available for acidic conditions. On the other hand, fundamental carbohydrate research showed that pH could play an important role in HTL bio-oil formation [13,14]. The reaction pathways of HTL of biomass change with acidic, neutral and alkaline conditions [15–20]. As shown in Fig. 1, under acidic conditions, the main conversion compounds are 5-(Hydroxymethyl)furfural (5-HMF) and levulinic acids. Under alkaline conditions, they become carboxylic acids such as lactic and acetic acids. Under neutral conditions, both the acidic and alkaline conversion products are formed, due to the self-disassociation of H₂O to H⁺ and OH⁻ at high temperatures. Our recent study [21] showed that these reaction pathways were not independent on each other. Under weak alkaline conditions, the reaction pathway can change gradually from alkaline to acidic one. The carboxylic acids produced under initial alkaline conditions could neutralize the input alkalis and the aqueous reaction media become acidic, activating the acidic pathway. Since HTL bio-oils are extracted from the corresponding aqueous products, the influence of acidic, neutral and alkaline conditions on HTL reaction pathways and liquid products are expected to change HTL bio-oil yields and compositions.

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Following up on our previous studies on the effect of alkalinity on the change of the HTL pathway, the objective of this study is to better understand the mechanism of HTL of biomass under acidic and neutral conditions by comparing with HTL under alkaline con-
ditions. Our focus is on the differences between acidic, neutral, and alkaline HTL of biomass to bio-oil using identical biomass feed-
stock in the same reactor. Then, based on the experimental data and analyses, different strategies will be recommended for practical applications of acidic, neutral and alkaline HTL. To our best knowledge, only He et al. [22] mentioned the differences in the bio-oil yields of HTL of swine manure under all three types of conditions with pH 4, pH 7 and pH 10. However, their research was not focused on understanding of the mechanisms behind these differences. They only compared the yields of the HTL bio-oils.

2. Materials and methods

Cellulose (Sigma Aldrich Cat No. C6413) was used as a feedstock in this study. We did not study lignin as feedstock because only alkali lignin was commercially available, which was already the product of biomass treatment in alkaline solutions. If alkali lignin was used as a feedstock, the results on acidic and neutral HTL of lignin to bio-oil would be misleading.

The solutions of pH 3, pH 7 and pH 14 were selected to represent acidic, neutral and alkaline conditions, respectively. The pH 3 acidic solutions were prepared using hydrochloric acid (HCl). pH 3 was chosen because the rate of hydrolysis of cellulose was greater than that at pH 4–7 [23]. In addition, pH 3 solution causes less corrosion of metal reactor as compared to that with pH 1–2. The pH 14 solutions were prepared using sodium hydroxide (NaOH). Alkali metal hydroxides solutions were widely used for alkaline HTL of biomass to bio-oil [5,8,24,25] and HTL bio-oil yields usually increased with solution alkalinitities [26]. During the preparation of the above acidic and alkaline solutions, their pH values were monitored online by a pH meter (Oakton Ion 5) with the accuracy of ±0.01.

All tests were carried out in a 69 ml tubing reactor that was previously reported by Dolan et al. [27] It was made of stainless steel 316 with two reducing unions. One reducing union can be sealed using a stainless steel cap and the other connected to a needle valve. The whole reactor system was rated to 320 °C and 3000 psig.

In a typical test, 1 g of cellulose with 30 ml of solutions was first loaded to the reactor from the end with a stainless steel cap. After loading and sealing the reactor, air in its headspace was removed through the needle valve using a vacuum pump and the headspace was then filled with N2 from a gas cylinder. The reactor was heated in a muffle furnace (StableTemp Muffle Furnaces, Cole-parmer) with a preset temperature of 280–320 °C. These temperatures were chosen because subcritical water favors bio-oil products [28]. Xu and Lad [8] and Qian et al. [29] compared sub/supercritical liquefaction of woody biomass using water and both found that more bio-oil was produced with subcritical water than supercritical water. Supercritical water usually is employed for bio-gas production by steam forming [30,31].

Although the temperature inside the muffle furnace had reached the preset value, it was not the same temperature in the reactor. The temperature inside the reactor was monitored by a K-type thermocouple. The moment when the temperature inside the reactor reached the preset value (same as that in the muffle furnace) was defined as time zero for the residence time. After heating the reactor with the desired residence time, it was removed from the furnace and submerged into a water bath (at room temperature) to quench further reactions.

After cooling and opening the reactor, the slurry was collected and filtered by Whatman No.1 filter paper. The residual solids on the filter paper were dried at 105 °C in an oven until their weight became constant. The residual solid yield was defined as the mass ratio of the residual solids to the input cellulose. The filtrate was measured in terms of mass and volume. Subsequently, the filtrate was extracted using dichloromethane (CH2Cl2) at the volumetric ratio of 1 (filtrate) to 1 (CH2Cl2) for 30 min in a 125 ml separation funnel. The extract was then treated at 40 °C in a rotary evaporator (BUCHI RE-121 Rotavpoar with BUCHI 461 water bath) to remove dichloromethane. The remaining liquid was bio-oil [3,5]. The bio-
oil yield was calculated as the mass ratio of the bio-oil to the input cellulose. The mass of produced gases was calculated based on the mass balance. The gas yield was similarly determined as the mass ratio of the gases to the input cellulose. The yield of aqueous products from cellulose was also calculated based on the cellulose mass balance, which was equal to 100% minus the yields of residual sol-
ids, bio-oil and gas products.

The chemical compositions of the HTL bio-oils were analyzed using gas chromatography (GC, Varian 430 equipped with a capillary column (CP 7717) and with a FID detector). The GC had been
calibrated for typical HTL bio-oil compounds using standard chemicals such as acetone, methanol, acetic acid, propionic acid, isobutyric acid, butyric acid, iso-valeric acid, n-valeric acid, isocaproic acid, caproic acid, heptanoic acid, dihydroxyacetone, lactic acid, levulinic acid, and 5-HMF [32]. In a typical GC analysis, 1 μl of bio-oil was injected into the GC, and the GC separation program was set as follows: injection temperature of 230 °C, oven temperatures from 30 °C to 230 °C with heating speed of 10 °C/min, and final temperature of 230 °C for 10 min. Test under each condition in this study was repeated at least three times until the error between the results was less than 5%. The mean value for each condition is reported as follows.

3. Results and discussion

3.1. Chemical compositions of bio-oils

As shown in Table 1, the main compounds of the bio-oils were greatly influenced by the acidic, neutral and alkaline conditions. 5-HMF was the main compound of the HTL bio-oil produced under acidic conditions. Under neutral conditions, 5-HMF remained a major compound, but the yields of carboxylic acids became apparent. Under alkaline conditions, the compounds of the bio-oil were primarily C2–5 carboxylic acids (acetic, lactic, propionic, butyric and caproic acids) and dihydroxyacetone.

The GC results above were consistent with the main reaction pathways illustrated in Fig. 1. 5-HMF was the main compound of HTL with cellulose as a feedstock under acidic conditions. And the carboxylic acids were the main products of HTL of cellulose under alkaline conditions. These similarities between HTL bio-oil and HTL liquid products confirmed that acidic, neutral and alkaline conditions influenced the compositions of not only liquid products but also HTL bio-oils.

Furthermore, the differences between the compositions of the HTL bio-oils indicated that sometimes it is misleading to compare the yields of HTL bio-oils from different research groups without considering the chemical compositions. Comparison of yields is supposed to be based on the assumption of the same chemical compositions. Data in literature with higher yields were usually supposed to be based on the assumption of the same chemical compositions. Therefore, attention ought to be paid to HTL bio-oil compositions, particularly when research focuses on the optimization of conversion parameters to improve HTL bio-oil yields.

### Table 1

Main components of acidic, neutral and alkaline HTL bio-oil.

<table>
<thead>
<tr>
<th>No</th>
<th>Retention time (min)</th>
<th>Compounds</th>
<th>Concentrations (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH = 3</td>
</tr>
<tr>
<td>1</td>
<td>5.50</td>
<td>Acetic acid</td>
<td>9.34</td>
</tr>
<tr>
<td>2</td>
<td>6.39</td>
<td>Propionic acid</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>6.68</td>
<td>Isobutyric acid</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>7.35</td>
<td>Butyric acid</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>7.78</td>
<td>Iso-valeric acid</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>9.18</td>
<td>Isocaproic acid</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>10.68</td>
<td>n-Caprylic acid</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>12.10</td>
<td>Heptanoic acid</td>
<td>–</td>
</tr>
<tr>
<td>9</td>
<td>12.10</td>
<td>Dihydroxyacetone</td>
<td>0.87</td>
</tr>
<tr>
<td>10</td>
<td>12.85</td>
<td>Lactic acid</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>14.22</td>
<td>Levulinic acid</td>
<td>3.50</td>
</tr>
<tr>
<td>12</td>
<td>15.70</td>
<td>HMF</td>
<td>38.38</td>
</tr>
<tr>
<td></td>
<td>Total peak area (%)</td>
<td></td>
<td>93.9</td>
</tr>
</tbody>
</table>

(HTL conditions: 1 g cellulose, 30 ml solutions, 300 °C, and 0 min reaction residence time).

3.2. Bio-oil yields

The effects of conversion temperature on the HTL bio-oil yields at acidic, neutral and alkaline conditions are shown in Fig. 2. It is noted that regardless of pH levels, the HTL bio-oil yields all first increased and then decreased with temperatures in the range of 275–320 °C. And, the maximum bio-oil yields under acidic, neutral and alkaline conditions were all obtained at 300 °C.

The effects of residence time on the yields of HTL bio-oils are presented in Fig. 3. It can be seen that the trends of the bio-oil yields against residence time were similar. The bio-oil yields under acidic, neutral and alkaline conditions all decreased with increasing residence time, ranging from 0 to 30 min. With a residence time of 0 min, the bio-oil yields under acidic, neutral and alkaline conditions were 34.0 wt.%, 28.2 wt.% and 5.8 wt.%, respectively. But, as the residence time was extended to 30 min, the corresponding bio-oil yields decreased to 7.9 wt.%, 3.6 wt. % and 3.0 wt.%, respectively.

Despite the similar trends of HTL bio-oil yields against the conversion temperature and the residence time, the mechanisms behind were quite different. Under acidic HTL conditions, the decrease in bio-oil yields at high temperature and long residence time were mainly attributed to the formation of residual solids as evidenced in Fig. 4A. At pH = 3, the yields of HTL bio-oil and residual solids at 300 °C were 34.0 wt.% and 17.4 wt.%, respectively. At 320 °C, however, the yield of residual solids increased to about 50 wt.% and the corresponding bio-oil yield decreased to only 6.1 wt.%. Similarly, when the bio-oil yield decreased from 34.0 wt.% (with a residence time of 0 min) to 7.9 wt.% (with a residence time of 30 min) at 300 °C, the corresponding yield of the residual solid increased from 17.4 wt.% to 31.7 wt.% (Fig. 4B).

Under acidic conditions, the main component of acidic HTL bio-oil (5-HMF) is an active chemical and tends to form hydrothermal char/solid by polymerization. Titirici et al. [33] compared the solid hydrothermal carbon materials from starch, sucrose, maltose and glucose by using 13C solid-state CP-MAS NMR and showed that 5-HMF was the core structure of hydrothermal carbon. Baccile et al. [34] further applied a combination of advanced solid-state 13C NMR techniques to characterize hydrothermal carbon from glucose and found that 65% of hydrothermal carbon existed in the form of HMF ring structure. Therefore, it mainly was the formation of residual solids from 5-HMF that caused the decrease in the yields of bio-oil under acidic conditions.

Under neutral conditions, the decrease in HTL bio-oil yields at high temperatures and long residence times was a result of increased residual solids as well as gaseous products. As shown in
Fig. 5A, when bio-oil yield decreased from 28.4 wt.% at 300 °C to 3.0 wt.% at 320 °C, the yields of residual solids and gas products increased to 64.1 wt.% and to 6.0 wt.%, respectively. Similarly, as the bio-oil yields decreased with the residence time of from 0 min to 30 min at 300 °C (Fig. 5B), the corresponding yields of residual solids and gases increased to 30.9 wt.% and to 3.0 wt.%, respectively.

The bio-oil yields were likely to be reduced by the polymerization of HMF to residual solids because 5-HMF was one main compound of the bio-oil produced under neutral conditions [35]. Fig. 5 does show that the yields of residual solids increased as both yields of HMF and bio-oil decreased with the increase of temperature and the reaction residence time. High temperature and long residence time can also promote the decomposition of HMF to gases, resulting in the decrease in the yields of HTL bio-oil under neutral conditions. Chuntanapum and Matsumura [36] studied the decomposition of 5-HMF in pure water and found that the corresponding gas yield increased with temperature (300, 350, 400 and 450 °C) as well as residence time (0–7 min). Another means for the production of gases may originate from the decomposition of short chain acid and aldehyde components formed under neutral conditions. Kruse and Gawlik studied hydrothermal conversion of biomass at the temperatures of 350–410 °C with the pressures of 30–50 MPa, and they found that low molecular weight acids and aldehydes from cellulose can be easily converted to gases [37].
Under alkaline conditions, it was mainly the formation of gases from the decomposition of HTL compounds that led to the decrease in bio-oil yields at high temperatures (>300 °C). As shown in Fig. 6A, when the yields of the HTL bio-oil under alkaline conditions decreased from 5.8 wt.% at 300 °C to 0% at 320 °C, the corresponding yields of gaseous products increased from 0 to 10.1 wt.%. Meanwhile, the yields of the aqueous products and the residual solids remained nearly constant. This indicates that HTL bio-ols under alkaline conditions at high temperatures were unstable and could be easily decomposed to gases. This observation was consistent with the literature on subcritical hydrothermal gasification (HTG) of biomass. For example, Fang et al. [38] studied hydrothermal gasification (HTG) of cellulose with and without alkali and found that the yields of gases under alkaline conditions were approximately 50% higher than those under neutral conditions on a carbon basis and that the gas yields in the presence of alkalis apparently increased with the temperatures (220–340 °C). Onwudili and Williams also investigated the role of alkali in HTG of different biomass and found that the intermediates (bio-oil compounds) produced under alkaline conditions were more easily gasified to gases than those produced under neutral conditions [39].

The yields of HTL bio-oil under alkaline conditions also decreased with the increase of residence time. As shown in Fig. 6B, as the bio-oil yields decreased from 5.8 wt.% with 0 min residence time to 3.1 wt.% with a residence time of 30 min at 300 °C, the corresponding yields of gases increased from 5.0 wt.% to 18.2 wt.% in our previous study on HTL of cattle manure under alkaline conditions, a similar correlation between the yields of bio-oil and gas products was reported [5]. This is because acids and aldehydes were the key intermediates for gas products from HTG [37,39]. They were also the main components of HTL bio-oil under alkaline conditions. It was likely that a long residence time allowed more of these intermediates to be decomposed to gases. Our experiment data (Fig. 6B) showed that the concentrations of carboxylic acids in the liquid products decreased as the bio-oil yields under alkaline conditions decreased with the long residence time.

Note that the highest HTL bio-oil yields were always obtained under acidic conditions, followed by neutral and alkaline conditions, as shown in Figs. 3 and 4. The main reason behind this difference was related to the extraction efficiency of major compounds of the HTL bio-ols. Carboxylic acids were the main compounds in the HTL bio-ols under of alkaline conditions. These acids are polar chemicals and are less likely to be extracted by non-polar solvents. On the other hand, the primary component of acidic and neutral HTL bio-ols, 5-HMF, is a less polar chemical and can be easily extracted by non-polar solvents such as dichloromethane, diethyl ether and supercritical CO₂ [40]. As supported by our experiment data, the mass ratios of the bio-oil to the total liquid products under acidic and neutral conditions were between 0.34 and 0.69, while the ratios under alkaline conditions were only 0.02–0.08.

4. Conclusions

In this paper we compared hydrothermal liquefaction (HTL) of cellulose to bio-oil under acidic, neutral and alkaline conditions using identical feedstock in the same reactor. All experimental data obtained in this study led to one conclusion that HTL of biomass to bio-oil under acidic, neutral and alkaline conditions are different in terms of bio-oil chemical composition and yield. Based on the results above, the following specific conclusions can be made.

1. The compositions of HTL bio-oil depend on the acidic, neutral and alkaline conditions. The bio-oil produced from cellulose under acidic and neutral conditions, was mainly composed of 5-HMF. However, the main compounds of the bio-oil produced under alkaline conditions were C_{2-5} carboxylic acids. The difference in chemical composition indicated that it is necessary to clarify the pH conditions for HTL bio-oil formation. Although they were all referred to as HTL bio-oil in literature, they actually had different properties due to their different chemical compositions.

2. Different reaction mechanisms were involved for HTL under acidic, neutral and alkaline conditions, although HTL bio-oil yields showed similar trends against conversion temperatures and reaction residence time. The decrease in the yield of HTL bio-oil under acidic conditions was mainly caused by the polymerization of HMF to solids. Under neutral conditions, bio-oil yields decreased because of the conversion of 5-HMF to both solids and gases. Under alkaline conditions, HTL bio-oil was mainly decomposed to gases through short chain acids and aldehydes in the bio-oil.

5. Implications

1. Since HTL of biomass to bio-oil under acidic, neutral and alkaline conditions followed different reaction pathways, different approaches need to be taken in order to improve HTL bio-oil yields. For HTL processes under acidic and neutral conditions, HTL bio-oil yields can be increased by preventing polymerization of HMF. For HTL process under alkaline conditions, this can be done by inhibiting the decomposition of bio-oil to gases. One practical method that may help in this regard is consideration of reactor material. Common reactor materials, such as nickel, are known to be effective catalysts for hydrothermal gasification [38]. Glass reactors or reactors with different coatings may decrease the decomposition of bio-oil to gases.
(2) Because short residence time favors the yields of HTL bio-oil, equipment size can be reduced for a given throughput. However, given that hydrothermal solids are formed during the acidic and neutral HTL processes, more research would be needed to prevent the plugging of reactors. In addition, for HTL processes under alkaline conditions, corrosion resistant materials are required for reactor due to the relatively high concentrations of carboxylic acids in HTL bio-oil.

References