Improved two-step hydrothermal process for acetic acid production from carbohydrate biomass

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Abstract

An improved two-step process for converting carbohydrate biomass to acetic acid under hydrothermal conditions is proposed. The first step consists of the production of lactic acid from carbohydrate biomass, and the second step consists of conversion of the lactic acid obtained in the first step to acetic acid using CuO as an oxidant. The results indicated that CuO as an oxidant in the second step can significantly improve the production of high-purity acetic acid from lactic acid, and the maximum yield of acetic acid was 61%, with a purity of 90%. The yield of acetic acid obtained using the improved two-step hydrothermal process from carbohydrate biomass, such as glucose, cellulose and starch, was greater than that obtained using traditional two-step process with H_2O_2 or O_2. In addition, a proposed pathway for the production of acetic acid from lactic acid in the second step with CuO was also discussed. The present study provides a useful two-step process for the production of acetic acid from carbohydrate biomass.

Key words

carbohydrate biomass; lactic acid; CuO; acetic acid; hydrothermal reactions

1. Introduction

Energy shortages and environmental problems have attracted global attention toward the development of clean and sustainable energy sources to replace petroleum resources [1−3]. Biomass, which is the most abundant and cleanest renewable resource, has been the focus of attention for converting into fuels and chemicals [4−12]. Acetic acid, a very important organic chemical in industrial applications, is obtained from natural gas. Acetic acid can also be used to produce calcium-magnesium acetate, which is known as an environmentally friendly deicer. Among these processes, hydrothermal treatment is an interesting alternative for transforming the biomass into acetic acid because of its unique properties of high-temperature water. For example, the ionization constant (K_w) of high-temperature water is maximum at a temperature near 300 °C under saturated vapor pressure, under which K_w

is approximately 1000 times greater than that of water at normal temperature and pressure [13−15].

Previously, our group [16−22] reported a two-step process for improving the yield of acetic acid from carbohydrates. The two-step process consists of both a hydrothermolysis without any oxygen supply (first step) followed by a subsequent oxidation reaction (second step). The products in the first step are 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA) and lactic acid, and then these intermediate products are converted to acetic acid by oxidation [17]. Subsequently, a further study reported an alkali two-step process for the production of acetic acid from carbohydrates. The first step is to produce lactic acid from carbohydrates in the presence of alkali, and the second step subsequently converts the formed lactic acid into acetic acid [18]. However, the results were still unsatisfactory. For example, the second step of the process for converting lactic acid to acetic acid via oxidation requires a supply of H_2O_2 or O_2 during the transformation

(Scheme 1). The use of H_2O_2 or O_2 as oxidants in the conversion of carbohydrate biomass into acetic acid was relatively costly and corrosive. Therefore, to improve the production of acetic acid and to satisfy the requirements for practical applications, developing a new solid oxidant to replace H_2O_2 or O_2 is of great significance and is highly desirable.
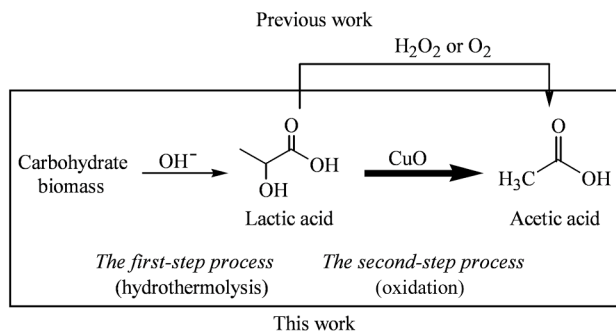
Scheme 1. Previous work and our concept for the two-step process of carbohydrate biomass to acetic acid

In our recent works, we found that CuO could be reduced to Cu by biomass in hydrothermal reactions [23−25]. More recently, we reported that the use of CuO as an oxidant could efficiently convert glucose and cellulose to low-molecular-weight carboxylic acids under hydrothermal conditions [26,27]. Based on these findings, we hypothesized that CuO might serve as an oxidant to replace H_2O_2 or O_2 in the second step of the oxidation process. With this in mind, in this study, we proposed an improved two-step process for producing acetic acid from carbohydrate biomass using CuO as an oxidant in the second step (Scheme 1).

2. Experimental

2.1. Materials

All the reagents used in this study were analytical-grade reagents (≥99%). CuO and sodium hydroxide were obtained from Sinopharm Chemical Reagent (China). Lactic acid (1.0 N) was purchased from Alfa Aesar Chemical Industries. Glucose, cellulose and starch were purchased from Sinopharm Chemical Reagent (China).

All the experiments were conducted in a batch reactor made from SUS 316. The reactor consisted of a piece of stainless steel 316 tubing (3/8 inch diameter, 1 mm wall thickness and 120 mm length) with an internal volume of 5.7 mL. Schematic drawings of the experimental set-up can be found elsewhere [19]. The reaction time was shorter than the apparent reaction time because the time required to increase the temperature of the reaction medium from room temperature to 300 °C was approximately 15 s. In this study, 0.1 mol/L lactic acid was used in all the experiments.

2.2. Procedure for the conversion of lactic acid to acetic acid with CuO

The desired amounts of lactic acid, CuO, NaOH and deionized water were placed in the batch reactor. Then, the reactor was placed horizontally in a salt bath that had been preheated to the desired temperature. In the salt bath, the reactor was shaken horizontally to enhance the mixture. After the desired reaction time, the reactor was transferred immediately from the salt bath into a cold water bath to quench the reaction. After the reaction, the liquid samples were collected and analyzed by HPLC.

2.3. Two-step process for the conversion of carbohydrate biomass to acetic acid

In the first-step reaction, various desired carbohydrate biomass, alkali and deionized water were added into the batch reactor. Sequentially, the reactor was placed horizontally in a salt bath that had been preheated to 300 °C. After 1 min, the reactor was transferred immediately from the salt bath into a cold water bath to quench the reaction. After the first-step reaction, CuO was added into the cooled reactor to start the second-step reaction in the same procedure as in the first-step. After 60 min, the reaction was quenched. The liquid samples were collected and analyzed by HPLC.

2.4. Analytical methods

After the reaction, the liquid samples were collected and analyzed using high performance liquid chromatography (HPLC, Agilent 1200LC). Formic acid, acetic acid and lactic acid were quantified using HPLC. The mobile phase used during the HPLC analyses was 2 mmol/L $HClO_4$ with a flow rate of 1 mL/min. The carbon balance was determined using a total organic carbon analyzer (TOC, Shimadzu, V-CPN).

Solid samples were also collected and analyzed using X-ray diffraction (XRD) with a Bruker D8 advance X-ray diffractometer equipped with Cu K_α radiation to determine their compositions and phase purities. The concentrations of metal ions in the solution were measured by inductively coupled plasma (ICP, Perkin Elmer, Optima 2100DV).

The purity of acetic acid was defined as the percentage of carbon in a liquid sample of acetic acid against the TOC of the liquid sample after the reaction. The yield of acetic acid was calculated using the following formula. The yield was obtained from three replicate experiments, and the relative error was less than ±5%.

$$\text{Yield (wt\%)} = \frac{\text{C in acetic acid (g)}}{\text{C in the initial substrates (g)}} \times 100\%$$

3. Results and discussion

3.1. Investigating the role of CuO for oxidizing lactic acid into acetic acid

Initially, the effect of CuO as an oxidant for the production of acetic acid from lactic acid was investigated at 300 °C for 5 min with and without NaOH and CuO. 300 °C and 5 min were selected because of optimum reaction conditions