

## Chapter 2

# Hydrothermal Conversion of Cellulose into Organic Acids with a CuO Oxidant

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**Abstract** In this chapter, we review some recent progress on the acid/base-catalyzed hydrothermal conversion and oxidation of cellulose into organic acids mainly in our research group. A novel one-pot production of organic acids and metal copper from cellulose and CuO under alkaline hydrothermal conditions is introduced based on our former research. The mechanism of formation of organic acids and metal copper is discussed. A principal reaction pathway from cellulose to organic acids and their reactions are also discussed. The results show that from cellulose to organic acids, the production processes are mainly composed of four stages of reactions. The reaction conditions were also optimized for production of organic acids and copper. These results show that a selective production of organic acids including lactic acid, glycolic acid, acetic acid, and formic acid can be achieved by varying reaction temperature and time and ratio of CuO and NaOH addition.

## 2.1 Introduction

To decrease the dependence of the human race on fossil resources and relieve the global warming caused by anthropogenic CO<sub>2</sub> emission, renewable and green resources of fuels and chemicals should be found. Cellulosic biomass emerges as a promising source for many reasons. First, cellulosic biomass is sustainable as long as light, water, CO<sub>2</sub>, and some other necessary conditions are provided. Secondly,

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cellulosic biomass is nonedible in comparison with starch or corn. So, it will not conflict with the need of human beings for food. Some solid wastes mainly composed of cellulose such as paper, sawdust, and municipal wastes can also be used. Thirdly, biomass is commonly recognized as carbon neutral that has no net release of  $\text{CO}_2$ .

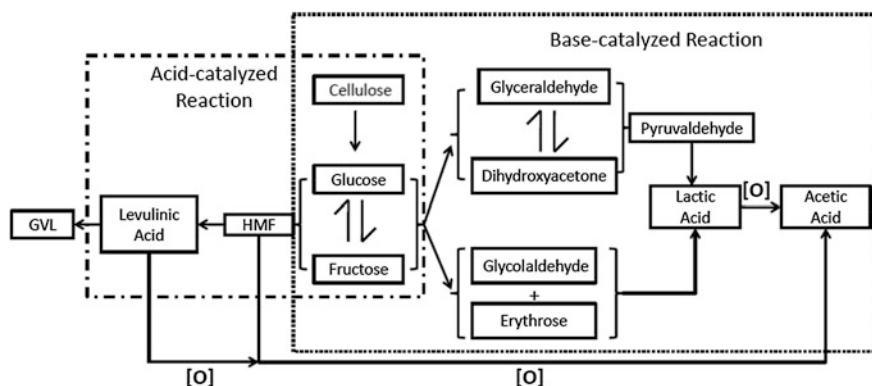
Many effective chemical methods for transformation of cellulose into valuable chemicals have been developed and reviewed [1, 2]. Generally speaking, gasification, pyrolysis, liquefaction, and solidification are the main approaches for transformation of cellulosic biomass leading to different products. For instance,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  are normally formed from gasification when using oxygen as the gasifying agent which can then be synthesized to liquid alkanes and alcohols by Fischer-Tropsch process [3]. Oxygen containing low molecular weight organics is formed through liquefaction technology such as 5-hydroxymethyl-2-furaldehyde (HMF) [4]. Carbons can also be formed to be employed as energy and storage materials by solidification [5].

Recently, hydrothermal technology applied in transformation of biomass to gas, liquid, and carbon products has attracted attention for its high efficient and environment-friendly advantages [5–10]. High temperature water has a lot of unique features. For example, water around 250–300 °C has high ion product ( $k_w$ ), which can act both as acid and base catalyst [6]. The low dielectric constant of high temperature water can greatly increase solubility of nonpolar feedstock. Hydrothermal reaction can quickly hydrolyze insoluble cellulose into water-soluble saccharides and desirable chemicals afterwards [10, 11]. Besides, direct use of wet biomass is available without the drying process, which can decrease the cost a lot. Readers are suggested to find classic reviews [5–10] on hydrothermal technology. In this chapter, selective conversion of cellulose into desired products (HMF and organic acids) is discussed through acid/base-catalyzed and oxidation reactions and recent progress in organic acid production by  $\text{CuO}$  oxidant under hydrothermal conditions in our group is reviewed.

## ***2.1.1 Conversion of Cellulose by Acid/Base Catalyst***

### **2.1.1.1 Acid Catalyst**

Figure 2.1 shows a principal reaction pathway of cellulose by hydrothermal conversion. It is well known that cellulose can decompose into HMF by acid-catalyzed reaction and lactic acid by base-catalyzed reaction without adding any catalyst under hydrothermal conditions as high-temperature water can act both as acid and base catalyst [6, 12]. However, the yields of some specific value-added products, such as HMF and lactic acid, are low without adding catalyst. Therefore, it is expected that the selective production of HMF and lactic acid can be enhanced by adding acid or base catalyst under hydrothermal conditions.



**Fig. 2.1** A principal reaction pathway of cellulose by hydrothermal conversion

As shown in Fig. 2.1, HMF is produced from the acid-catalyzed dehydration of C6-sugars (i.e., hexoses) in the furanose form [13, 14]. Hence, fructose which contains 21.5 % of furanose tautomers in aqueous solution can be converted into HMF easier than glucose which contains only 1 % of furanose tautomers in aqueous solutions. However, acid catalyst can improve the yield of HMF from glucose by increasing isomerization of glucose into fructose followed by Brønsted acid-catalyzed dehydration of fructose to HMF [4]. Mineral acids (HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) [15] and acid metal salts [16] are usually adopted acid. The rehydration of HMF with two molecules of water would produce levulinic acid and formic acid [17]. Levulinic acid can be further converted into g-valerolactone (GVL) via hydrogenation with hydrogen [18], which can be converted to liquid alkenes in the transportation fuel range [19]. Kinetics studies [20–22] show that humins formation from glucose and HMF cannot be neglected. The activation energy of its formation from glucose and HMF was estimated at 51 and 142 kJ/mol, respectively, while dehydration of glucose to HMF and rehydration of HMF to levulinic acid was 160 and 95 kJ/mol, respectively [22].

Currently, numerous researches [16, 23–25] on production of HMF from cellulosic biomass have been concentrated on the temperature range of 100–200 °C. To minimize the formation of humins and enhance selectivity toward HMF, a biphasic solution with water and organic phase was adopted that would continuously extract HMF as it is produced [16, 23–25]. Dumesic et al. reported a 61 % yield of HMF from glucose using a biphasic reactor of water/tetrahydrofuran with AlCl<sub>3</sub>·6H<sub>2</sub>O catalyst at 160 °C [23]. However, hydrothermal reactions can afford a fast transformation of biomass within a few minutes [26] compared with the case in lower temperature range that normally needs 30 min to hours [16]. Yoshida et al. obtained the best yield of HMF (65 %) from fructose achieved at a temperature of 513 K for a residence time of 120 s [26]. Our study [15] found the highest yield of levulinic acid is about 55 % at 523 K for 5 min with HCl as a catalyst, and the total highest yields of HMF and levulinic acid are about 50 %, and the total highest yields of HMF and levulinic acid are about 50 %, and the total highest yields of HMF and levulinic acid are about 50 %.

which occurred at 523 K for 5 min with  $\text{H}_3\text{PO}_4$  as a catalyst. For the three mineral acids ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$ ), it was found that not only the pH, but also the nature of the acids, had great influence on the decomposition pathway [26]. At lower pH, a rehydration of HMF to levulinic and formic acids was favored, whereas at higher pH, polymerization reactions was favored [26]. The order for the production of HMF using the three acids is in the sequence of  $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HCl}$ . By contrast, the order for production of levulinic acid follows  $\text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$  [15].

### 2.1.1.2 Base Catalyst

Lactic acid has received attention as a building block for biodegradable lactic acid polymers with limited environmental impact. Currently, the fermentation of starch is the main method for producing lactic acid. Bioconversion (bacterial fermentation), however, is not available directly to cellulose and lignocelluloses. In general, pretreatment is needed, and also a large amount of residue is acquired for further treatment. Besides, the fermentation is a complex and sensitive process requiring 2–8 days to complete the reaction, of which the pH and temperature must be carefully monitored. In contrast, hydrothermal reactions have been shown to convert cellulose and lignocelluloses into lactic acid directly and effectively.

Researchers [27–31] have examined intermediate products for hydrothermal degradation of glucose and cellulose at a reaction temperature of nearly 300 °C. As shown in Fig. 2.1, through these studies it was revealed that fructose and some compounds containing three carbon atoms (C3 carbon compounds), such as glyceraldehyde, dihydroxyacetone, and pyruvaldehyde, are formed by the base catalytic role of high-temperature water. Furthermore, there is isomerization occurring between glyceraldehyde and dihydroxyacetone followed by their subsequent dehydration to pyruvaldehyde [30]. These C3 carbon compounds are considered as the precursors of lactic acid from transformation of pyruvaldehyde [27]. On the other hand, the intermediates glycolaldehyde and erythrose transformed from glucose [28, 29] can also produce lactic acid [31]. Although these intermediates from C2–C3 or C3–C4 bond cleavage by reverse aldol condensation from hexoses can all produce lactic acid, glyceraldehyde can produce a higher yield of lactic acid [31]. Thus, it is suggested that if the selective bond cleavage can be achieved between these two bond cleavages, the yield of lactic acid can be higher.

Our recent studies [32, 33] show that the addition of base catalyst ( $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$ ) can increase the yield of lactic acid. The highest yield of lactic acid from glucose was 27 % with 2.5 M  $\text{NaOH}$  and 20 % with 0.32 M  $\text{Ca}(\text{OH})_2$  at 300 °C for 60 s [32]. A recent study by Labidi et al. [34] also found that the highest yield lactic acid of 45 % from corn cobs was obtained using 0.7 M  $\text{Ca}(\text{OH})_2$  at 300 °C for 30 min. The reason that base catalyst increases the yield of lactic acid can be attributed to the enhancement of reaction pathway for lactic acid production discussed above. Another reason may be that the lactate formed actually by alkaline

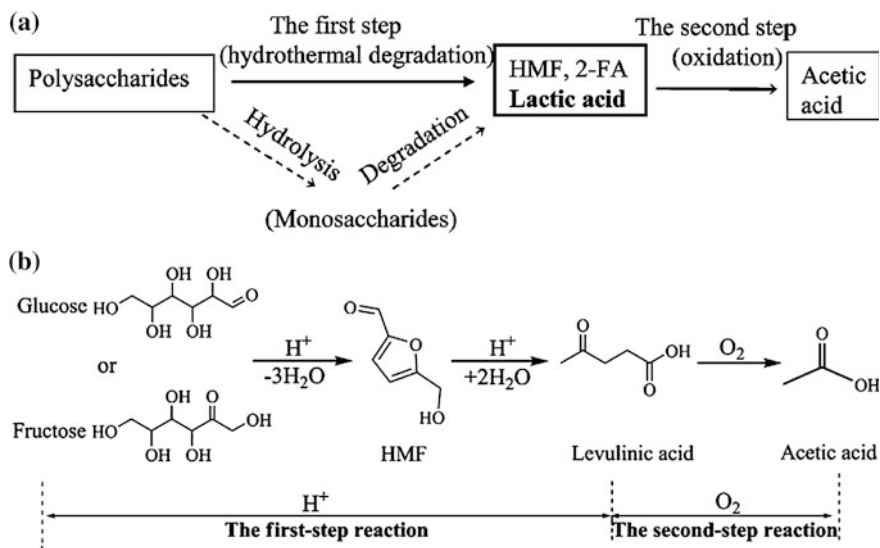
solution prevents it from decomposition [35]. For comparison with NaOH and  $\text{Ca}(\text{OH})_2$  [32], at lower alkaline concentration,  $\text{Ca}(\text{OH})_2$  promotes more effectively for production of lactic acid than NaOH in the same  $\text{OH}^-$  concentration. This is probably because  $\text{Ca}^{2+}$  is more capable than  $\text{Na}^+$  for forming complexes with two oxygen atoms in the hexoses. When  $\text{Ca}(\text{OH})_2$  increased higher from 0.32 to 0.4 M, it did not lead to increase in lactic acid yield, while the optimum  $\text{OH}^-$  concentration for NaOH was 2.5 M. This difference can be attributed to the fact that the saturated solubility of NaOH is higher than that of  $\text{Ca}(\text{OH})_2$ .

### ***2.1.2 Conversion of Cellulose by Acid/Base Catalyst Coupling with Novel Oxidant***

#### **2.1.2.1 $\text{H}_2\text{O}_2$ Oxidant**

Hydrogen peroxide,  $\text{H}_2\text{O}_2$  is an attractive oxidant for liquid-phase reactions in an economically, technically, and environmentally satisfying manner [36]. In hydrothermal reactions, it has been adopted to convert biomass into stable oxidation products such as acetic acid [37–39]. Acetic acid is also an important raw material in the industry primarily for producing vinyl acetate monomer (VAM) and acetic anhydride, and a solvent for purified terephthalic acid (PTA) production [40]. More than 60 % of the world acetic acid production employs the methanol carbonylation methods with drawbacks of catalyst solubility limitations and the loss of expensive Rh metal due to precipitation in the separation sections [40]. Thus, the development of an environmentally friendly and highly effective method for converting biomass into acetic acid is strongly desired. Daimon et al. [37] studied the production of low molecular weight carboxylic acids by the hydrothermal treatment of representative organic waste and compounds with  $\text{H}_2\text{O}_2$ . They found that acetic acid was dominant among the several carboxylic acids obtained including formic, propanoic, succinic, and lactic acids. About 29 mg/g yield of acetic acid from glucose was obtained. The reactions of  $\text{H}_2\text{O}_2$  in the supercritical water were also investigated experimentally and theoretically [41–43]. It was found that the rate of dissociation of  $\text{H}_2\text{O}_2$  in supercritical water is density-dependent and faster than its high pressure limit rate in the gas phase.

A strategy for improving acetic acid yield consisting of two steps was proposed by our group [12, 44]. As shown in Fig. 2.2, the two-step process consists of both a hydrothermal reaction without a supply of oxygen (the first-step reaction) and an oxidation reaction (the second-step reaction). In Fig. 2.2a, the first step is to accelerate the formation of HMF, 2-FA, and lactic acid because these furans and lactic acid can produce a large amount of acetic acid by their oxidation. In Fig. 2.2b, the first step is a reaction in the presence of an added acid catalyst that accelerates the formation of levulinic acid. The second step is to further convert the furans and lactic acid or levulinic acid produced in the first step into acetic acid



**Fig. 2.2** Two proposed two-step processes for enhancing acetic acid yield. **a** Reprinted with permission from Ref. [12]. Copyright 2005 American Chemical Society. **b** Reprinted with permission from Ref. [44]. Copyright 2012 American Chemical Society

by oxidation with newly supplied  $H_2O_2$ . It was shown that the acetic acid yield was greatly increased by the two-step process. The yield of acetic acid increased to 23 % from glucose and 26 % from fructose at 523 K for 300 s with HCl and  $H_2O_2$  [44].

On the other hand, if the method of hydrothermal treatment by adding base catalyst and  $H_2O_2$  together was adopted, high yield of formic acid can be obtained [35]. Formic acid is an important organic chemical because it can be seen as an energy material that produces hydrogen as well as its other chemical application [45]. Formic acid is probably formed mainly from the direct oxidation of glucose by  $\alpha$  scission [35]. The addition of alkali was considered as an effective way to prevent oxidative decomposition of formic acid [35]. The highest yield of formic acid through hydrothermal oxidation of glucose in the absence of alkali was about 24 %. In the case of adding alkali, the yield of formic acid increased to about 75 % from glucose [35].

### 2.1.2.2 CuO Oxidant

Recently, we have found that some metal oxides, such as CuO, could be reduced to its metal form with carbohydrates [46–48], which suggest that these metal oxides show oxidative potential for carbohydrates. That is, metal oxide might have the effect of promoting the production of organic acids from carbohydrates. With these in mind, a new process for selective production of acetic acid and lactic acid using

CuO as oxidant from glucose was proposed [49]. CuO has an obvious promotion effect on the production of acetic acid and lactic acid from glucose in the presence of NaOH [49]. Furthermore, we extended the feedstock from glucose to cellulose, and proposed a process for production of organic acids and refined copper in one-pot reaction from cellulosic biomass. An overall reaction scheme from cellulose to organic acids with a CuO oxidant under alkaline hydrothermal conditions was formulated based on these results. In the following, the progress on the production of organic acids and copper from glucose and cellulose with CuO in our group was reviewed including some recent unpublished results.

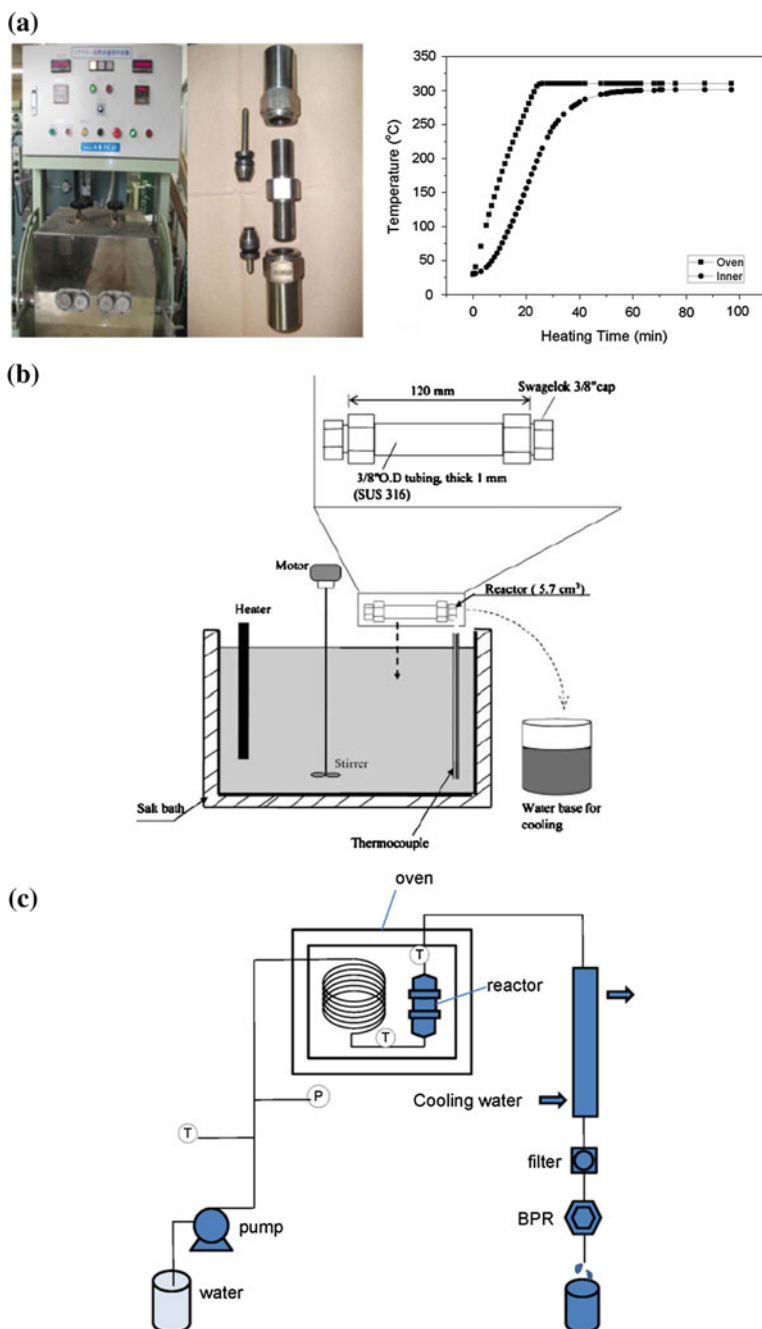
## 2.2 Conversion of Cellulose with CuO

In this section, there are three types of reactors used. Figure 2.3 shows a schematic diagram of the reactors used. As shown in Fig. 2.3, two types of batch reactor and a continuous flow type reactor were adopted. The detailed experimental methods can be found in our previous reports [12, 49]. The biggest differences are their heating time and flow type. As shown in Fig. 2.3a, the time required to heat up the oven from room temperature to 300 °C was 23 min. It needs another 38 min for the reactor to reach 300 °C and become stable. For the smaller tube reactor (see Fig. 2.3b), the time required to raise the temperature of reaction medium from 20 to 300 °C was about 15 s, which was faster than the former one. Therefore, the real reaction time performed in the former reactor was longer than that in the latter because of the heating time difference, although their nominal reaction times were the same. As shown in Fig. 2.3c, compared with the batch reactors, the continuous flow type reactor can be conducted at low temperatures and very short residence times (less than 1 min).

### 2.2.1 Conversion of Glucose

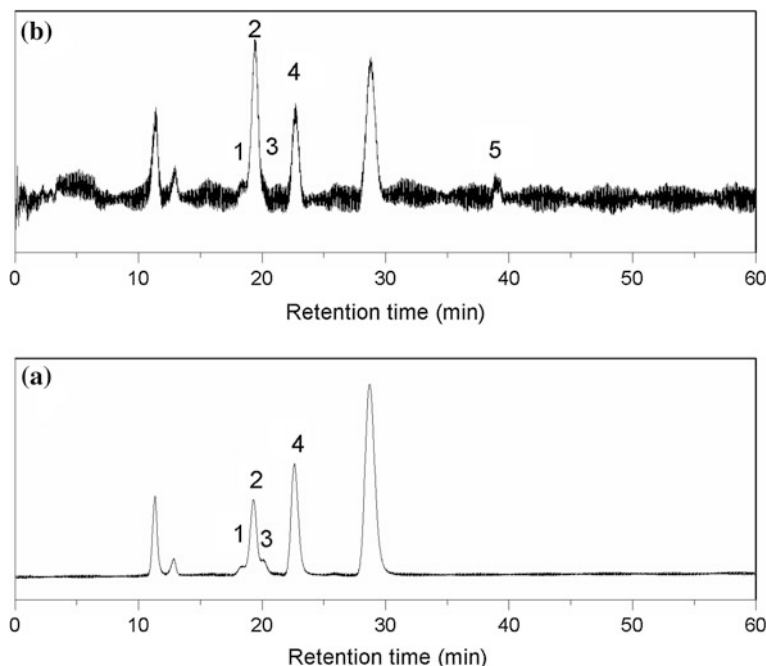
#### 2.2.1.1 Effect of CuO on Products

Experiments with glucose were conducted in the presence and absence of CuO at 300 °C for 1 min using batch reactor 1. 300 °C was chosen because our previous research [10] on conversion of cellulosic biomass into chemicals showed that 300 °C was the optimum reaction temperature under hydrothermal conditions. As shown in Fig. 2.4, glycolic acid, lactic acid, formic acid, and acetic acid have been detected in the presence of CuO. As illustrated in Fig. 2.5, in the case without CuO (entry 1), the yields of these organic acids were all low, below 1.0 %. The conversion of glucose was above 99 %, 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 lactic acid was observed. This result suggests that CuO had a promotion



**Fig. 2.3** Schematic diagram of reactors used. **a** Batch reactor 1: photo and its heating time profile, reproduced from Ref. [49] by permission of John Wiley & Sons Ltd; **b** Batch reactor 2, reprinted with permission from Ref. [12]. Copyright 2013 American Chemical Society; **c** Diagram of continuous flow reactor, reproduced from Ref. [49] by permission of John Wiley & Sons Ltd

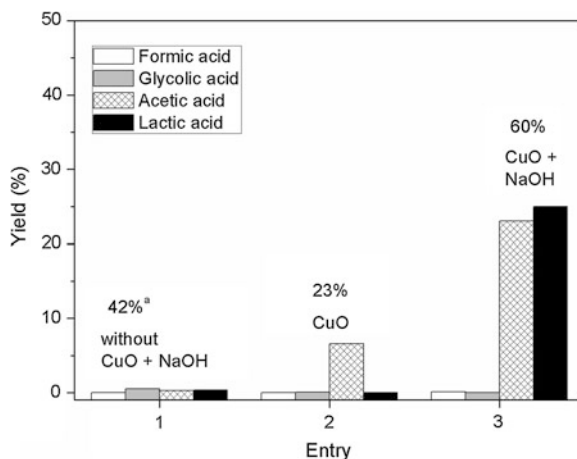




**Fig. 2.4** **a** HPLC–UV chromatogram obtained from 0.0525 g D(+)-glucose, 2 mmol CuO, and 1 M NaOH after 1 min of reaction at 300 °C. 1: glycolic acid, 2: lactic acid, 3: formic acid, and 4: acetic acid. **b** HPLC–RI chromatogram obtained from 0.0525 g D(+)-glucose, 2 mmol CuO, and 1 M NaOH after 1 min of reaction at 300°C. 1: glycolic acid, 2: lactic acid, 3: formic acid, 4: acetic acid, and 5: 5-HMF. Reactor used: batch reactor 1. Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd

effect on the acetic acid yield. In addition, as mentioned above, some researchers [33, 50] have proved that alkali had an obvious catalysis effect on the production of lactic acid from carbohydrate biomass under hydrothermal conditions. Thus, an experiment with glucose was conducted in the presence of CuO and NaOH to examine the role of  $\text{OH}^-$  in the production of organic acids in the presence of CuO. The yield of lactic acid 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  $\text{OH}^-$ . As shown in Fig. 2.5, 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 lower than that 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  $\text{OH}^-$  can protect glucose from carbonization into solids [51]. These observations further suggest that  $\text{OH}^-$  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 lactic acid and acetic acid.

**Fig. 2.5** 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. Reactor used: batch reactor 1) (<sup>a</sup> the percentage of TOC in the liquid samples to the total input carbons based on carbon number after reactions). Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd



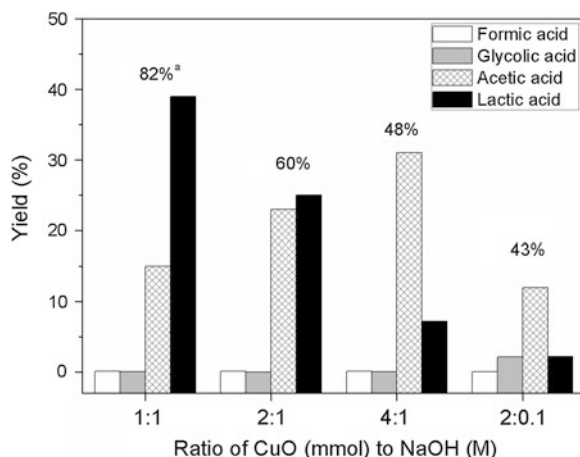
### 2.2.1.2 Effect of the Ratio of CuO:NaOH

The optimization ratio of CuO to NaOH for obtaining high yields of lactic acid and acetic acid was studied. As shown in Fig. 2.6, when fixing NaOH concentration to 1 M, the yield of acetic acid increased from 15 to 31 % with the increase of the amount of CuO from 1 to 4 mmol, which further confirmed that CuO had a selective production for acetic acid. However, the yield of lactic acid decreased from 39 to 7.2 % with the increase of the amount of CuO from 1 to 4 mmol. When lowering the NaOH concentration to 0.1 M with 2 mmol CuO, both yields of lactic acid and acetic acid decreased. This result indicates that a low concentration of alkali was disadvantageous for the production of lactic acid 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 lactic acid and acetic acid.

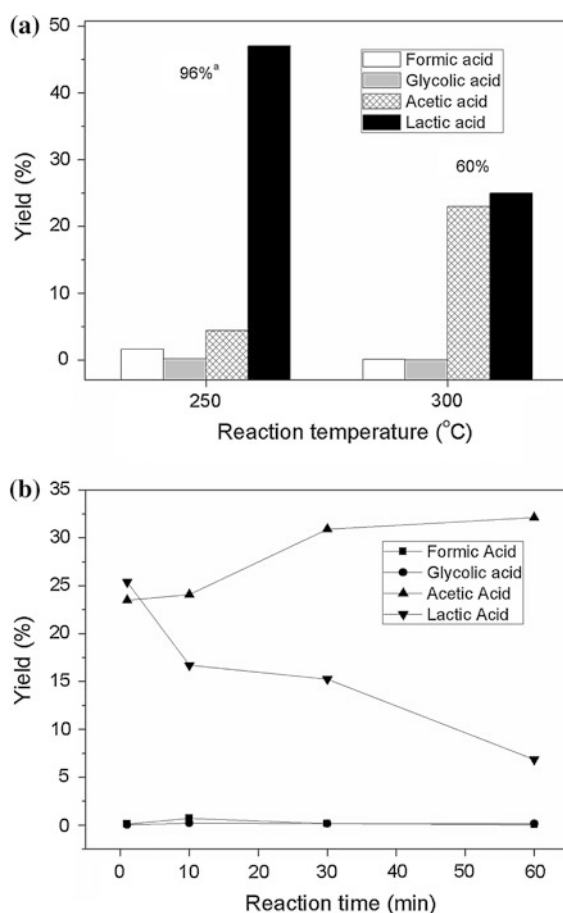
### 2.2.1.3 Effect of Reaction Temperature and Time

Figure 2.7a shows the effect of reaction temperature at 250 and 300 °C for 1 min on yields of lactic acid and acetic acid. The yield of lactic acid 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 acid and glycolic acid were very low at both temperatures. Figure 2.7b shows the effect of reaction time on yields of organic acids. Similarly, with increase in reaction time the yield of acetic acid increased, while the yield of lactic acid increased. A high yield of acetic acid (32 %) was obtained for 60 min. The yields of formic acid and glycolic acid were very low, below 1.0 %. It is suggested that the increase in acetic acid and the decrease in lactic acid with the increase in reaction temperature and time are probably because the formation of acetic acid is through the oxidative decomposition of lactic acid in the presence of CuO.

**Fig. 2.6** 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. Reactor used: batch reactor 1 (<sup>a</sup> the percentage of TOC in the liquid samples to the total input carbons based on carbon number after reactions). Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd



**Fig. 2.7 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; <sup>a</sup> 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). Reactor used: batch reactor 1. Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd



As discussed above, a longer reaction time and higher reaction temperature was not advantageous for a high yield of lactic acid in the presence of CuO. That is, a higher yield of lactic acid may 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 lactic acid, 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 lactic acid was obtained in the continuous flow reactor compared to that in the batch reactor (see Fig. 2.8). The highest yield of lactic acid (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 lactic acid reported so far obtained from glucose under hydrothermal conditions.

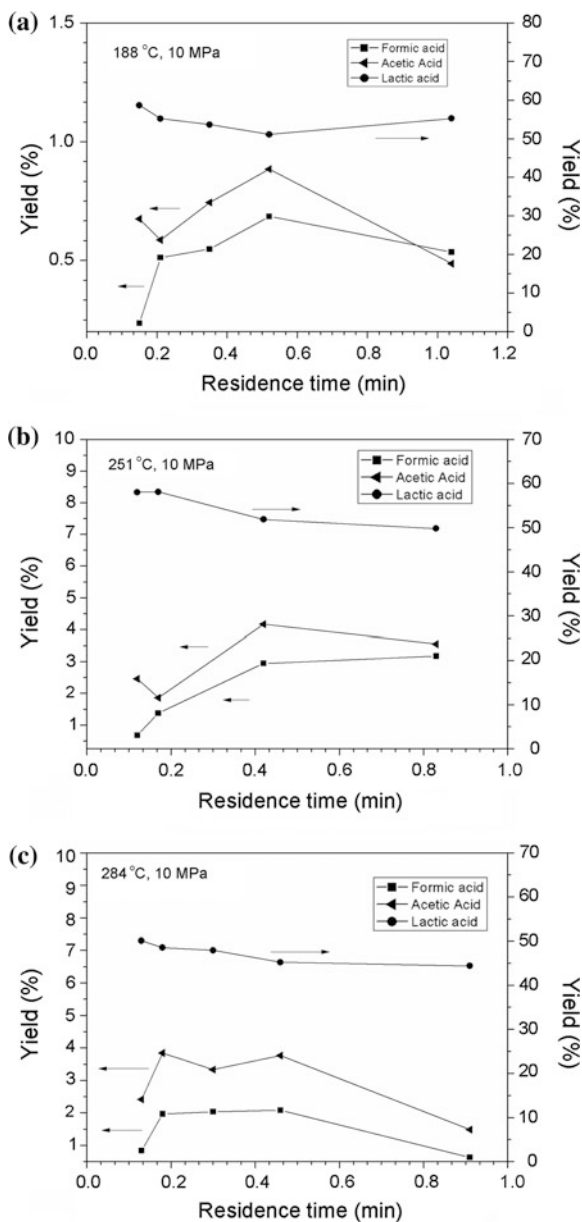
Similarly to the results obtained in the bath reactor, there is a tendency of decrease in yield of lactic acid with the increase in the residence time. For acetic acid, the yields were below 5 %, which were much lower than the results obtained in the batch reactor at all temperatures. These results suggest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

## ***2.2.2 Reactions of Intermediates and Organic Acids with CuO***

### **2.2.2.1 Reactions of Intermediates and Organic Acids**

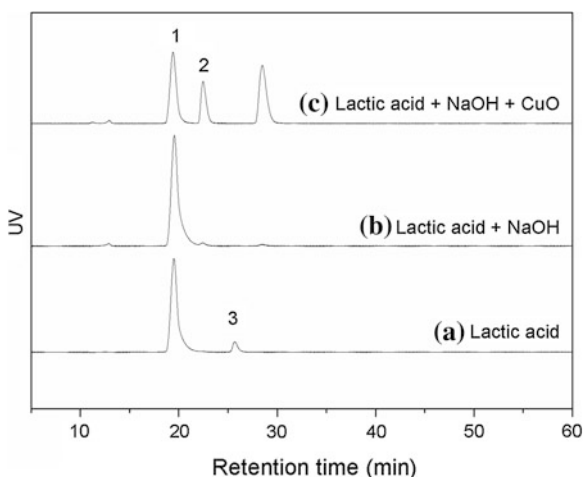
It has been reviewed before that aldose, aldehydes, and ketones, such as fructose, erthrose, glyceraldehyde, glycolaldehyde, pyruvaldehyde, and hydroxyacetone, are first formed as intermediates from glucose and then transformed into lactic acid under alkaline hydrothermal conditions. Therefore, fructose, erythrose, glycer-aldehyde, glycolaldehyde, and pyruvaldehyde were chosen as starting materials to examine their availability to produce organic acids with CuO. In the presence of CuO (without NaOH) at 300 °C for 1 min, a yield 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, respectively [49]. For all these experiments, no peaks of starting materials and lactic acid were observed maybe because their concentrations were below the detection limit [49]. Due to the uncertainty in the purity of erythrose, the quantification is not available [49]. These results show that those selected intermediates were able to produce acetic acid with CuO by acid/base-catalyzed reactions. According to our recent studies

**Fig. 2.8** 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). Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd



performed in the batch reactor 2 at 300 °C for 30 s, in the presence of CuO and NaOH, the intermediates of glyceraldehyde and glycolaldehyde were transformed into lactic acid mainly with glycolic acid, acetic acid, and formic acid (unpublished results), suggesting lactic acid was still initially mainly formed in the

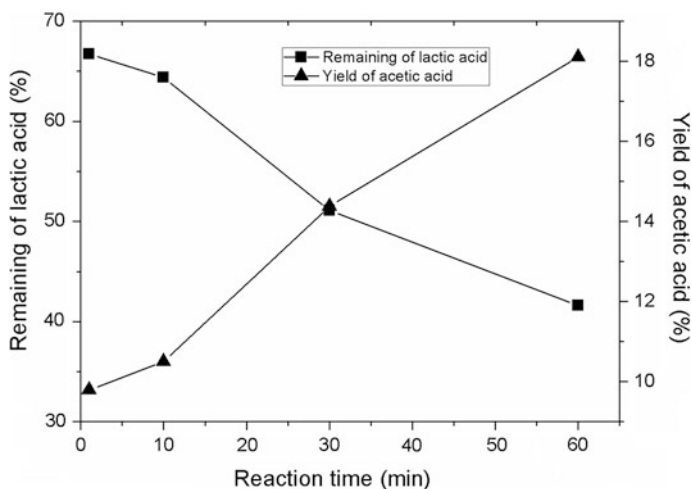
**Fig. 2.9** HPLC–UV chromatogram obtained from 0.35 M lactic acid, 2 mmol CuO, and 1 M NaOH at 300 °C for 1 min (1: lactic acid, 2: acetic acid, and 3: propionic acid). Reactor used: batch reactor 1. Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd



transformation of these intermediates in the addition of CuO under alkaline hydrothermal conditions.

Later, to examine the conversion of lactic acid into acetic acid, experiments with lactic acid as a starting material in the presence and absence of CuO were performed. As shown in Fig. 2.9a, lactic acid slightly decomposed and no peak of acetic acid was observed without CuO and NaOH. From Fig. 2.9b, in the case of adding 1 M NaOH without CuO, 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 lactic acid can be improved with CuO. Figure 2.10 shows the change in the decomposition of lactic acid and the yield of acetic acid with CuO and NaOH by varying reaction time from 1 to 60 min. The remaining lactic acid 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. Therefore, in the presence of CuO and NaOH, the high yield of acetic acid obtained in Sect. 2.1 was mainly attributed to the decomposition of lactic acid because lactic acid was initially formed with low yield of acetic acid at the same reaction time (see Fig. 2.8) and then lactic acid can be transformed into acetic acid.

For the reactions of other acids, such as glycolic acid, acetic, and formic acid, according to our recent study performed in the batch reactor 2 (unpublished results), they are relatively stable in the presence of NaOH whose conversions were lower than 10 % at 300 °C for 180 s. The presence of CuO (in addition of CuO and NaOH) can enhance the conversion of these acids except acetic acid compared with the case only in addition of NaOH. The conversion of these acids decreased in the following order: formic acid > glycolic acid > lactic acid > acetic acid in the



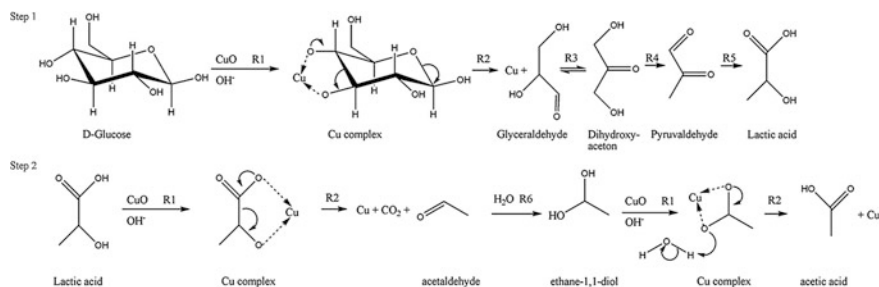
**Fig. 2.10** Effect of reaction time on conversion of lactic acid and yield of acetic acid (0.35 M lactic acid, 2 mmol CuO, and 1 M NaOH at 300 °C). Reactor used: batch reactor 1. Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd

presence of CuO. Acetic acid, glycolic acid, and lactic acid can all produce formic acid and formic acid can be further reacted to produce gas [52]. The fact that the yield of formic acid and glycolic acid from glucose performed in the batch reactor 1 was relatively low was attributed to the easy decomposition of these two acids in the presence of CuO and long heating time of batch reactor 1.

#### 2.2.2.2 Role of CuO and Possible Mechanism

A possible mechanism of conversion of glucose into lactic acid and acetic acid in the presence of CuO was proposed and is presented in Fig. 2.11. At the beginning of reaction, a strong base (NaOH) under hydrothermal conditions may enhance the solubility of CuO to form hydroxo complex [53]. 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). Simultaneously, lactic acid is formed as the main product from the transformation of complex and glyceraldehyde [10]. Then, the formed lactic acid is further oxidized into acetic acid via a similar transformation by formation of Cu complex with the release of CO<sub>2</sub> as shown in Fig. 2.11.

The detailed discussion on reduction of CuO into Cu<sub>2</sub>O and Cu by glucose and cellulose is given in Sects. 2.3.1 and 2.3.2.



**Fig. 2.11** Reaction pathway of production of lactic 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). Reproduced from Ref. [49] by permission of John Wiley & Sons Ltd

## 2.2.3 Conversion of Cellulose with CuO

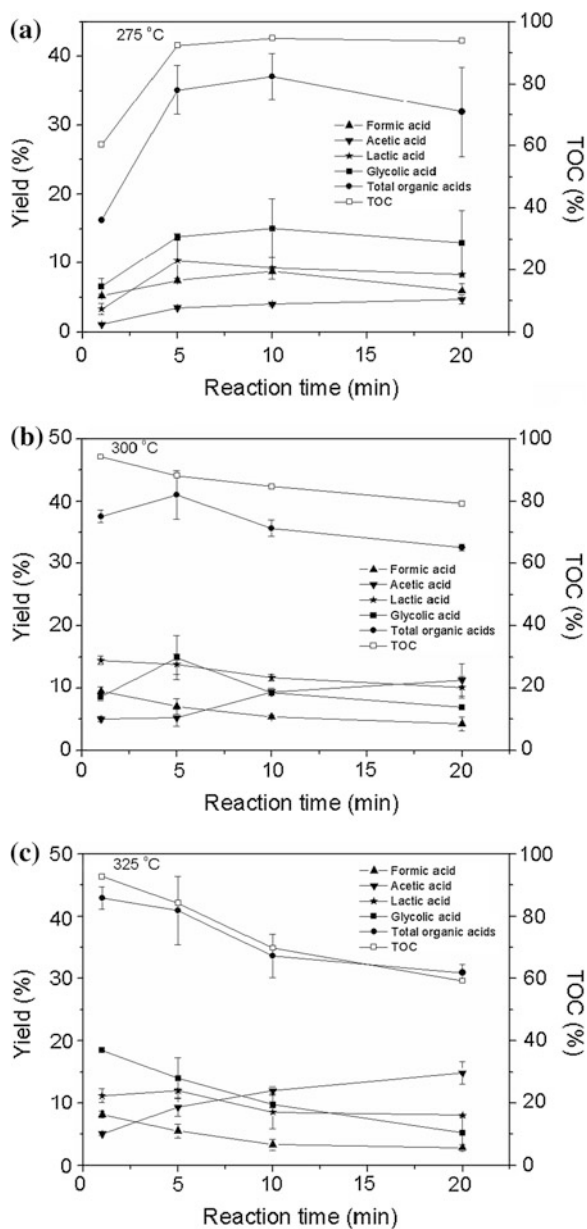
### 2.2.3.1 Effect of Reaction Temperature and Time

The feedstock in this section is extended to cellulose rather than its monomer glucose to investigate the reaction pathway of cellulosic biomass in this reaction system and optimize reaction conditions. Experiments of cellulose with CuO and NaOH under different reaction temperatures and time were conducted and the yield of organic acids and total organic carbon (TOC) are given in Fig. 2.12. As shown in Fig. 2.12, the total organic acids yield first increased and then decreased after 10 min at 275 °C, while it decreased after 5 min in the case of 300 °C and decreased after 1 min at 325 °C along with a similar trend of TOC yield. The higher the reaction temperature is, the sooner the yield of total organic acids will reach its highest value. The following decrease can be attributed to the reactions of carboxylic acids by decarboxylation or decarbonylation that lead to decrease in carbon yield.

For specific organic acids, it can be seen from Fig. 2.12 that mainly four kinds of organic acids including lactic acid, glycolic acid, acetic acid, and formic acid have been detected to be the same as the result obtained from glucose. Acetic acid increased with the increase in reaction time at all temperatures, which can be ascribed to the fact that it is very stable and can be obtained from lactic acid with CuO. 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 the yield was observed, showing the competitive reactions between the formation and decomposition of these acids. These results suggest us that a selective production of these organic acids can be achieved by varying reaction temperature and time. It can be also found that an initial short reaction time, such as 5 min at 300 °C, mainly accounts for the formation of organic acids from cellulose. After that, the decomposition of organic acids dominates the whole process.



**Fig. 2.12** Effect of reaction temperature and time on the yields of organic acids. Reaction conditions: 0.035 g cellulose, 2.0 mmol CuO, 1.0 mol/L NaOH, 2 mL water. Reactor used: batch reactor 2. Unpublished results



### 2.2.3.2 Reaction Scheme

On the basis of these results, we therefore propose a principal reaction pathway (Fig. 2.13) showing that cellulose is first hydrolyzed to glucose and fructose, then degraded into two carbons or three carbons aldehydes and ketones, and these

aldehydes and ketones are subsequently transformed to carboxylic acids which can be further degraded from higher carbon numbers acid to lower carbon numbers acid. It can be concluded that the overall reaction pathways consist of four reaction stages: (i) stage from polysaccharide to monosaccharide; (ii) stage from monosaccharide to aldehydes and ketones; (iii) stage from aldehydes and ketones to carboxylic acids; (iv) stage of reactions of carboxylic acids.

## 2.3 Reduction of CuO with Cellulose

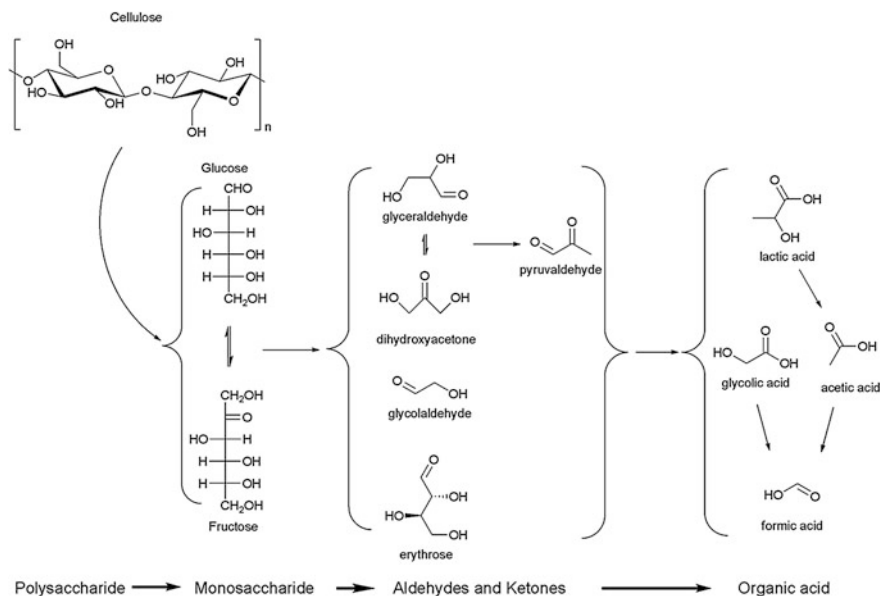
In the studies of conversion of cellulose with CuO, Cu<sub>2</sub>O and Cu were found in solid products. This indicated that CuO can be reduced directly by cellulose. It is well known that Cu existing in nature is mainly in the form of ores containing oxygen or sulfur. Direct reduction of Cu oxides to Cu with cellulose as reductant is significant for green Cu smelting process. Compared to traditional CuO reducing agents in smelting, such as carbon, heavy oil, petroleum gas, and ammonia [54–56], cellulose is an environment-friendly reductant. This is because cellulose is one of the most abundant carbon neutral and renewable resources. Moreover, cellulose can reduce CuO efficiently at lower hydrothermal temperatures (<250 °C). Meanwhile, cellulose was converted into value-added chemicals (lactic acid, acetic acid, et al.). Thus, cellulose is a promising green reducing agent in Cu smelting.

In this section, we outline some recent advances on the conversion of CuO to Cu by using cellulose under alkaline hydrothermal conditions. Experiments in this study were carried out in a Teflon-lined batch reactor with an inner volume of 20 mL.

### 2.3.1 Examination of the Reduction of CuO to Cu with Cellulose

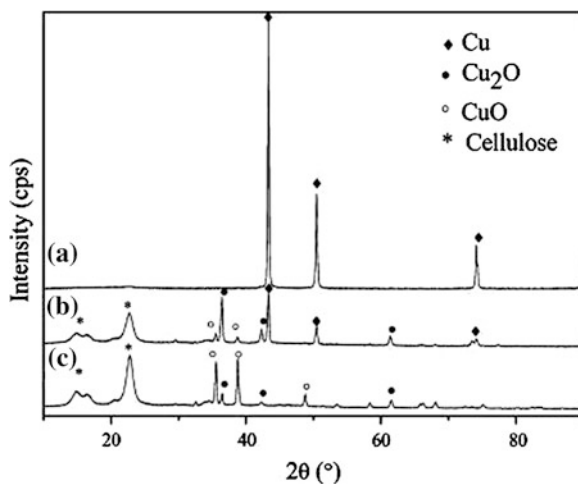
Figure 2.14 shows the XRD patterns of solid samples obtained after hydrothermal reactions at 250 and 180 °C with and without 0.50 mol/L NaOH. CuO can be partly reduced to Cu<sub>2</sub>O and Cu, even at a lower temperature of 180 °C (see Fig. 2.14b), and only a Cu peak was observed when the temperature was increased to 250 °C. These results indicate that CuO can be completely reduced to highly pure Cu at 250 °C. Comparing the XRD patterns in the presence and absence of NaOH at the temperature of 180 °C (see Fig. 2.14b, c), it is clear that only a small quantity of Cu<sub>2</sub>O and no Cu was produced, which suggest that alkali was favorable for the reduction of CuO to Cu<sub>2</sub>O and Cu.

The particle size distributions for the original CuO and Cu obtained after the reaction at 250 °C for 1.5 h without any further processing were measured using a



**Fig. 2.13** Proposed reaction pathway from cellulose to organic acids

**Fig. 2.14** XRD patterns of the solid samples at **a** 250 °C, 0.50 mol/L NaOH, 1.5 h; **b** 180 °C, 0.50 mol/L NaOH, 3 h; and **c** 180 °C, without NaOH, 3 h. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society



laser particle size analyzer. As shown in Table 2.1, the average particle sizes of the initial CuO and the Cu obtained were 6.19  $\mu\text{m}$  (standard deviation (SD) = 3.50  $\mu\text{m}$ ) and 1.46  $\mu\text{m}$  (SD = 1.03  $\mu\text{m}$ ), respectively. The range of the Cu particle size distribution was narrower than that of CuO, indicating that the particle size of Cu obtained after the reaction was more uniform.

**Table 2.1** Distribution of particle size of the purchased CuO with 200 mesh and the obtained Cu with cellulose after the reaction at 250 °C with 0.50 mol/L NaOH after 1.5 h<sup>a</sup>

	av diam (μm)	D10 (μm)	D50 (μm)	D90 (μm)
Purchased CuO (200 mesh)	6.19	2.53	5.77	10.33
Obtained Cu	2.41	0.76	1.64	5.01

<sup>a</sup> D10, D50, and D90 mean that 10, 50, and 90 % of the powder particles are smaller than this value, respectively

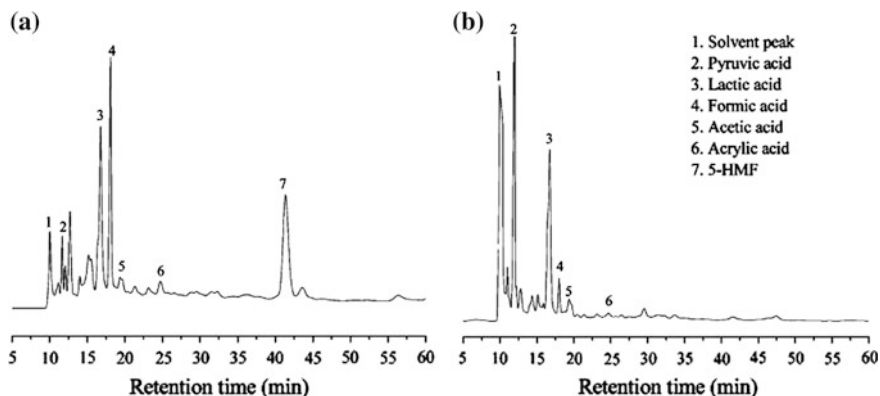
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To determine the effect of CuO on the conversion of cellulose, the liquid products obtained after the hydrothermal degradation of cellulose with and without CuO were analyzed by HPLC. As shown in Fig. 2.15, lactic acid, formic acid, acetic acid, pyruvic acid, and some other low molecular weight carboxylic acids were detected in the absence and presence of CuO. However, in the presence of CuO, the amount of acetic acid increased from 2.0 to 4.0 g/L, the yield of formic acid decreased by 85 %, and the amount of lactic acid increased slightly. The increase of acetic acid may be attributed to the oxidative decomposition of lactic acid in the presence of CuO, as discussed above. Therefore, the production of lactic acid from cellulose was promoted in the presence of CuO. Moreover, the decrease of formic acid may be due to further oxidative decomposition to CO<sub>2</sub> [57].

### 2.3.2 Effects of Reaction Conditions on the Conversion of CuO into Cu

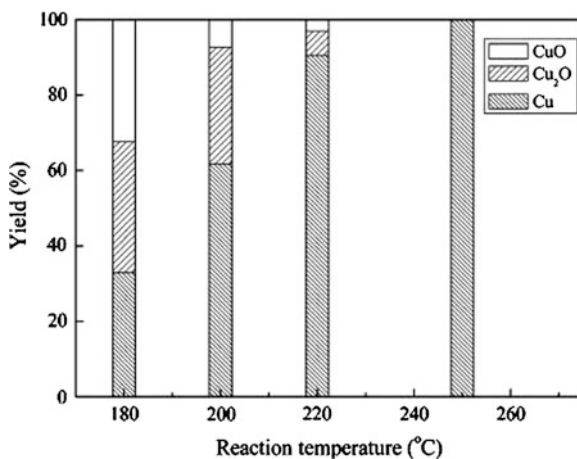
The effects of the reaction temperature, reaction time, and concentration of alkali on the reduction of CuO to Cu were investigated to determine the optimum conditions for the conversion of CuO into Cu. The yield of Cu<sub>2</sub>O or Cu was defined as the ratio of the Cu<sub>2</sub>O or Cu to the solid sample obtained based on the mass by XRD analysis. The Rietveld method is a standard technique for quantitative phase analysis. The Rietveld calculations in this work were performed by the software TOPAS 4.2 from Bruker AXS GmbH, Germany. This software is based on the fundamental parameter approach (FPA), which considers the geometric and unit-specific parameters [58].

The influence of reaction temperature on the reduction of CuO with cellulose was determined by varying the temperature from 180 to 250 °C after 2 h (Fig. 2.16). The yield of Cu greatly increased with the increase in reaction temperature. When the temperature increased to 250 °C, the CuO was completely reduced to Cu after 1.5 h. However, at temperature of 180 °C, the yield of Cu was only approximately 71 %, even for the longer reaction time of 8 h. As shown in the XRD patterns (Fig. 2.14b), there was unreacted cellulose remaining in the solid sample, which indicates that, at lower temperature, not all of the cellulose took



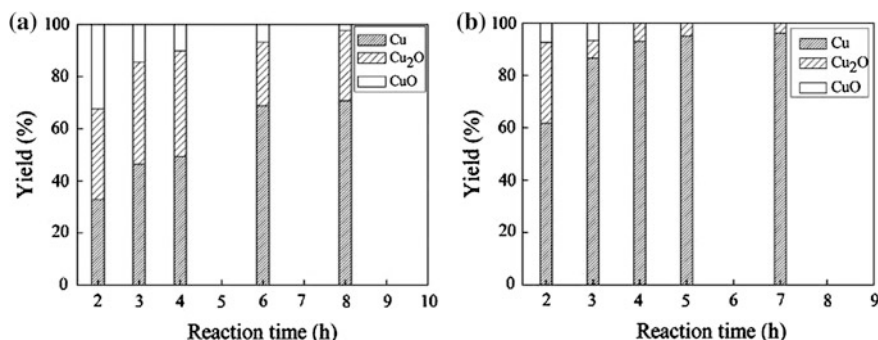
**Fig. 2.15** HPLC chromatograms of liquid samples **a** without CuO and **b** with CuO at 250 °C, 1.5 h, 0.50 mol/L NaOH. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society

**Fig. 2.16** Yields of Cu and Cu<sub>2</sub>O with the variation of reaction temperature at 0.50 mol/L NaOH, 2 h. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society



part in the reduction reaction, leading to less conversion of CuO. These results suggest that the degradation of cellulose played an important role in the reduction of CuO to Cu. Moreover, in the view of thermodynamics of the reaction,  $\Delta G_{\text{red}}$  (the Gibbs free energy for the reduction of oxides) slowly decreases as the temperature increases [59]. Therefore, the improvement in the reduction of CuO to Cu at a higher temperature, that is, above 200 °C, could be attributed to the decrease in  $\Delta G_{\text{red}}$ .

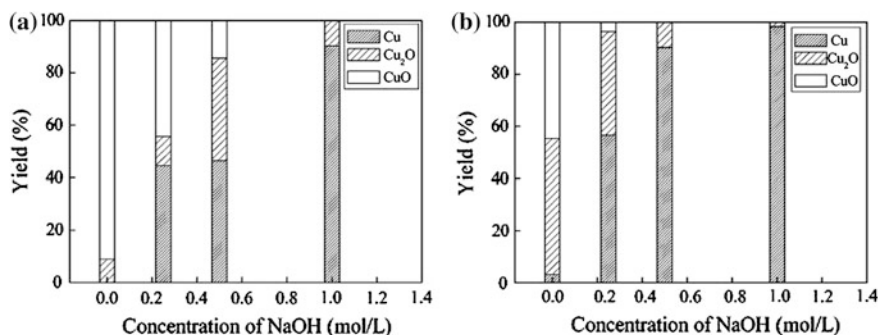
As shown in Fig. 2.17, the yield of Cu increased from 61 % after 2 h to 93 % after 4 h at 200 °C, and no further obvious increase in the yield of Cu was observed after 6 h. Similar increase tendency was observed at 180 °C.



**Fig. 2.17** Yields of Cu and Cu<sub>2</sub>O with reaction time at temperatures of **a** 180 and **b** 200 °C, respectively, at 0.50 mol/L NaOH. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society

A large amount of Cu<sub>2</sub>O was produced at a lower temperature after a short reaction time (Figs. 2.16 and 2.17), which suggests that the formation of Cu from CuO is a multistep reaction that proceeds via the formation of Cu<sub>2</sub>O. The first step in the reduction of CuO to Cu<sub>2</sub>O is exothermic with a calculated  $\Delta_r H_m$  of  $-1306.94$  kJ/mol, and the second step for reduction of Cu<sub>2</sub>O to Cu is endothermic with a calculated  $\Delta_r H_m$  of  $703.07$  kJ/mol. Therefore, CuO can easily be converted to Cu<sub>2</sub>O at a lower temperature after a short reaction time, whereas a higher temperature is necessary to convert Cu<sub>2</sub>O into Cu.

Experiments were conducted at 180 °C and 200 °C to investigate the effect of alkali by varying the concentration of NaOH from 0 to 1.0 mol/L. As shown in Fig. 2.18, a higher NaOH concentration was favorable for the reduction of CuO. The yield of Cu increased greatly with the increase in NaOH concentration and exceeded 90 % with 0.50 mol/L NaOH at 200 °C after 3 h. The notable increase in the conversion of CuO with the increase in NaOH concentration probably occurred for three reasons. First, alkali can promote the hydrolysis of cellulose. It has been reported that, NaOH can readily break the hydrogen bonds in cellulose and promote the degradation of cellulose in favor of C–C bond cleavage under hydrothermal conditions [60, 61]. Second, NaOH promoted the conversion of glucose into lactic acid due to its alkali catalytic activity which shows reducing function for CuO as discussed later [33, 62]. Moreover, according to the Pourbaix diagram in electrochemistry, the  $E_h$  (reduction potential) decreases as pH increases [63, 64]. Therefore, the increase of Cu with the increase of alkali concentration is probably due to the reduction of  $E_h$  by OH<sup>−</sup> ions. To maintain the safety of the experiments and the durability of the reactor, the optimum concentration of NaOH was set at 0.50 mol/L.



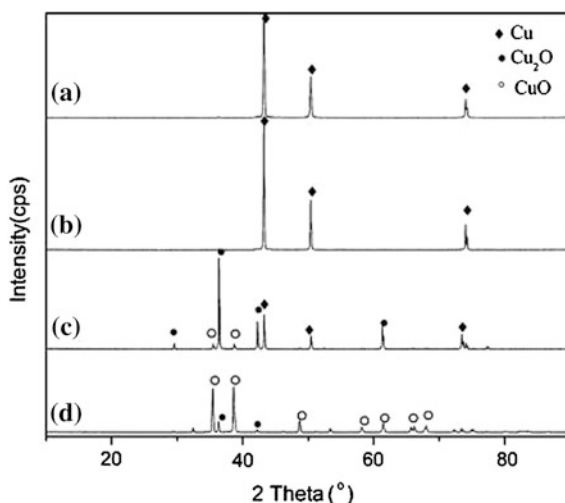
**Fig. 2.18** Effect of concentration of NaOH on yields of Cu and Cu<sub>2</sub>O at temperatures of a 180 and b 200 °C, respectively, 3 h. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society

### 2.3.3 Proposed Mechanism of Reduction of CuO to Cu with Cellulose

Generally, cellulose is a nonreducing sugar and is insoluble in water at a temperature; however, cellulose can be easily hydrolyzed to oligosaccharides and monosaccharides in HTW even without base or acid, due to inherent acid and base catalytic roles of HTW [65, 66]. Therefore, cellulose may first be hydrolyzed into glucose under the alkaline hydrothermal conditions [38], which subsequently is used for the reduction of CuO. Moreover, it is known that hydrogen or syngas can be produced from the hydrothermal gasification of biomass under subcritical water conditions [67–70]. Therefore, there are two possible explanations for the reduction of CuO to Cu in the presence of cellulose. One explanation is that CuO is reduced by the glucose formed by the hydrolysis of cellulose. The other explanation is that CuO is reduced by a reducing gas, such as CO and H<sub>2</sub> [71, 72], formed by the decomposition of cellulose. To test the latter hypothesis, gas samples were collected and examined by GC-TCD. Nearly no reducing gas, such as H<sub>2</sub> and CO, was produced, and approximately 58 % (v/v) of the gas collected was CO<sub>2</sub>. Therefore, it was reasonable to propose that CuO was reduced by glucose formed by the hydrolysis of cellulose. The possible mechanism of reduction of CuO by glucose under hydrothermal conditions has been discussed in Sect. 2.2.2.2.

As mentioned above, the increase of acetic acid obtained in the presence of CuO is probably due to the oxidation of lactic acid. To test this assumption, further experiments with lactic acid as a reductant in the presence of CuO at 250 °C after 3 h were carried out under acidic, neutral, and alkaline conditions by adjusting the pH with NaOH. As shown in Fig. 2.19, which depicts the XRD patterns of the solid products after reactions with lactic acid at pH 12.0, 6.0, and 3.0, the peak of Cu was higher at a lower pH, and the peak of CuO was not observed at pH 3.0. These results indicate that acidic conditions are favorable for the reduction of CuO

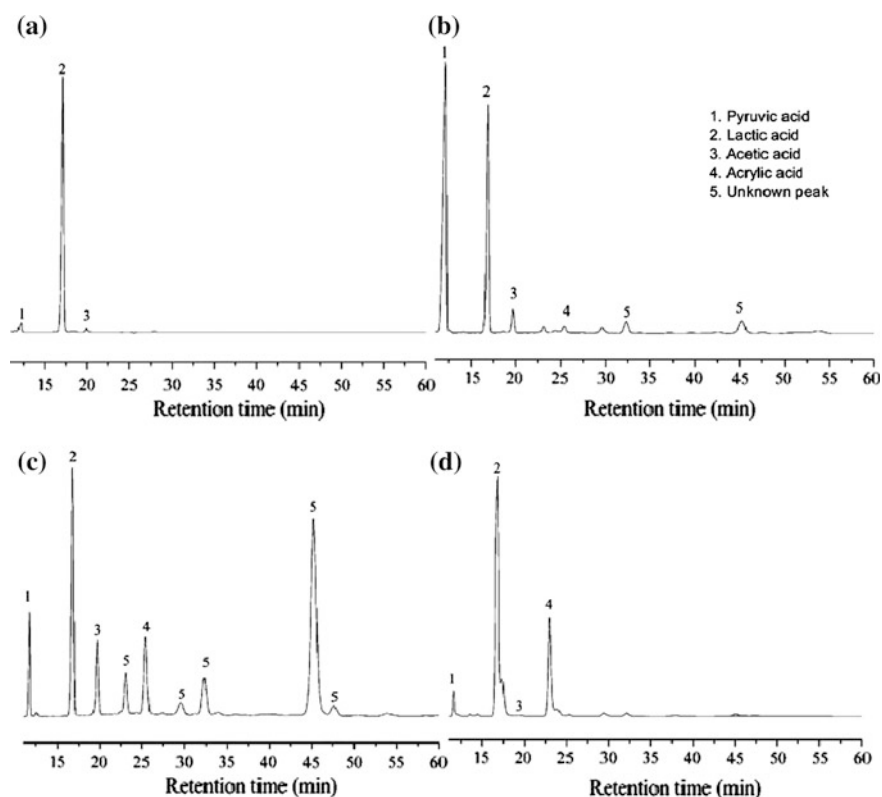
**Fig. 2.19** XRD patterns of solid samples with lactic acid at temperature of 250 °C, 3 h, and **a** Cu = 6 mmol, pH 3.0; **b** CuO = 6 mmol, pH 3.0; **c** CuO = 6 mmol, pH 6.0; and **d** CuO = 6 mmol, pH 12.0. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society



to Cu with lactic acid as reductant. Figure 2.19a is the XRD pattern of solid sample after the blank experiment with Cu and lactic acid, which indicated that there were no reactions with Cu and lactic acid. Figure 2.20 shows the HPLC chromatograms of the liquid products obtained under the same conditions. These chromatograms show that the pyruvic acid and acetic acid were present in the liquid samples. Comparing the HPLC chromatograms at different pH values, the lactic acid peak was smaller and the acetic acid peak became higher with a decrease in the pH, thereby indicating that the increase of acetic acid could be attributed to the oxidation of lactic acid [73]. These results also demonstrate that acidic conditions are favorable for the decomposition of lactic acid, perhaps because organic acids are difficult to degrade under alkaline conditions, as demonstrated by our previous report [35]. A comparison of the HPLC chromatograms of the liquid samples obtained under the same conditions with and without CuO (Fig. 2.20c, d) reveals that the peak area of the acetic acid increased in the presence of CuO, indicating that CuO can promote the decomposition of lactic acid and improve the yield of acetic acid. Furthermore, a series of experiments with acetic acid (0.50 mol/L) and CuO at 250 °C were conducted to investigate the reducing capacity of acetic acid for CuO. As shown in Fig. 2.21, the reduction of CuO was not observed at pH 6.0 and 12.0, respectively, and a small amount of CuO was reduced to Cu<sub>2</sub>O at pH 3.0. In contrast with experiments with lactic acid, the reducing ability of acetic acid is much lower in the reduction of CuO under hydrothermal conditions. Therefore, CuO can be reduced not only by cellulose but also by the products of cellulose decomposition, such as lactic acid.

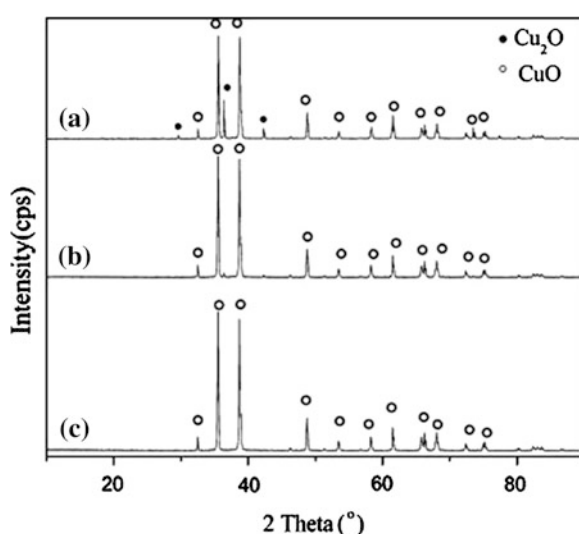
Based on the reduction of CuO to Cu by cellulose as reducing agent under mild hydrothermal conditions, a facile and green process for producing Cu from CuO was proposed. As shown in Fig. 2.22, highly pure Cu can be obtained easily.

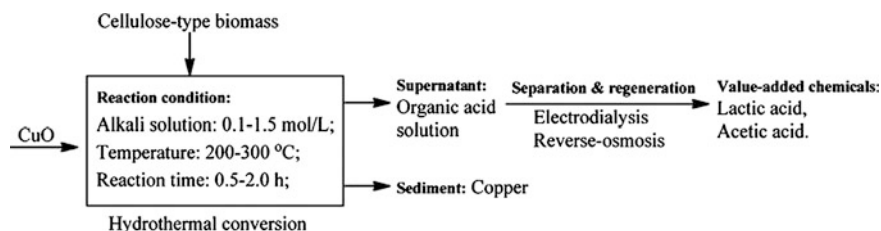




**Fig. 2.20** HPLC chromatograms of liquid samples in the presence of CuO and lactic acid with different pH values, **a** pH = 12.0, **b** pH = 6.0, **c** pH = 3.0, **d** pH = 3.0 (without CuO), at 250 °C, 3 h. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society

**Fig. 2.21** XRD patterns of solid samples in the presence of CuO and acetic acid at temperature of 250 °C, 3 h, and **a** pH 3.0 **b** pH 6.0, and **c** pH 12.0. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society





**Fig. 2.22** Proposed flow sheet for converting CuO into Cu. Reprinted with permission from Ref. [47]. Copyright 2012 American Chemical Society

At the same time, some value-added chemicals, such as lactic acid and acetic acid, were also produced by suitable management [49]. Work along this line is now in progress.

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