Selective Conversion of Glucose into Lactic Acid and Acetic Acid with Copper Oxide Under Hydrothermal Conditions

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Biomass as a source for chemicals production attracts growing attention due to the decreasing storage of fossil fuels and global warming caused by emission of CO_2. In this study, conversion of glucose with copper oxide (CuO) was studied under alkaline hydrothermal conditions using a batch reactor and continuous flow reactor. CuO, as an oxidant, greatly improves the yields of lactic acid (LA) and acetic acid from glucose and was reduced into Cu_2O and Cu. Selective production of LA with the highest yield of 59% and acetic acid with the highest yield of 32% can be achieved by controlling reaction time, temperature, and addition of CuO. A possible mechanism of conversion of glucose with CuO was proposed. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 2096–2104, 2013

Keywords: glucose, lactic acid, acetic acid, copper oxide, hydrothermal reactions

Introduction

Biomass has wide applications as a source of clean energy and as a raw material for different chemical stocks.[1–4] Promising target chemical products are organic acids, such as lactic acid (LA) and acetic acid.[5–7] LA is receiving an increasing attention as a building block for the synthesis of chemicals, such as acrylic acid, pyruvic acid, 2,3-pentanedione, 1,2-propanediol, and LA esters, and also as a material for producing biodegradable LA polymers.[8] Acetic acid is also an important raw material in industry primarily for producing vinyl acetate monomer and acetic anhydride and a solvent for purified terephthalic acid production.[9] At present, the fermentation of starch is a dominant method for producing LA. Bioconversion (bacterial fermentation) can obtain a high yield of LA[8]; however, bioconversion is not directly available to cellulose and lignocelluloses. More than 60% of the world acetic acid production uses the methanol carbonylation methods with drawbacks of catalyst solubility limitations and the loss of expensive Rh metal due to precipitation in the separation sections.[9] Thus, the development of an environmentally friendly and highly effective method for converting biomass to useful chemicals, such as LA and acetic acid, is strongly desired.

The hydrothermal process is one of the most promising processes for the conversion of various biomass to value-added products among the several biomass conversion processes, because water at high temperature and pressure behaves as an environmental friendly reaction medium with unique properties.[10–12] The high natural concentrations of the H^+ and OH^- resulting from the high ion product constant (K_w) of subcritical and supercritical water favor acid- or

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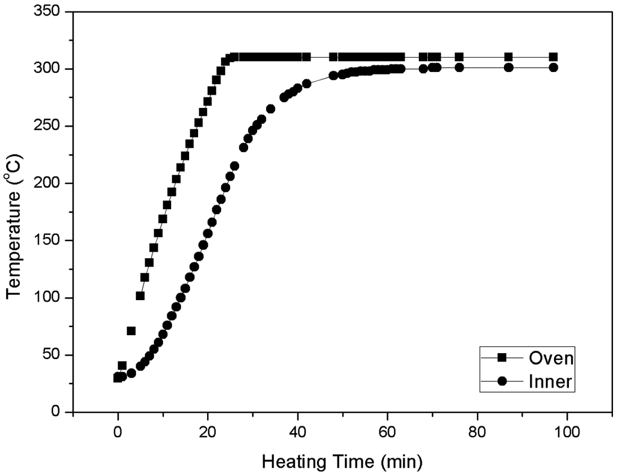

Figure 1. Inner temperature of the batch reactor and oven temperature with the increase of heating time when the oven was set at 310°C.

base-catalyzed reactions. Many investigations have demonstrated that cellulose can be easily degraded into oligomers and glucose under hydrothermal conditions,[13,14] and thus hydrothermal process can directly be available to cellulose and lignocelluloses. There have been many researches[1,2,5,7,15–17] involving in conversion of various biomass into chemicals via hydrothermal process.

Our group has conducted many works concerning the production of LA and acetic acid from carbohydrate under hydrothermal conditions.[1,5,7,15–19] The highest yield of LA (27%) from glucose was obtained.[18] It should be noted that the LA from hydrothermal method is not directly available for producing LA polymers due to its racemic property. A two-step hydrothermal process to improve the production of acetic acid from carbohydrate was proposed.[7] The first step was to accelerate the formation of 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA), and LA, and the second step was to further convert the furans (HMF, 2-FA) and LA produced in the first step to acetic acid by oxidation with newly supplied oxygen. An acetic acid yield of 16.3% was obtained from cellulose. Further improvement on the yield of acetic acid to 23% from glucose and 26% from fructose was realized by adjusting the first step in acidic condition.[19] However, the use of oxygen was a drawback in hydrothermal oxidation of carbohydrate into acetic acid due to its high cost on compressing air or oxygen into the reactor. Therefore, it is highly desirable to develop a new solid oxidant to replace air or oxygen. Recently, we investigated the possibility of reduction of CuO into Cu in the presence of glucose or cellulose under hydrothermal conditions,[20,21] to develop an alternative for replacing the traditional copper smelting methods that are energy-intensive and nonenvironmental.[22] Results[20,21] showed that CuO can be reduced into Cu in the presence of cellulose or glucose under mild conditions. These facts suggested us a new way to enhance the production of carboxylic acids from carbohydrates with metal oxide as an oxidant. Thus, we extended our research to investigate the use of metal oxide as an oxidant to enhance the production of carboxylic acids from carbohydrates. Our preliminary study have compared the oxidative potential of different metal oxides, including Al_2O_3, ZnO, Fe_2O_3, Fe_3O_4, TiO_2, Ni_2O_3, and CuO, and found that CuO showed the best performance among these metal oxides. Simultaneously, the obtained copper can be directly used as an important metal in many fields. Thus, in this article, we reported these new findings of the production of carboxylic acids from carbohydrates with CuO as an oxidant.

Experimental

Materials

Glucose was used as a model compound of carbohydrate, because it is the primary intermediate formed during the conversion of carbohydrates. D(+)-glucose (98%), D(−)-fructose (minimum 99.0%), DL-LA (85–92%), acetic acid (99.9%), formic acid (99%), glycolic acid (99%), pyruvaldehyde solution (30–40%), copper oxide (14-24 mesh, 99%), and sodium hydroxide (97%) were purchased from Wako Pure Chemicals Industries Ltd. Cellulose (200 mesh, ≥99%), D(−)-erythrose (minimum 50%), glyceraldehyde dimer (95%), and glycoaldehyde dimer were purchase from Sigma–Aldrich. Deactivated fused silica was purchased from Agilent Technology.

Experimental procedure

Most experiments were conducted in a batch reactor in this study. The experimental setup has been described in detail elsewhere,[23] and only a brief description is given below. The batch experiments were conducted in an 8.8-mL batch reactor (AKICO, Japan) lined with SUS-316. After loading the starting materials, the reactor was purged with argon and sealed. In all experiments, the filling rate was set at 34%. The reactor was loaded to an electric furnace (AKICO, Japan) and heated to the desired temperature. In a preparatory experiment, the temperature in the reactor was measured by a thermocouple inserted into the reactor. In a typical experiment in which the furnace temperature was set at 310°C, as shown in Figure 1, the time required to heat up the oven from room temperature to 300°C was 23 min. And it needs another 38 min for the reactor to reach 300°C and becomes stable. Zero reaction time was defined as the time when the reactor temperature reached the desired temperature. The reactor was shaken in a front–back motion at ~60 cycles per minute for all experiments. After the reaction, the reactor was taken out from the electric furnace and quickly quenched in a water bath at room temperature. After cooling, the reactor was opened, and then liquid and solid fractions were collected and analyzed. In this study, due to the reactor's limitation, the gaseous fraction was not collected.

A continuous flow reactor was also used in this study. Figure 2 shows a schematic diagram of the continuous flow reactor. The experimental setup has been described in detail elsewhere,[24] and only a brief description is given below. The reactor was made from 1/4 (inch) stainless-steel tubing (SUS316) with a volume of about 1.5 mL and length of 10 cm. About 1.5 g of CuO was loaded into the reactor with both ends supported by about 0.2 g of deactivated fused silica. Feed solution containing 1.75 wt % glucose and 1 M NaOH was introduced into the reactor using a high-pressure pump (Jasco) at a flow rate of 1–10 mL/min. They were sufficiently degassed using ultrasonication for 30 min before reaction. Then, the pressure in the reactor was adjusted at 10 MPa using a back-pressure regulator (AKICO). When the system reached the desired pressure and steady state was achieved, an electric furnace was used to heat the reactor. The temperature of the reactor was measured using a K-type thermocouple connected to the reactor. The residence time

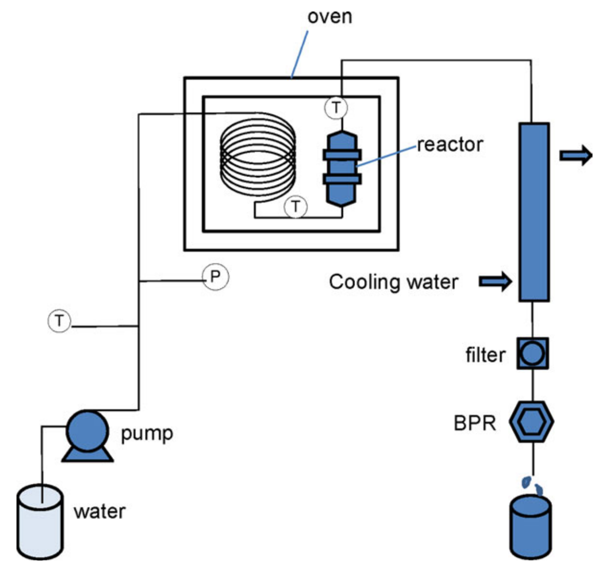

Figure 2. Diagram of continuous flow reactor.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the solution in the reactor, τ, was evaluated from the following equation

$$\tau = \frac{V(1-\varepsilon)}{F}\frac{\rho_{T,p}}{\rho_{T_0,P}} \tag{1}$$

where V is the reactor volume (mL), ε is the filling rate of solid (%), F is the flow volume (mL/min), and $\rho_{T,p}$ and $\rho_{T_0,P}$ indicate the density of water at the reaction temperature and under ambient conditions, respectively (kg/m^3). After the feed solution passed through the reactor, the reaction was rapidly quenched with a double-tube-type heat exchanger to terminate further reactions of the products. The products were subsequently collected in a sampling bottle at a fixed time.

Product analysis

Identification and quantitative analysis for liquid samples were conducted using high-performance liquid chromatography (HPLC) with refraction index (RI; RI-2031 plus; Jasco) and ultraviolet–visible (870-UV; Jasco) detectors. Sugar-SH1011 (Showa Denko) was used as the column medium. Perchloric acid (1 mmol/L) was used as the mobile phase, and bromothymol blue solution was used as coloring reagent, mixed in the immediate aftermath of the column, to detect organic acids. For evaluation of the liquid organic carbon, a total organic carbon analyzer (TOC-5050A; Shimadzu) was used. The copper ion in solution was analyzed by ICP (Optima 2100DV, Perkin Elmer). The conversion (X), yield (Y), and selectivity (S) were based on the following equations

$$X = \frac{\text{Moles of carbon in glucose consumed}}{\text{Moles of carbon in glucose input}} \times 100 \tag{2}$$

$$Y = \frac{\text{Moles of carbon in organic acid}}{\text{Moles of carbon in glucose input}} \times 100 \tag{3}$$

$$S = Y/X \times 100 \tag{4}$$

Solid samples were washed with distilled water several times and dried in air and then characterized by X-ray diffraction (XRD, Rigaku RAD-1B) using Ni-filtered Cu Kα radiation at an acceleration voltage of 35 kV and emission current of 15 mA. The step scan covered angles of 20–90° (2θ), at a rate of 0.2°/s. Scanning electron microscopy (SEM, JEOL) was used to characterize the surface of solids.

Results and Discussion

Effect of CuO on products from glucose

Experiments with glucose were conducted in the presence and absence of CuO at 300°C for 1 min using a batch reactor. 300°C was chosen, because our previous research[2] on conversion of carbohydrate biomass into chemicals showed that 300°C was the optimum reaction temperature under subcritical water conditions. As shown in Figure 3, glycolic acid, LA, formic acid, and acetic acid were commonly formed in the presence and absence of CuO. However, as illustrated in Figure 4, in the case without CuO (Entry 1), the yields of these organic acids were all low, below 1.0%. In this study, the conversion of glucose was all above 99%, and thus, the yield almost equals the selectivity. In the case of adding CuO, the yield of acetic acid increased to 6.6%, and no formation of LA was observed. This result suggests that CuO had a promotion effect on the acetic acid yield. In addition, our previous researches[1,5] have proved that alkali had an obvious catalysis effect on the production of LA from carbohydrate biomass under hydrothermal conditions. Thus, an experiment with glucose was conducted in the presence of CuO and NaOH together to examine the role of OH$^-$ in the production of organic acids in the presence of CuO. The yield of LA and acetic acid increased to 25 and 23%, respectively, suggesting that the role of CuO for the production of organic acids can be improved in the presence of OH$^-$. As shown in Figure 4, in the case of adding CuO alone, the percentage of TOC in the liquid samples to the total input carbons based on carbon number was 23%, even

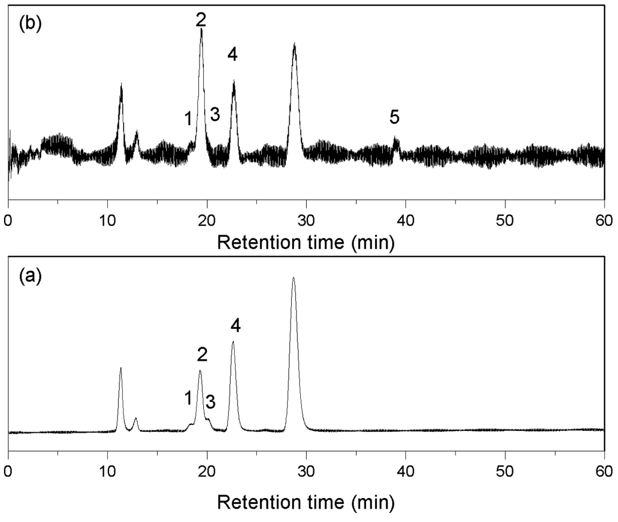

Figure 3. (a) HPLC-UV chromatogram obtained from 0.0525 g D(+)-glucose, 2 mmol CuO, and 1 M NaOH after 1 min of reaction at 300°C. 1: glycolic acid, 2: LA, 3: formic acid, and 4: acetic acid.

(b) HPLC-RI chromatogram obtained from 0.0525 g D(+)-glucose, 2 mmol CuO, and 1 M NaOH after 1 min of reaction at 300°C. 1: glycolic acid, 2: LA, 3: formic acid, 4: acetic acid, and 5: 5-HMF.

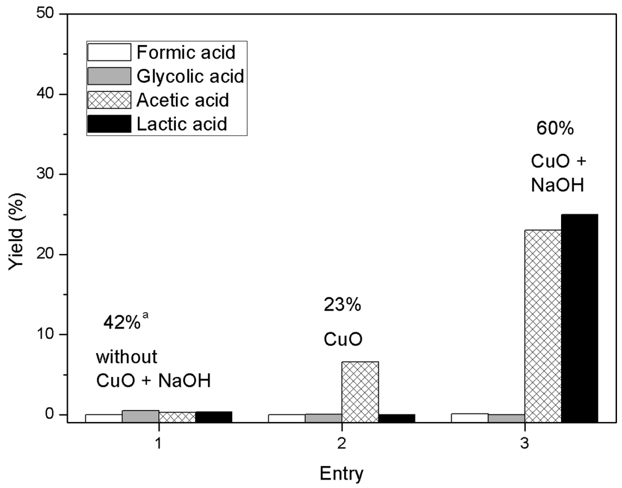

Figure 4. Effect of CuO on the yields of organic acid from glucose at 300°C for 1 min (Entry 1: without addition; Entry 2: 2 mmol CuO; and Entry 3: 2 mmol CuO and 1 M NaOH (^{a}the percentage of TOC in the liquid samples to the total input carbons based on carbon number after reactions).

lower than that of without CuO and NaOH (42%). This percentage increased to 60%, when NaOH was added in the presence of CuO (see Entry 3), which suggests that OH^- can protect glucose from carbonization into solids.[25] These observations further suggest that OH^- was crucial in the conversion of glucose into organic acids. Therefore, the combination of CuO and NaOH was adopted in the following for selective production of LA and acetic acid.

Effect of ratio of CuO:NaOH on the production of LA and acetic acid

The optimization of ratio of CuO to NaOH for obtaining high yields of LA and acetic acid was studied. As shown in Figure 5, when fixing NaOH concentration to 1 M, the yield of acetic acid increased from 15 to 31% with the increase of amount of CuO from 1 to 4 mmol, which further confirmed that CuO had a selective production for acetic acid. However, the yield of LA decreased from 39 to 7.2% with the increase of amount of CuO from 1 to 4 mmol. When lowering the NaOH concentration to 0.1 M with 2 mmol CuO, both yields of LA and acetic acid decreased. The result indicates that a low concentration of alkali was disadvantageous for the production of LA and acetic acid. Thus, the ratio of 2 mmol CuO to 1 M NaOH was adopted in the following discussion for attaining both high yields of LA and acetic acid.

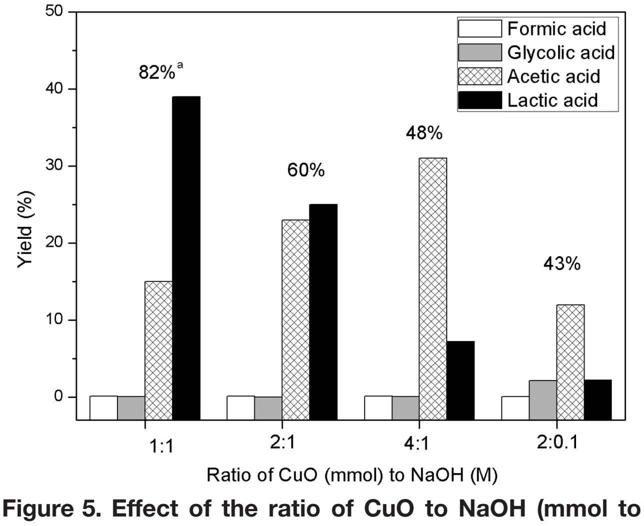

Figure 5. Effect of the ratio of CuO to NaOH (mmol to M) on the yields of organic acid from glucose at 300°C for 1 min (^{a}the percentage of TOC in the liquid samples to the total input carbons based on carbon number after reactions).

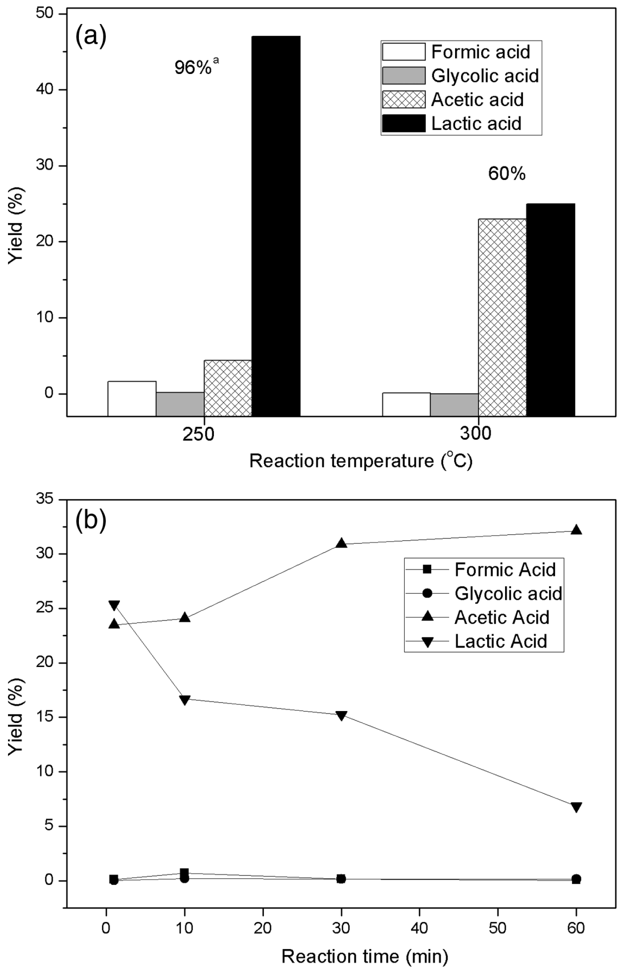

Figure 6. (a) Effect of reaction temperature on the yields of organic acid (reaction conditions: 0.0525 g glucose, 2 mmol CuO, 1 M NaOH, and 1 min of reaction time; ^{a}the percentage of TOC in the liquid samples to the total input carbons based on carbon number after reactions); (b) effect of reaction time on the yields of organic acid (reaction conditions: 0.0525 g glucose, 2 mmol CuO, 1 M NaOH, and 300°C).

Effects of reaction temperature and time on yields of LA and acetic acid

Figure 6a shows the effect of reaction temperature at 250 and 300°C for 1 min on yields of LA and acetic acid. The yield of LA decreased from 47 to 25%, and the yield of acetic acid increased from 4.4 to 23% with the increase in reaction temperature from 250 to 300°C. The yields of formic

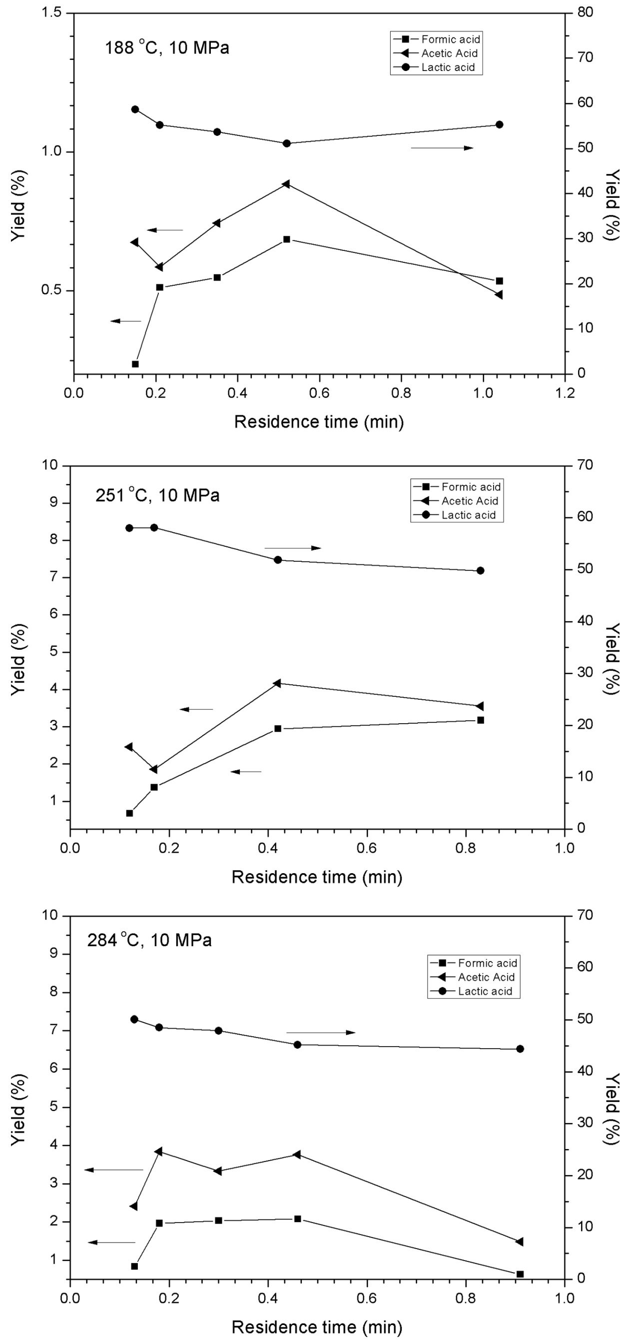

Figure 7. Yields of organic acid with different residence times using the continuous flow reactor (1.75 wt % glucose feed solution; 1 M NaOH; and 1.5 g CuO).

acid and glycolic acid were very low at both temperatures. Figure 6b shows the effect of reaction time on yields of organic acids. Similarly, with the increase in reaction time, the yield of acetic acid increased, whereas the yield of LA increased. The highest yield of acetic acid (32%) was obtained for 60 min. The yields of formic acid and glycolic acid were very low, below 1.0%. The increase in acetic acid and the decrease in LA with the increase in reaction temperature and time are probably, because the formation of acetic acid is through the oxidative decomposition of LA in the presence of CuO, as discussed later.

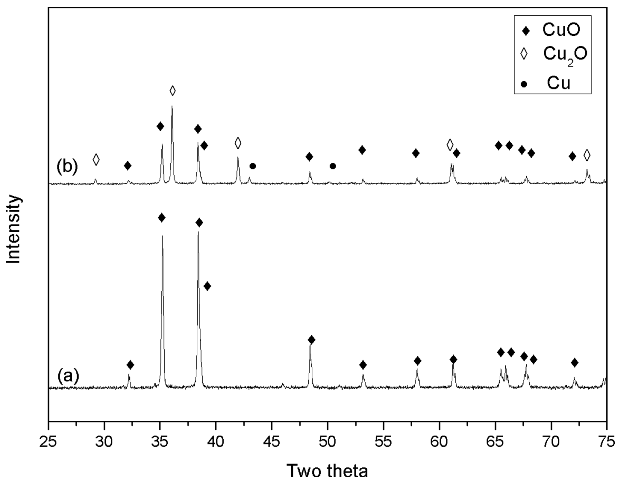

Figure 8. XRD patterns of solid residues after the reaction: (a) raw CuO particles and (b) 0.0525 g glucose, 4 mmol CuO, 1 M NaOH; 300°C, and 1 min.

Production of LA and acetic acid with a continuous flow reactor

As discussed before, a longer reaction time and higher reaction temperature did not favor a high yield of LA in the presence of CuO. That is, a higher yield of LA can be obtained in a short reaction time. However, a short reaction time is not available with the used batch reactor system due to the long heat-up time. Thus, to obtain a higher yield of LA, experiments were conducted in a continuous flow reactor, which can be conducted at low temperatures and short residence times. The temperature range was set from 188 to 284°C, and the residence time was set at 0–1 min under a stable pressure (10 MPa). As expected, a much higher yield of LA was obtained in the continuous flow reactor compared with that in the batch reactor (see Figure 7). The highest yield of LA (59%) was obtained at 188°C with a short reaction time of 0.15 min. To the best of our knowledge, it is the highest yield of LA reported so far obtained from glucose under hydrothermal conditions. Moreover, no significant peaks of new intermediates were observed by HPLC analysis compared with those in the batch reactor.

Similar to the results obtained in the bath reactor, there is a tendency of decrease in yield of LA with the increase in the residence time. For acetic acid, the yields were below 5%, which were much lower than the results obtained in the batch reactor at all temperatures. These results suggest that in the initial time of reactions, glucose first transformed into LA, which was then converted into acetic acid, and the conversion of glucose to LA was fast and conversion of LA to acetic acid was relatively slow. These suggest that selective production of LA and acetic acid can be achieved by controlling reaction time and temperature.

Table 1. IC in the Liquid Phase After Reactions (0.0525 g Glucose, 300°C, and 1 min)

	Entry			
	1	2	3	4
IC (ppm)	46.3	161	592	2244

Entry 1: without CuO and NaOH; Entry 2: 2 mmol CuO; Entry 3: 1 M NaOH; Entry 4: 2 mmol CuO + 1 M NaOH.

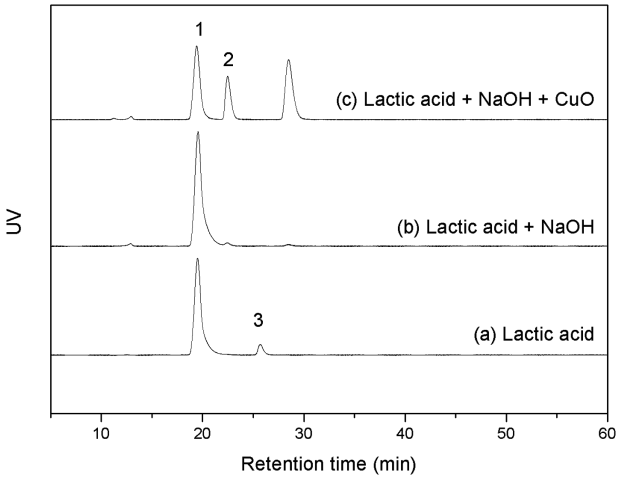

Figure 9. HPLC-UV chromatogram obtained from 0.35 M LA, 2 mmol CuO, and 1 M NaOH at 300°C for 1 min (1: LA, 2: acetic acid, and 3: propionic acid).

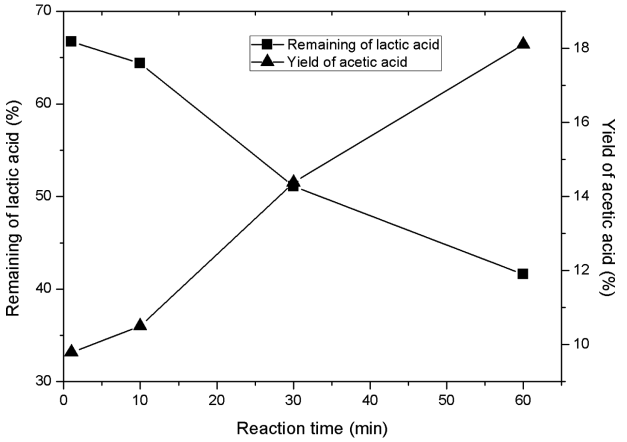

Figure 10. Effect of reaction time on conversion of LA and yield of acetic acid (0.35 M LA, 2 mmol CuO, and 1 M NaOH at 300°C).

It should be notable that the amount of CuO would decrease after a run in the continuous experiments due to the reduction of CuO into Cu as will be discussed later. In this study, the addition of CuO was excessive. However, a continuous flow reactor with the slurry containing both biomass and CuO as a feed proposed in our previous research[26,27] should be used in an industry-scale production.[26,27]

Role of CuO and possible mechanism

Figure 8 shows XRD patterns of solid residues after the reactions and raw CuO powder. The peaks of Cu_2O and Cu were found in solid residues after the reactions, indicating that CuO was reduced. The liquid sample after the reaction in the batch reactor at 250°C was characterized by ICP. The result showed that no copper ion was detected. That is, there was no loss of copper in the solution, and almost 100% copper as solid can be obtained. Our previous reports[20,21] have showed that completely reduced Cu from CuO can be available after 1.5 h with glucose or cellulose at 250°C. In this study, the conversion of glucose was above 99% after 1 min in the batch reactor, whereas a large proportion of CuO was not reduced at the same reaction condition according to XRD result (Figure 8). These results indicated that CuO could also be reduced by other decomposed products of glucose, such as LA.[20]

In addition, as shown in Table 1, in the case of adding CuO (Entry 2), the inorganic carbon (IC) in the liquid phase after the reaction was 3.5 times as that without addition of CuO (Entry 1). The IC in Entry 4 (CuO + NaOH) was 3.8 times as that only adding NaOH (Entry 3). The increase in IC may be attributed to the increase in CO_2 in liquid samples, because CO_2 dissolved strongly in alkaline solution and liquid samples was not adjusted with an acid for IC analyses. Also, CO_2 was detected for gaseous samples in the presence of both CuO and NaOH.[20] These results suggest that CuO promoted the oxidation of glucose to CO_2, particularly for the presence of alkali. The decrease of the percentage of TOC in the liquid samples from 82 to 48% with the increase of CuO from 1 to 4 mmol (see Figure 5) further verified this assumption.

Furthermore, as discussed in section "Effects of reaction temperature and time on yields of LA and acetic acid," CuO may promote conversion of LA into acetic acid. To examine this possibility, experiments with LA as a starting material in the presence and absence of CuO were performed. As shown in Figure 9a, LA slightly decomposed and no peak of acetic acid was observed without CuO and NaOH. From Figure 9b, in the case of adding 1 M NaOH without CuO,

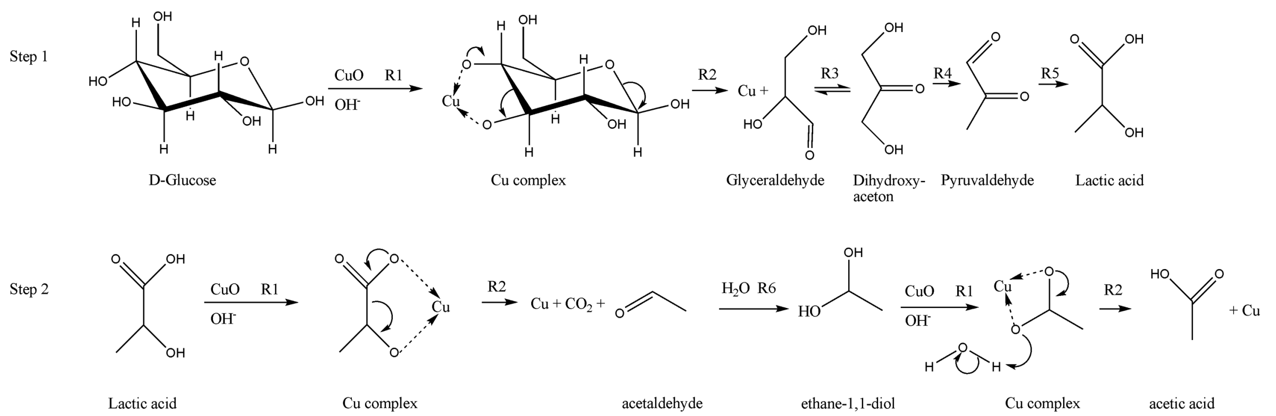

Figure 11. Reaction pathway of production of LA and acetic acid from D-glucose with CuO under alkaline hydrothermal conditions (R1: coordination; R2: redox; R3: Lobry de Bruyn-Alberda van Ekenstein transformation (LBAE); R4: elimination; R5: benzilic acid rearrangement; and R6: hydration).

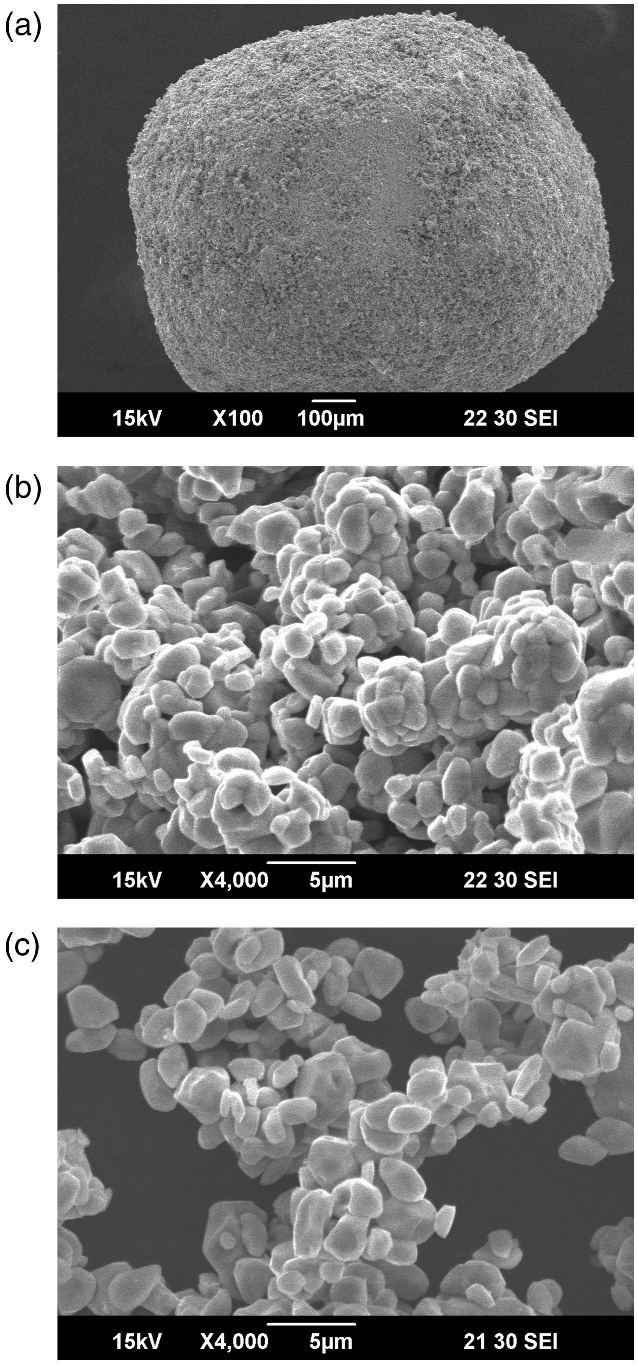

Figure 12. SEM photos of solid residues after the reaction: (a,b) raw CuO particles and (c) 0.0525 g glucose, 4 mmol CuO, 1 M NaOH, 300°C, and 1 min.

the peak of acetic acid was found. The yield and selectivity of acetic acid were 2.3 and 17%, respectively. When adding 2 mmol CuO in the presence of 1 M NaOH, the yield and selectivity of acetic acid increased to 9.8 and 29%, respectively. These results suggest that production of acetic acid from LA can be improved with CuO. Figure 10 shows the variation of the decomposition of LA and the yield of acetic acid with CuO and NaOH by varying reaction time from 1 to 60 min. The remaining of LA decreased from 66.7 to 41.6%, and the yield of acetic acid increased from 9.8 to 18.1% in accordance with the increase in reaction time from 1 to 60 min. The selectivity of acetic acid became stable with the increase in reaction time. In addition, CuO was also reduced into Cu_2O and Cu according to XRD results for the experiments with LA as the starting material.

Many researchers have studied and summarized the reaction pathway of conversion of glucose into LA under alkaline hydrothermal conditions.[2,5,28,29] It is generally believed that aldose, aldehydes, and ketones, such as fructose, erthrose, glyceraldehyde, glycoaldehyde, pyruvaldehyde, and hydroxyacetone, are first formed as intermediates and then transformed to LA. Based on the previous researches and results in this study, a possible mechanism of conversion of glucose to LA and acetic acid in the presence of CuO was proposed and is presented in Figure 11. At the beginning of reaction, a strong base (NaOH) under hydrothermal conditions may enhance the solubility of CuO to form hydroxo complex.[30] Subsequently, dissociated Cu(II) ions from the hydroxo complex may coordinate with hydroxyl oxygen atoms of glucose to form a comparatively stable coordination compound. The short distance between oxygen and Cu atoms in the coordination compound is favorable for electron transfer from the oxygen atom to Cu(II) ion, resulting in the reduction of Cu(II) into Cu(0). Simultaneously, LA is formed as the main product from the transformation of complex and glyceraldehyde.[2] Then, the formed LA is further oxidized into acetic acid via a similar transformation by formation of Cu complex with the release of CO_2 as shown in Figure 11.

For the source of acetic acid, it was still elusive that whether acetic acid can be directly from the decomposition of the intermediates from glucose, such as aldose, aldehydes, and ketones with CuO. Therefore, fructose, erythrose, glyceraldhyde, glcoaldehyde, and pyruvaldehyde were chose as a starting material to examine their availability to produce acetic acid with CuO at 300°C for 1 min. For all these experiments, no peaks of starting materials and LA were observed, and peak of acetic acid was found after the reactions. A selectivity of 2.7% from fructose, 13.3% from glyceraldehyde, 1.7% from glcoaldehyde, and 18.5% from pyruvaldehyde for production of acetic acid was observed. Due to the uncertainty in the purity of erythrose, the quantification is unavailable. These results showed that those selected intermediates were able to produce acetic acid directly. However, the high yield of acetic acid was probably mainly attributed to the decomposition of LA, because the intermediates from glucose, such as aldehydes and ketones, were fast transformed into LA as discussed in section ''Production of LA and acetic acid with a continuous flow reactor.''

The morphology of solid residues after reactions was characterized by SEM. As shown in Figure 12, the particle size of commercial CuO was ~1.3 mm and was composed of a lot of 1–5 μm small particles. As shown in Figure 12c, the CuO particles after the hydrothermal reaction were crushed to small powders with a diameter of approximately 1–3 μm.

Examination of lactic and acetic acids from cellulose

To further examine the feasibility of this process, an experiment with cellulose and CuO was conducted in the batch reactor under a condition for achieving higher yields of lactic and acetic acids in the case of using glucose. As shown in Table 2, the yields of acetic acid and LA from cellulose were lower compared to that with glucose. However, when comparing yield from cellulose with different hydrothermal processes, the yield of acetic acid with the proposed process was approximately the same as that obtained by the

Table 2. Comparison of Yields of Acetic Acid and LA by Different Hydrothermal Methods

Feedstock	Method	Yield		References
		Acetic Acid	LA	
Cellulose	Conventional wet oxidation	9.0%	–	7
Cellulose	Two-step process	16%	–	7
Cellulose	Alkaline	–	19%	18
Cellulose	Our proposed method	8.2%*	12%*	This study

*0.035 g cellulose, 2 mmol CuO, 2.5 M NaOH, 300°C, 1 min; This experiment was conducted in a SUS 316 lined batch reactor, and details can be found in our previous report.[7]

conventional wet oxidation, which cannot produce LA,[7] and the yield of LA from the proposed process was slightly lower than that by the conventional alkaline hydrothermal method, which cannot produce acetic acid.[18] These results show that CuO is also effective for enhancing the production of acetic and LAs from cellulose. Moreover, the yields of acetic and LAs should increase by optimizing reaction conditions, because the optimization of reaction conditions for achieving higher yields is generally different between glucose and cellulose.

At present, our results demonstrated a possibility of the production of lactic and acetic acids from carbohydrate with CuO as an oxidant. From the view of thermodynamics, this process should be energy efficient, because the reaction of conversion of carbohydrate into lactic and acetic acids with CuO as an oxidant is exothermic if assuming that glucose is decomposed into LA (50%, on carbon basis), acetic acid (33%), and formic acid (17%). As for the separation of products in an industry-scale production, the reduced copper as solid can be separated by a simple precipitation method. For the products of LA and acetic acid, our previously proposed process,[26] in which electrodialysis and reverse osmosis were used, may be suitable. Moreover, other membrane technology such as nanofiltration[31] may also be considered. Finally, the residual alkaline solution could be recycled to the reactor.

Conclusions

CuO had an obvious promotion effect on the production of LA and acetic acid in the presence of NaOH. High yield and selectivity of LA or acetic acid can be obtained with CuO under alkaline hydrothermal conditions by controlling reaction time and temperature. The possible mechanism may be that glucose is first converted into LA that is then oxidized into acetic acid. Fructose, erthyrose, glyceraldehyde, glcoaldehyde, and pyruvaldehyde, as common intermediates under alkaline hydrothermal conditions, can also lead to acetic acid formation in addition of CuO.

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