Homogeneous Degradation of Cellulose in Its Aqueous Solution at Mild Temperature under Atmospheric Pressure

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Degradation of cellulose to chemicals is one of major routes for biomass conversion. Here, a new simple and two-step method has been developed to convert cellulose in its homogeneously alkaline solution to organic acids under atmospheric pressure at mild temperature. At first, cellulose was degraded to small molecular intermediates at 110 °C for 3 h under atmospheric pressure, and then it was oxidized with H₂O₂ at 50 °C for 4 h. Under the optimal condition, 73.5% conversion of cellulose could be achieved, and the yield of organic acids was 32.8% (formic acid), 11.6% (lactic acid), and 2.3% (oxalic acid), respectively. It is noteworthy that the new strategy reduces energy consumption in the process of reaction, unlike the hydrothermal reaction under high temperature and high pressure.

Key words: Cellulose, Degradation, Homogeneous, Organic acids

I. INTRODUCTION

In recent decades, as we all know, the serious energy crisis, environmental pollution and the greenhouse effect have gained more and more attention with the expansion of the demand for energy and chemicals. Therefore, the conversion of biomass is becoming increasingly attractive as renewable feedstock for the production of chemicals and fuels [1–3]. Cellulose is the most abundant renewable molecules in biomass for the production of value-added fuels and platform molecules, and unlike starch, which is inedible [4]. The conversion of cellulose into valuable chemicals such as formic acid, lactic acid, and oxalic acid has attracted much attention. For example, formic acid was produced from direct conversion of cellulose with CuO as an oxidant [5]. Formic acid and lactic acid were produced from cellulose by the hydrothermal reaction [6]. Lactic acid was obtained from corn cobs with alkaline hydrothermal treatment [7].

However, because of the complex hydrogen bonding structure of cellulose composed of glucose units linked by β-1,4-glycosidic bonds, the processes usually are heterogeneous where cellulose powder is usually used as the feedstock, resulting in a slow degradation rate. Dissolution of cellulose will accelerate the degradation of cellulose, as cellulose chains are well-extended and dispersed in its homogeneous solution. In this case, two kinds of solvents, ionic liquids and alkaline aqueous solutions, were used for dissolving cellulose [8–12]. For example, lignocellulosic biomass was converted to 5-hydroxymethyl furfural (HMF) and furfural in ionic liquid [13]. However, ionic liquids are difficult in recovery, exorbitant in price and tough in reutilization, which limit their application in a large scale application at present. It is known that homogeneous aqueous solution of cellulose could be formed in 5wt%–7wt% [11] or 7wt%–12 wt% [14] NaOH aqueous solution with/without urea through various freezing-thawing processes, where OH⁻ breaks the hydrogen bonds, Na⁺ hydrations stabilize the hydrophilic hydroxyl groups, and urea stabilizes the hydrophobic part of cellulose [15]. The formation of homogeneous solution in aqueous phase provides a chance to prepare organic acids in the homogeneous cellulose solution by an alkaline hydrothermal reaction. For instance, oxalic acid was produced from cellulose in alkaline solution under low O₂ pressure [16]. And formic acid, lactic acid, and malonic acid were gained from cellulose homogeneous alkaline solution [17]. However, these reactions all occurred under the high-temperature, high-pressure water vapor environments, which required a great deal of energy consumption and special reactors. In order to further save energy and reduce the cost of reactors, we conceived a new method to degrade cellulose to organic acids in its homogeneous solution, especially under atmospheric pressure.

It has been reported that NaOH would promote the retrograde aldol condensation of the carbohydrates and degradation from cellulose to organic acids [18]. H₂O₂ was used as an oxidant that was applied to conversion of glycerol and glucose to organic acids, which occurred at mild temperature [19]. Formic acid was prepared by hydrothermal oxidation of glucose with only H₂O₂ al-
though it happened at high temperature [20]. Hence, in this work we accomplished the following work: firstly, an alkaline aqueous solution of cellulose was prepared by a modified freezing-thawing process, and then the well-dispersed cellulose chains were degraded to mild molecular weight sugars or organic acids at mild temperature, which was finally oxidized to formic acid and oxalic acid by H$_2$O$_2$ as only oxidant at mild temperature. It is also worth mentioning that reactions of two steps were all carried out in an open system under atmospheric pressure.

II. EXPERIMENTS

A. Materials

Microcrystalline cellulose (M$_w$=1.08×10$^5$ g/mol by an Ubbelohde viscometer using DMAC/LiCl as solvent) powder was purchased from Shanghai Hengxin Chemical Reagent Co. Ltd. Sodium hydroxide was analytical grade, and standard samples of formic acid, lactic acid and oxalic acid were all purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water with resistivity of 18 MΩ·cm was produced by a Milli-Q (Millipore, USA) and was used for solution preparation.

B. Preparation of the homogeneous cellulose solution

Here, an alkaline aqueous solution of cellulose was prepared by a modified freezing-thawing process [11]. 3 g NaOH and 45 g deionized water were subjected into a beaker, and a mixture was obtained under stirring. Then, this mixture was kept in a freezer until it became a frozen solid. After thawing, 1.5 g microcrystalline cellulose was slowly added in ice bath with vigorous stirring for 15 min. The new mixture was kept in freezer (−32 °C) for 20–25 min, resulting in an ice-water mixed solution. Next, the ice-water mixture was stirred for 3–5 min at room temperature, resulting in a uniform mixture which was then immediately transferred and kept in a freezer (−32 °C) for 4 h. At last, the homogeneous cellulose solution was obtained after the frozen solid was thawed at room temperature (without stirring).

C. Open-system degradation of cellulose at mild temperature

The reaction was divided into two processes. First, 4.95 mL homogeneous cellulose solution was added into a 50 mL round-bottom flask with a reflux condenser and a magnetic stirrer. Then the flask was immersed in an oil bath preheated to the required temperature and occasionally shaken during the reaction in order to prevent the mixture sticking to the flask wall. After the desired reaction time, the flask was taken out and immersed into a cold water bath. The procedure mentioned above was called the pretreatment reaction. Second, the cooled flask was immersed in a water bath for the reaction at mild temperature with adding H$_2$O$_2$. After the known reaction time, the flask was immediately quenched in a cold water bath.

D. Characteristics and analysis of the product

The cooled solution was filtered through a filter (0.22 μm in pore size), then the filtrate was neutralized by sulfuric acid and analyzed by high performance liquid chromatography (HPLC, LC-20AD, Shimadzu) with a UV detector (210 nm), using a C-18 column, 0.1%H$_3$PO$_4$ as the mobile phase with flow rate of 0.8 mL/min at 40 °C. The residue was collected, dried and then weighed to calculate the feedstock conversion.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the typical photoimage of the as-prepared cellulose alkaline aqueous solution, and it is transparent, indicating a well dissolving of cellulose chain. After the first-step reaction at 100 °C under atmospheric pressure, a brown solution was obtained (Fig.1(b)), indicating the efficient degradation of cellulose. Then, after the second-step reaction with H$_2$O$_2$ oxidation, a little brown solution was formed as shown in Fig.1(c), and no precipitation appeared even adding acid into it to neutralize, indicating a high conversion of cellulose. HPLC measurements were used to analyze the product, and the major contents were small molecular organic acids, such as formic acid (FA), acetic acid (AA), oxalic acid (OA), and lactic acid (LA), with other unknown compounds.

A. Effect of the pretreatment reaction on the cellulose conversion

First of all, we explored the optimization of reaction conditions for cellulose conversion in a Parr reaction. Table I shows the conversion of cellulose with the varied of reaction time (1, 2, 3, or 4 h) at 110 °C. The highest
### TABLE I The effect of the reaction time on cellulose conversion$^a$.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>$t$/h</th>
<th>Conversion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>68.8</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>70.3</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>73.5</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>71.2</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 4.95 g cellulose solution, 110 °C.

### TABLE II The effect of the reaction temperature on cellulose conversion$^a$.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T$/°C</th>
<th>Conversion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>71.3</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>73.5</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>70.8</td>
</tr>
<tr>
<td>4$^b$</td>
<td>110</td>
<td>52.1</td>
</tr>
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</table>

$^a$ Reaction conditions: 4.95 g cellulose solution, 3 h.  
$^b$ 0.15 g microcrystalline cellulose suspension, 0.3 g NaOH, and 4.5 mL H$_2$O.

conversion (73.5%) was obtained with reaction time of 3 h. This result is possibly decreased because that part of intermediates aggregated and adsorbed on the residual of the cellulose with the increase of reaction time after 3 h. Low molecular weight sugars can be found in the intermediates by the HPLC measurements using an amine column, indicating the intermediates are oligomers of sugar, but the accurate structure is still unclear.

This hypothesis may be also used to explain the results of Table II, the conversion of cellulose with the reaction time (3 h) at 100 °C (71.3%), 110 °C (73.5%) or 120 °C (70.8%). As the reaction temperature increased, the rate of reactions and the formation of intermediates was also increased. In summary, the highest conversion (73.5%) was obtained at 110 °C with 3 h. In addition, the low conversion (52.1%) of microcrystalline cellulose in its heterogeneous aqueous solution confirmed cellulose with the advantage of the faster reaction rate in its homogeneous aqueous solution.

#### B. Effect of reaction temperature on the yield of organic acids

Next, the effect of reaction temperature on the yield of organic acids was studied. Figure 2 shows the yield of FA, LA and OA with reaction time (4 h) at 45, 50, 55, or 60 °C, respectively. The yield of FA (31.1%, 32.8%, 31.2% and 29.7%) and OA (1.8%, 2.3%, 2.2%, and 1.8%) were increased at first and then decreased with the increase in temperature. With the reaction temperature increase, the reaction rate gets faster, but the decomposition rate of H$_2$O$_2$ is also faster which is bad for oxidation reaction. Obviously, the yield of LA (11.2%, 11.4%, 12.0% and 13.1%) was slightly controlled by the H$_2$O$_2$ amounts at 45–60 °C. This hypothesis will be further proven later.

#### C. Effect of reaction time on the yield of organic acids

Similarly, effect of reaction time on the yield of organic acids has been investigated (Fig.3). As the reaction time increased, the yields of FA (29.1%, 32.8%, 32.6%, and 32.8%) and OA (2.0%, 2.3%, 2.2%, and 2.3%) were increased at first and finally no longer changed with the increased reaction time, but the yield of LA (11.5%, 11.6%, 11.5% and 11.5%) has changed little. It is apparent that FA and OA were not increased after H$_2$O$_2$ run out, when the amount of H$_2$O$_2$ was fixed, the yield of LA looked pretty much the same.

#### D. Effect of H$_2$O$_2$ amounts on the yield of organic acids

Figure 4 illustrates the effect of H$_2$O$_2$ amounts on the yield of organic acids. Because excess H$_2$O$_2$ amounts can oxidize OA to CO$_2$, the yield of OA (1.6%, 2.1%,...
FIG. 4 Effect of H$_2$O$_2$ amounts on the yield of organic acids. Reaction conditions: 4.95 g cellulose solution, 3 h, 110 °C, then 50 °C, 0.1, 0.15, 0.2, 0.3, 0.4, or 0.5 mL H$_2$O$_2$, 4 h.

<table>
<thead>
<tr>
<th>Volume of H$_2$O$_2$ / mL</th>
<th>Y (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>0.15</td>
<td>15</td>
</tr>
<tr>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>0.3</td>
<td>25</td>
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<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>0.5</td>
<td>35</td>
</tr>
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</table>

Scheme 1 Reaction pathway for the production of formic acid, lactic acid and oxalic acid by open-system degradation of cellulose at mild temperature.

IV. CONCLUSION

In summary, a new two-step method for production of organic acids has been developed by an open-system degradation of cellulose at mild temperature. It’s effective to prepare formic acid (32.8%), lactic acid (11.6%) and oxalic acid (2.3%) via the optimum condition (first at 110 °C with 3 h and then 50 °C with 4 h) and in the meantime, it’s beneficial to reduce energy consumption. We believe this new strategy can be applied in other conversion of sugars.

V. ACKNOWLEDGMENTS

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