One-Pot Hydrothermal Conversion of Cellulose into Organic Acids with CuO as an Oxidant

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ABSTRACT: A one-pot hydrothermal conversion of cellulose with CuO as an oxidant was investigated under alkaline conditions. The results showed that a high yield of organic acids, mainly including acetic acid, glycolic acid, lactic acid, and formic acid, was obtained from cellulose. The highest total yield of the four organic acids reached 43.0% at 325 °C for 1 min. CuO can effectively increase the total yield of organic acids, and Cu2O and Cu0 can be produced from the proposed process. A reaction pathway of cellulose conversion into organic acids in the presence of CuO was investigated and proposed. The present study is expected to be a link in the development of a new and green method of both cellulose conversion and CuO smelting.

1. INTRODUCTION

In recent decades concerns about the depletion of fossil fuel reserves and global warming caused by anthropogenic CO2 emission have spurred the search for renewable chemicals and fuel sources. Cellulosic biomass emerges as a very promising source because biomass originates from fixation of CO2 by photosynthesis and, unlike starch or corn, cellulosic biomass is nonedible. Many effective methods for conversion of cellulose into valuable chemicals have been proposed and studied.1,2

Because of the insolubility of cellulose, hydrothermal technology shows highly efficient and environmentally friendly advantages that can fast hydrolyze insoluble cellulose into water-soluble saccharides and desirable chemicals afterward with only water as the solvent3,4 because high-temperature water has many unique inherent qualities, such as high ionic product constant (Kw), acting as both an acid and base catalyst.5 Therefore, acid- or base-catalyzed reactions could occur under hydrothermal conditions even without the addition of acid or base. The acid-catalyzed reaction of cellulose under hydrothermal conditions easily led to the formation of 5-hydroxymethylfurfural (HMF) or levulinic acid with a low concentration of acid.6,7 Hydrothermal pretreatment of lignocellulosic materials by dicarboxylic maleic and oxalic acids can also produce a liquid stream rich in pentose sugar oligomers with fewer further degradations by varying reaction conditions.8 Carboxylic acids including lactic acid can be obtained under base-catalyzed hydrothermal conditions.9–11 In addition, hydrothermal oxidation of cellulose could be used to produce organic acids such as formic acid and acetic acid with H2O2 or O2 as oxidants.12

However, the usage of H2O2 or O2 will lead to a high cost because of the high price of H2O2 or the high energy needed to compress gaseous O2 into the reacting system. Recently, we have found that some metal oxides such as CuO and NiO could be completely reduced to its zerovalent metal in the presence of carbohydrates,13–15 which suggests that those metal oxides having oxidative potential might have the function of promoting the oxidation of carbohydrates into organic acids. A recent work showed that CuO has a promotion effect on the production of acetic acid and lactic acid from glucose.16 The usage of CuO as an oxidant has the additional benefit of developing a new and green process for copper manufacturing14,16 because only water is used as a reaction medium in this process. The reduction of CuO and production of organic acids from cellulose can be obtained in one-pot reaction. Moreover, the proposed process should be expected to be green compared to conventional copper production processes, in which sulfuric acid is used as a leaching agent and organic solvents as extractants. These findings gave us the motivation to extend the feedstock from glucose to cellulose as well as other saccharides and to investigate other organic acid production except for lactic acid and acetic acid. Herein we report a production of organic acids in a one-pot reaction from cellulosic biomass with CuO as an oxidant.

2. EXPERIMENTAL SECTION

2.1. Experimental Materials. α-Cellulose, glycolaldehyde dimer, pyruvic acid (98.0%), glycolic acid (99.0%), and acetic acid (≥99.7%) were purchased from Sigma-Aldrich. Glucose
(>99.9%), d-fructose (>99.9%), sucrose (>99.9%), chitosan (>98.0%), d-(−)-xylose (>99.9%), NaOH (≥96.0%), FeO₃ (≥99.0%), MnO₂ (≥97.5%), ZnO (≥99.0%), and NiO (≥99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium-d-gluconate (≥98%), ethylene glycol (≥99.99%), CuO (≥99.0%), and Cu (≥99.7%) were purchased from Shanghai Richjoint Chemicals. D-(+)−cellobiose was purchased from Toronto Research Chemicals Inc. D,L-glycer-aldehyde dimer (>93.0%) was purchased from Apollo Scientific. Lactic acid (1.0 N) was purchased from Alfa Aesar. Formic acid (~98%) was purchased from Fluka. Al₂O₃ (≥99.0%) was purchased from Shanghai Wusi Chemicals. For product analysis and derivatization, perchloric acid (70%) was purchased from Sigma-Aldrich. Potassium biphthalate (≥99.8%), tetradecyl trimethylammonium bromide (TTAB, 99%), methanol (≥99.5%), dichloromethane (≥99.95%), H₂SO₄ (95.0−98.0%), Na₂SO₄ (≥99.0%), and NaCl (≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All these reagents were used without further purification.

2.2. Experimental Procedure. All of the experiments were conducted in a SUS 316 batch reactor (9.5 mm diameter, 1 mm wall thickness, and 120 mm length) with an internal volume of 5.7 mL. A 0.035 g cellulose sample and 2.0 mL of deionized water (35% water content) was added into the reactor which was then sealed. The reactor, which was shaken to enhance mixing and heat transfer during the reaction, was heated to the reaction temperature in a preheated salt bath. After the reaction, the reactor was taken out of the salt bath and immediately placed into a cold water bath to stop the reaction. The real reaction time is a little shorter than the apparent reaction time because initial reaction time (about 15 s) was required to raise the temperature of the reaction medium from room temperature to the salt bath temperature. Each experiment was conducted at least twice.

2.3. Product Analysis. After the reactions, the resultant aqueous phase samples were prepared for total organic carbon (TOC), capillary electrophoresis (CE), high-performance liquid chromatography (HPLC), and gas chromatography coupling with mass spectrometer (GC-MS) analysis. The solids residues were collected and analyzed by X-ray diffraction (XRD). The gaseous products were analyzed using a gas chromatograph equipped with thermal conductivity detector (GC-TCD).

The liquid samples after the reactions were collected, diluted, and filtered with a 0.22 μm filter membrane. TOC was measured at a total organic carbon analyzer (TOC-v, Shimadzu). TOC yields were defined as the percentage of the TOC content of the aqueous phase products in the TOC of the initial substrate. Formic acid, acetic acid, glycolic acid, and lactic acid were quantified by CE (Beckman, P/ACE MDQ) with TTAB as background electrolyte (pH 5.6) at 254 nm. Fused-silica capillary (Beckman) of 67 cm (50 cm effective length) with 0.075 mm I.D. was used. The temperature of the capillary cassette was 25 °C, and the sample injection was performed in the hydrodynamic mode by applying a 0.5 psi pressure for 5 s. A negative voltage of 20 kV was applied for the separation, and indirect detection was used. Pyruvic acid was quantified by HPLC (Agilent 1200 LC) equipped with two Shodex KC-811 columns and UV detector. The mobile phase is 2 mM HClO₄ with flow rate of 1 mL min⁻¹. The conversion X, yield Y, and selectivity S of organic acids were defined based on the following equations:

\[
X = \frac{\text{moles of carbon in feedstock consumed}}{\text{moles of carbon in feedstock input}} \times 100
\]

\[
Y = \frac{\text{moles of carbon in organic acid}}{\text{moles of carbon in feedstock input}} \times 100
\]

\[
S = \frac{Y}{X} \times 100
\]

3. RESULTS AND DISCUSSION

3.1. Potential of CuO for Enhancing the Production of Organic Acids as an Oxidant. First, the aqueous products from conversion of cellulose were analyzed to study whether CuO can enhance the oxidation of cellulose to produce organic acids. As can be seen from Figure 1, carboxylic acids from one carbon number to three carbon numbers were detected as the major products, and the highest TOC content of the aqueous phase products in the TOC of the resultant aqueous phase product was added into 10 mL of H₂SO₄/methanol solution in a vial. Then the capped vial was placed in a shaker for 24 h and maintained at 30 °C. After esterification, the sample was put into a separating funnel and combined with 6 mL of dichloromethane and saturated NaCl solution afterward. After the sample was shaken for about 1 min, the lower separated phase in the funnel was separated and followed by adding Na₂SO₄ to remove water. The sample was injected in an Agilent 7890A GC-MS equipped with an HP-INNOWAX column and 5975 mass selective detector. The column was maintained at 40 °C for 2 min, then ramped at 7 °C/min to 230 °C, and held at 230 °C for 20 min.

Solid samples were washed with distilled water several times, dried, and then characterized by XRD (Shimadzu, 6100) using Ni filtered Cu Kα radiation at an acceleration voltage of 40 kV and emission current of 30 mA. The step scan covered angles of 20−70° (2θ) at a rate of 0.1° s⁻¹. The quantitative analysis of XRD for compositions of Cu/Cu₂O/Cu was determined by the widely used Rietveld method.¹ The gas samples were separated by a carbon molecular sieve (TDX-01) column and detected with TCD in a GC system (HP-5890 Series II).
CuO, especially lactic acid and acetic acid from cellulose. However, other metal oxides exhibit no obvious promotion effect on the total organic acid yield. In the case of adding \( \text{Al}_2\text{O}_3 \), \( \text{MnO}_2 \), \( \text{ZnO} \), or \( \text{Ni}_2\text{O}_3 \), the total organic acid yield decreased slightly compared with that of the case in the absence of these oxides. These results indicate that CuO can increase the production of these four organic acids. As shown in Figure 4, with the increase in the reaction time (Figure 4a) and reaction temperature (Figure 4b), the amount of both \( \text{Cu}_2\text{O} \) and Cu increased, while the amount of CuO decreased, which suggest that CuO acted as an oxidant. It is noteworthy that CuO was not completely reduced into Cu; however, the complete reduction of CuO can be achieved by adding more cellulose or prolonging reaction time up to 2 h.\(^{14}\) Considering that the use of more cellulose or reaction time would decrease the yield of total organic acids as will be discussed later, a proper initial amount of cellulose (0.035 g) and reaction time (minutes) was adopted to balance the yield of organic acids and copper. Besides, there were no peaks of cellulose found in the XRD patterns of solid residues, suggesting that cellulose was all transformed. Because CuO was reduced into Cu, an experiment with adding Cu was conducted to examine the possibility of Cu as a catalyst. As shown in Figure 3, the yield of total organic acids decreased a little with the addition of Cu, and the products distribution with the addition of Cu was similar to that in the absence of Cu, which indicates that Cu had little effect on the production of organic acids. Therefore, the increase in the yield of organic acids can be attributed to the oxidation effect...

Figure 1. Typical HPLC chromatograms (a, b) and electropherogram (c) of the liquid sample after the reaction. Reaction conditions: 0.035 g of cellulose, 2.0 mmol of CuO, 1.0 mol L\(^{-1}\) \( \text{NaOH} \), 2.0 mL of water, 300 °C, 5 min.

Figure 2. GC-MS chromatogram of the aqueous phase products after esterification. Reaction conditions: 0.035 g of cellulose, 2.0 mmol of CuO, 1.0 mol L\(^{-1}\) \( \text{NaOH} \), 2.0 mL of water, 300 °C, 5 min. Peaks in the GC-MS chromatogram were not calibrated, and only qualitative information is given (chemical structure and corresponding name before esterification). The reaction of pyruvic acid with methanol by acid catalyst is presented in Figure S3 of Supporting Information. There was acetal formation on the C==O group by methanol in addition to esterification.

Figure 3. Effect of various metal oxides on the yields of organic acids. Reaction conditions: 0.035 g of cellulose, 2.0 mmol of metal oxides or copper, 1.0 mol L\(^{-1}\) \( \text{NaOH} \), 2.0 mL of water, 300 °C, 1 min.
CuO. Moreover, because the residual oxygen was not removed from the reactor before heat-up, a controlled experiment to remove oxygen was conducted to examine the effect of residual oxygen on the yields of organic acids. As a result, the residual oxygen in the reactor had no significant effect on the yields of organic acids (see Table S1 of Supporting Information), which could be explained by the low dissolution of oxygen in water and an amount of CuO added that is much higher than that of residual oxygen.

3.2. Optimization of Reaction Conditions for Attaining High Yield of Total Acids. Effects of reaction conditions on the production of organic acids were studied to examine the effects and determine the optimum conditions. As shown in Figure 5a, an increase in the amount of CuO led to a steady increase in the total organic acid yield, but when CuO increased to 3 mmol in the presence of NaOH, the total organic acid yield decreased. The increase in the yield could be attributed to the improvement of the oxidation of cellulose. As will be discussed later, the presence of CuO can also enhance the oxidative decomposition of lactic, glycolic, and formic acids; thus, the decrease in the yield when CuO increased to 3 mmol could be attributed to the enhancement of oxidative decomposition for the formed lactic, glycolic, and formic acids. Lactic, glycolic, and formic acids can be subsequently oxidized into smaller acids or CO₂. In fact, as shown in Figure 5a for lactic acid, the yield decreased from 13.8% with 2.0 mmol of CuO to 5.4% with 3.0 mmol of CuO. As shown in Table 1, glycolic acid was decomposed into formic acid, and lactic acid into formic acid and acetic acid. Because the formation of acetic acid and formic acid from the decomposition of higher acids can compensate their decompositions, particularly for acetic acid which is relatively difficult to decompose, an increase in the yield of acetic acid and no significant change in the yield of formic acid were observed from 2.0 mmol of CuO to 3.0 mmol of CuO. Figure 5b depicts the effect of concentration of NaOH on the yield of organic acids. The total organic acid yield reached a maximum at 1.0 mol L⁻¹ NaOH and substantially decreased with a further increase in NaOH concentrations. The increase in the yield of organic acids with the increase in NaOH concentration is probably because NaOH would enhance the conversion from cellulose to organic acids, especially lactic acid,⁹ and also stabilize the formed organic acids in the form of salt.¹² The decrease in the yield of organic acids with the further increase in NaOH concentration was mainly attributed to the decrease in the yield of glycolic acid, as will be discussed later. It has been reported that excess NaOH can cause further

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**Figure 4.** XRD patterns of CuO after the reactions. Reaction conditions: 0.035 g of cellulose, 2.0 mmol of CuO, 1.0 mol L⁻¹ NaOH, 2.0 mL of water. (a) 300 °C, 1–20 min; (b) 275–325 °C, 5 min. The values below the XRD patterns are the percentage of CuO, Cu₂O, and Cu based on Cu atom after the reactions.

**Figure 5.** Effect of addition of CuO (a) and alkali (b) on the yields of organic acids. Reaction conditions: (a): 0.035 g of cellulose, 1.0 mol L⁻¹ NaOH, 2.0 mL of water; (b): 0.035 g of cellulose, 2.0 mmol of CuO, 2.0 mL of water; 300 °C, 5 min.
Degradation of organic acids.\textsuperscript{18,19} Oxidation of glycolic acid to formic acid and oxalic acid\textsuperscript{19} (detected by GC-MS as shown in Figure 2) was observed. For the combination effect of CuO and NaOH, a reaction of solely CuO and NaOH in the absence of glucose was conducted at 300 °C for 5 min. The solid residues were then characterized by XRD. As a result, CuO maintained its structure after the reaction (see Figure S1 of Supporting Information). Although the reaction of CuO and NaOH cannot be identified from XRD analysis of solid residue after reactions, it has been reported that CuO can produce hydroxo complex under alkaline hydrothermal conditions derived from thermodynamics calculation;\textsuperscript{20,21} we suggest that NaOH under hydrothermal conditions may enhance the solubility of CuO to form hydroxo complex that may lead to the rupture of glucose, which could result in the formation of more organic acids.\textsuperscript{16,22}

Furthermore, experiments under different reaction temperatures and times were conducted, and the yield of organic acids and total organic carbon (TOC) are given in Figure 6. The total organic acid yield first increased and then decreased after 10 min at 275 °C, while it decreased after 5 min at 300 °C and decreased after 1 min at 325 °C along with a similar trend of TOC yield. The results showed that temperature had an obviously positive effect on the yield of organic acids, which is possibly due to the significant change in water properties such as ion product at this temperature range in addition to the increase in reaction rate caused by the increase in temperatures. The following decrease can be attributed to the decomposition of carboxylic acids by decarboxylation or decarbonylation. TOC analyses showed that high concentration of carbonates was present in the liquid phase, which can be evidence that decarboxylation occurred with CO\textsubscript{2} as the product. Thus, it can be concluded that an initial short reaction time, such as 5 min at 300 °C, mainly accounts for the reaction stage of formation of acids, while reaction stage of decomposition of acids would dominate the further reaction process. As shown in Figure 6, the trend of TOC yield at all temperatures indicated a fast dissolution of cellulose into the aqueous solution. Except for 275 °C, the highest TOC yields were all obtained at 1 min at the other two temperatures. However, as shown in Figure 6, the quantified total organic acids (lactic, glycolic, acetic, and formic acids) did not equal the TOC yield, which indicates there were other products present in the aqueous solution, some of which were detected by GC-MS shown in Figure 2. These products may be attributed to side reactions and thus are not considered further. Regarding the insoluble products, there were no signals of carbon or other polymerization products found according to XRD results of solid residues shown in Figure 4, which suggests that no insoluble oligomers or polymerization products were formed. For specific organic acids, acetic acid increased with the increase in reaction time at all temperatures, which can be explained as the stability of acetic acid and its formation from the further oxidation of lactic acid with CuO (Table 1, entries 15 and 17). As for relatively decomposable acids, such as formic acid, glycolic acid, and lactic acid, a trend of first increase and then decrease or direct decrease in yield was observed as will be discussed later.

Experiments with various substrates of feedstock were conducted to investigate the difference in carbohydrate and examine the reaction pathway as well. It is commonly acknowledged that the hydrolysis of cellulose proceeds through depolymerization to form cellobiose followed by decomposition into glucose and fructose under hydrothermal conditions.\textsuperscript{23} First, several carbohydrates, including cellulose, cellobiose, sucrose, glucose, fructose, and xylose, were examined. As expected, they showed good potential for producing organic acids. As shown in Table 1, a similar yield of total organic acids was obtained from disaccharides of cellobiose (39.4%) and sucrose (44.0%) in comparison with that of cellulose (41.0%). Interestingly, the yields of glycolic acid from cellobiose or sucrose were about half that of cellulose, whereas the yields of lactic acid were approximately two times that of cellulose. As shown in Table 1 (entries 6 and 9), the same phenomenon was observed when using monosaccharides of glucose and fructose.

<table>
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<th>acetic</th>
<th>glycolic</th>
<th>lactic</th>
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<td>41.0 ± 3.9</td>
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\textsuperscript{a}Reaction conditions: 0.035 g of cellulose and other solid substrates, 2.0 mL of liquid substrates (0.3 mol L\textsuperscript{−1} ethylene glycol, 0.3 mol L\textsuperscript{−1} glycolaldehyde, 0.2 mol L\textsuperscript{−1} glyceraldehyde, 0.6 mol L\textsuperscript{−1} formic acid, 0.3 mol L\textsuperscript{−1} acetic acid, 0.3 mol L\textsuperscript{−1} glycolic acid, 0.2 mol L\textsuperscript{−1} lactic acid), 2.0 mmol of CuO, 1.0 mol L\textsuperscript{−1} NaOH, 2.0 mL of water, 300 °C. 0.070 g of cellulose. 0.105 g of cellulose. 0.009 g of glucose. ND = not detected.
glucose and fructose but with much higher yields of total organic acids (52.9% and 52.5%, respectively). When the reaction time was shortened to 60 s (Table 1 entry 8), the glycolic acid yield from glucose was still lower than that with cellulose. However, when the initial concentration of glucose was decreased (Table 1 entry 7), the glycolic acid yield jumped to the same level as that with cellulose. Therefore, in the conversion of cellulose, the high yield of glycolic acid was probably because the concentration of glucose from cellulose was at a low level during the reactions, which favored the production of glycolic acid. In addition, as can be seen from Table 1 (entries 1–3), increasing the concentration of cellulose decreased the yield of total organic acids. This is probably because the amount of CuO was not enough to oxidize cellulose. These results suggest to us that the concentration of substrate may have an influence on the reaction pathway and thus affect the yields of organic acids.

3.3. Proposed Reaction Mechanisms. To investigate the mechanism, further experiments with some possible intermediates from cellulose such as gluconic acid as well as the further degradation products from glucose or fructose such as aldehydes, alcohols and carboxylic acids used as starting materials were conducted. Identifications of liquid products from cellulose and glucose by HPLC analysis showed that no noticeable peak of gluconic acid was observed (see Figure S2 of Supporting Information), and as shown in Figure 2, there was no saccharinic acid detected by GC-MS. These results suggest that saccharinic acid is unlikely to form in this reaction system. Glyceraldehyde as an important intermediate via C3−C4 scission of glucose can transform to lactic acid followed by oxidative scission into acetic acid with the assistance of CuO.16,24 As shown in Table 1 entries 13 and 17, glyceraldehyde had a good selectivity for lactic acid, which can then selectively be converted to acetic acid. Glycolaldehyde, another intermediate formed by C2−C3 scission of glucose,24 did not show such high yield for organic acids compared with that of glyceraldehyde (Table 1 entry 12). In addition to lactic acid and acetic acid, the yields of glycolic acid and formic acid were also noticeable in this study. The oxidation of glycolaldehyde in the −CHO group by CuO as an oxidant can lead to glycolic acid formation. Besides, glycolaldehyde can produce formaldehyde and glycolaldehyde by retro-aldol reaction that can lead to formic acid and acetic acid, respectively. As shown in Table 1 entries 12 and 13, glycolaldehyde and glyceraldehyde can both form glycolic acid and formic acid with 100% conversion in 30 s. As can be seen from Table 1 entries 15–17, formic acid can have multiple sources including acetic acid, glycolic acid, and lactic acid in addition to aldehydes. For these produced organic acids, they can generally further decompose into smaller organic acids or gases (CO or CO2) by decarboxylation and decarbonylation under hydrothermal conditions.18,25 Our previous result showed that the addition of alkali could prevent the formic acid decomposition.12 As shown in Figure 7, the presence of CuO can enhance the decomposition of these acids, except acetic acid, compared with the case of adding NaOH, and the decreased order was formic acid > glycolic acid > lactic acid > acetic acid.

On the basis of these results and the traditional theory of conversion of sugar in alkaline solution at low temperatures, we therefore propose a reaction pathway for producing these four organic acids as shown in Figure 8. Cellulose is first hydrolyzed to cellobiose and then glucose or fructose under alkaline conditions. Subsequently, glucose or fructose is degraded into three-carbon aldehydes such as glyceraldehyde with CuO, and then both glyceraldehyde and dihydroxyacetone, which is an isomerization product of glyceraldehyde formed by the Lobry de Bruyn–Alberda van Ekenstein (LBAE) transformation, loses water to form pyruvaldehyde, which subsequently undergoes a benzilic acid rearrangement to form lactic acid.26−28 Finally, the lactic acid is oxidized into acetic and formic acids with CuO. As for the formation of glycolic acid, considering that (i) ethylene glycol can be selectively produced from hydrogenolysis of cellulose over CuCr catalyst,29 (ii) our previous research also found the presence of ethylene glycol in conversion of...
cellulose, ethylene glycol was detected (Figure 1) in this study by HPLC, and ethylene glycol can have a good selectivity (46%) for glycolic acid with CuO (see Table 1 entry 11), we propose the formation of glycolic acid via path II as shown in Figure 8. Glucose is first hydrogenated into ethylene glycol through some intermediates by copper species, and then ethylene glycol is oxidized into glycolic acid. A number of the organic acids (lactic, glycolic, fumaric acids) have recently been shown to undergo base-catalyzed degradation, releasing hydrogen as a main product. Thus, the hydrogen source for the hydrogenolysis of glucose is probably attributed to the base-catalyzed degradation of the formed organic acids. In this study, hydrogen was also detected by GC-TCD. Moreover, as mentioned before, there were some undetected products present in addition to the quantified four organic acids; thus, there are still other pathways or side reactions present in addition to the reaction pathways shown in Figure 8. If catalysts to inhibit the side reactions can be developed, then a higher yield of target acid would be expected.

4. CONCLUSIONS

A novel strategy for converting cellulose to organic acids and reducing CuO to Cu$_2$O or Cu in a one-pot reaction has been developed. Organic acids mainly include lactic acid, glycolic acid, acetic acid, and formic acid. The highest total yield of the four organic acids reached 43.0% at 325 °C for 1 min. The possible reaction mechanism of conversion of cellulose is through two pathways. One major pathway is from rupture of C$_3$–C$_4$ scission of glucose to three and lower carbon number acids by sequential reactions. Another possible pathway is the formation of ethylene glycol from glucose, which is then oxidized to glycolic acid.

ASSOCIATED CONTENT

* Supporting Information
  XRD pattern of CuO after the reaction (Figure S1), HPLC chromatograms of the liquid samples after the reactions (Figure S2)

Figure 8. Proposed reaction pathway from cellulose to organic acids.
S2), esterification and acetal formation of pyruvic acid with methanol by acid catalyst (Figure S3), and comparison of yields of organic acids in the presence and absence of oxygen (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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