Formation of Formic Acid from Glucose with Simultaneous Conversion of Ag₂O to Ag under Mild Hydrothermal Conditions

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ABSTRACT

Formation of formic acid from renewable biomass resources is of great interest since formic acid is a widely used platform chemical and has recently been regarded as an important liquid hydrogen carrier. Herein, a novel approach is reported for the conversion of glucose, the constituent carbohydrate from cellulose fraction of biomass, to formic acid under mild hydrothermal conditions with simultaneous reduction of Ag₂O to Ag. Results showed that glucose was selectively converted to formic acid with an optimum yield of 40.7% at a mild reaction temperature of 135 °C for 30 min. In addition, Ag₂O was used as a solid oxidant for the glucose oxidation, which avoids the use of traditionally dangerous liquid oxidant H₂O₂. Furthermore, complete conversion of Ag₂O to Ag can be achieved. This study not only developed a new method for value-added chemical production from renewable biomass but also explored an alternative low-carbon and energy-saving route for silver extraction and recovery.

Keywords: Biomass; Glucose oxidation; Formic acid; Solid oxidant; Hydrothermal reaction; Silver recovery
1. Introduction

Formic acid is an important chemical that is widely used in chemical, textile, leather, pharmaceutical, rubber, and other industries. Recent researches have demonstrated that formic acid can be used as a hydrogen storage material in the context of a future hydrogen economy. Current methods of formic acid production are mainly based on fossil resources with a negative impact on the environment. Developing alternative routes to directly produce formic acid from sustainable biomass or biomass-derived waste products is desirable from both ecological and economic perspectives. Various promising methods were proposed for the rapid conversion of biomass into high-value chemicals. Particularly, hydrothermal reaction is often used for biomass conversion since high-temperature water has unique properties as a reaction medium such as low dielectric constant, few and weak hydrogen bonds and high isothermal compressibility. However, in reported conversion routes of biomass to formic acid, $\text{H}_2\text{O}_2$, or $\text{O}_2$ were generally used as oxidants, and thus led to high energy costs due to the compressing gas or potential insecurity hazards. On the other hand, the poor selectivity of formic acid, high reaction temperature, or expensive and tedious preparation of noble-metal catalyst make these methods inappropriate for the synthesis of formic acid. For example, CuO was used in biomass conversion as a solid oxidant but only acetic acid was acquirable.
Recently, the cost of silver production increases rapidly with the decreasing natural silver resources, but silver has a huge demand for photography, radiography, electronics, photonics, catalysis, jewellery, silverware, dental material, medicines, and disinfectants in wastewater treatment\textsuperscript{33, 34}. Therefore, the market demand urgently requires the recovery of silver from silver-containing wastes through new cost-effective and environmentally friendly technologies\textsuperscript{35}. Many researchers studied the methods to recycle silver by chemical reduction, chemical replacement and ion exchange\textsuperscript{36-38}. However, these methods were short of economy and environmental friendliness due to the use of expensive resins or high energy input. Herein, we propose a new method for selective conversion of glucose into formic acid with easy separation by-product glycolic acid using Ag\textsubscript{2}O as a solid oxidant and a simultaneous transformation of Ag\textsubscript{2}O into Ag under mild hydrothermal conditions. Results show that glucose was selectively converted to formic acid with an optimum yield of 40.7\% and glycolic acid yield of 10\% at a mild reaction temperature of 135 °C for 30 min. The proposed method is not only a promising way for conversion of biomass into value-added chemicals but also an effective and green route for silver extraction.

2. Material and methods

2.1 Materials
In this research, glucose (99.9%), formic acid (98%), glycolic acid (98%), methanol (99.5%) and xylose (99.9%) were purchased from Sino-pharm Chemical Regent Co., Ltd. Sodium hydroxide (96%), acetic acid (99.5%) and lactic acid (85%) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Gluconic acid (49–53 wt% in water) was purchased from Sun Chemical Technology (Shanghai) Co., Ltd. Sorbitol (98%) was purchased from Innochem (Beijing) Technology Co., Ltd. Glycolaldehyde dimer was offered by Aladdin Reagent Company. Sodium oxalic (99.8%) and Pyruvaldehyde (40% w/w aq. solution) was purchased from Shanghai Titan Scientific Co., Ltd. Glyceraldehyde (85%) was obtained from Bide pharmatech Ltd. 1,3-dihydroxyacetone (98%) was provided by J&K Scientific Ltd. Ag₂O (99.7%, Macklin Biochemical Co., Ltd) was chose as the model compound of Ag(I) in basic solution, because Ag(I) ion could form AgOH and then generate Ag₂O at a high pH condition (pH > 11). The stoichiometric demand for complete oxidation of glucose to formic acid was defined as a 100% Ag₂O supply according to Eq. (1).

\[ C_{6}H_{12}O_{6} + 6Ag_{2}O \rightarrow 6HCOOH + 12Ag \] (1)

2.2 Conversion of Glucose

The conversion of glucose was conducted in a Teflon-lined stainless-steel batch reactor with an inner volume of 25 mL. In a typical procedure, desired amount of glucose, Ag₂O and 6.25 mL NaOH solution were first loaded into the reactor. Then the reactor was sealed and put into an isothermal oven
preheated to 135 °C for 30 minutes. After the desired reaction time, the reactor was taken out from the oven and cooled to room temperature.

2.3 Analytical Methods

After the reaction, liquid samples were filtered through a 0.22 μm membrane filter and analysed by an Agilent 1200 high-performance liquid chromatography (HPLC), which equipped with two KC-811 columns, a differential refractometer detector and a tunable ultraviolet/visible absorbance detector. A 2 mmol/L HClO₄ aqueous solution with a flow rate of 1.0 ml/min was used as the mobile phase of HPLC. Solid samples were washed with deionized water and then dried in a vacuum oven at 40 °C for 6 h. X-ray diffraction (XRD) patterns of the solid samples were collected by a Shimadzu 6100 X-ray diffractometer equipped with Cu Kα radiation at a scan rate of 2 °/min and with a 2θ ranging from 10° to 80°.

The conversion X and yield Y of products were defined based on the following equations:

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

\[
Y = \frac{\text{moles of carbon in product molecule}}{\text{moles of carbon in feedstock input}} \times 100%
\]

3. Results and discussions

3.1 Characteristics of Ag₂O/Ag with hydrothermal conversion of glucose to formic acid
A series of experiments with glucose and Ag$_2$O as reactants were carried out under mild hydrothermal conditions to investigate whether glucose could be selectively converted to formic acid. As shown in Figure 1, only lactic acid was detected from the liquid sample by HPLC analysis when glucose was reacted without Ag$_2$O under the basic hydrothermal condition. However, when Ag$_2$O was added, the product of formic acid was clearly increased and the formation of glycolic acid was also detected. The previous study has revealed that a relatively high yield of lactic acid can be obtained from the hydrothermal conversion of glucose under alkaline conditions. Notably, as show in Figure 1, the amount of lactic acid in the presence of Ag$_2$O was much less than that without Ag$_2$O, which suggested that glucose was selectively converted into formic acid through reacting with Ag$_2$O under mild hydrothermal conditions.

Figure 1. HPLC chromatography of liquid samples after reactions (a) with and (b) without 10 mmol Ag$_2$O (1 mmol glucose, 1 mol/L NaOH with 6.25 mL, 180 °C, 2 h).
To investigate the reduction of Ag$_2$O, solid samples were analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) methods. Figure 2 shows the XRD patterns of the Ag$_2$O before the reaction and solid products after the reaction. No Ag peak appeared in the solid sample before reaction (Figure 2a). However, four diffraction peaks were observed at 38.20°, 44.40°, 64.60° and 77.60°, respectively, which were indexed as the (111), (200), (220) and (311) orientations of cubic Ag (Figure 2b). These results indicated that the Ag$_2$O was converted into Ag after the reaction. Furthermore, the SEM image shows that the obtained Ag particle has a diameter of 0.1 – 0.3 μm (Figure 3).

Figure 2. XRD patterns of (a) Ag$_2$O before the reaction and (b) solid products after the reaction at 180 °C for 2 h (1 mmol glucose, 4 mmol Ag$_2$O, 1 mol/L NaOH)
Figure. 3 SEM image of the silver obtained after reaction (4 mmol Ag$_2$O, 1 mmol glucose, 135\(^\circ\)C, 2 h, 1 mol/L NaOH with 6.25 mL)

3.2 Investigating the influences of reaction conditions on yields of formic acid

Next, the relationship between reaction conditions and yields of formic acid from glucose were further investigated. Above all, the influence of reaction temperature was examined by varying the temperature from 105 to 210 \(^\circ\)C. As shown in Figure 4a, formic acid was identified as the major product. When the temperature increased from 105 to 135 \(^\circ\)C, the yield of formic acid increased from 22.9% to 29.1%. However, a further increase of the temperature led to slight decrease in the formic acid yield. For the production of glycolic acid, similar trend was observed. However, when the temperature increased to 210 \(^\circ\)C, lactic acid was detected at the cost of the yields of glycolic acid and formic acid. The change in the product yield and selectivity suggested that the temperature could affect the cleavage patterns of glucose and alter the reaction pathway. Furthermore, there was no glucose detected in the liquid phase after the reaction at all tested temperatures, which showed that glucose was
completely decomposed. Figure 4b shows the influence of reaction time on yields of different products and conversion of glucose in the hydrothermal oxidation of glucose to formic acid. In the first 30 min, the yield of formic acid dramatically increased to 29.7%, however, a slow decrease in the formic acid yield was observed when the reaction time prolonged to 240 min. Similar trends were observed for the glycolic acid yield. The decrease in the yields of formic acid and glycolic acid with a long reaction time is probably caused by the decomposition of the formed products under hydrothermal conditions.

The influence of the concentration of NaOH on the oxidation of glucose was also investigated. A sharp rise in glucose conversion was noted from 57.4% to 100% when NaOH concentration increased from 0 to 1 M (Figure 4c). This is probably because NaOH solution with higher concentration accelerated glucose conversion, which has been studied in detail in previous research. The yield of formic acid was less than 2% in the absence of NaOH. However, formic acid yield ascended simultaneously with increasing NaOH concentration and reached 34% at 0.75 M NaOH. The previous research has demonstrated that a certain amount of alkali could convert the formic acid to formate, which is more stable than formic acid under hydrothermal conditions. Thus, the addition of alkali could prevent the produced formic acid from being decomposed that resulted in the higher yield. However, further increasing the NaOH concentration exceeding 0.75 M got a decrease in the formic acid yield,
which is probably because the reaction pathway of glucose conversion was negatively affected by additional NaOH.

The effect of Ag₂O amount was examined (Figure 4d). The yield of formic acid first quickly increased from 1.1% to 33.1% when the Ag₂O addition increased from 0 to 116.7% relative to glucose, and then slowly ascended to 40.7% when the Ag₂O supply further increased to 266.7%. In addition, lactic acid with a yield of 44% without any formation of formic acid was observed in the absence of the oxidant. This result was similar with other literatures that glucose was dominantly isomerized into fructose and then cleaved into lactic acid via retro-aldol condensation under alkaline condition ²³, ³⁰. The above results indicated that the Ag₂O oxidant was advantageous for the oxidation of glucose to formic acid, and increasing the amount of Ag₂O had a positive effect on the formic acid yield.
Figure 4. Effect of (a) reaction temperature (7 mmol Ag$_2$O, 1 mol/L NaOH with 6.25 mL, 120 min), (b) reaction time (7 mmol Ag$_2$O, 1 mol/L NaOH with 6.25 mL, 135 °C), (c) NaOH concentration (7mmol Ag$_2$O, 135 °C, 30 min, 6.25 mL NaOH solution) and (d) amount of Ag$_2$O (0.75 mol/L NaOH 6.25 mL, 135 °C, 30 min) on yields of different products and conversion of glucose in the hydrothermal oxidation of glucose to formic acid (1 mmol glucose was used for all cases).

3.3 Investigating the oxidation pathways of glucose to formic acid

Oxidation pathways of glucose to formic acid were then investigated. Based on the previous research, glucose was probably first oxidized to gluconic acid under basic hydrothermal conditions, which was further converted to formic acid through a series of reactions. Thus, gluconic acid was first chosen as the starting material instead of glucose for the hydrothermal formic acid production. Results revealed that gluconic acid was completely converted and a formic acid
yield of 34.4% (Table 1, Entry 1), which is close to that obtained from glucose directly. This result indicates that the gluconic acid was a crucial intermediate for formic acid generation. Other organic acids, such as oxalic acid, glycolic acid, acetic acid and lactic acid, could be hardly converted under such hydrothermal condition (Table 1, Entries 2-5), which inferred that these organic acids were unlikely the intermediates for formic acid production. Meanwhile, methanol and sorbitol were completely converted but without any production of formic acid (Table 1, Entries 6 and 7), which suggested that these alcohols were unlikely the intermediates for formic acid production although they were more reactive than organic acids under hydrothermal condition.

Aldehyde/ketone species such as glycolaldehyde, pyruvaldehyde, glyceraldehyde and 1,3-dihydroxyacetone displayed high reaction activity under hydrothermal conditions and they were all had a 100% conversion (Table 1, Entries 8-11). Glycolaldehyde afforded formic acid and glycolic acid as the major products with yields of 24.1% and 16.5%, respectively, which indicated that the glycolaldehyde was likely an intermediate for formic acid generation. Formic acid yields obtained with pyruvaldehyde and glyceraldehyde were 3.2% and 1.1%, respectively. Especially, the major products of pyruvaldehyde were lactic acid and acetic acid with the yields of 53.6% and 21.4%, respectively. Hence, these two aldehydes were unlikely the
key intermediates for formic acid production. When 1,3-dihydroxyacetone was engaged as the substrate, glycolic acid was identified as the major product with formic acid, lactic acid and acetic acid as side products. Thus, the 1,3-dihydroxyacetone was unlikely the key intermediates for formic acid production. Furthermore, xylose was tested and displayed high activity to produce formic acid (Table 1, Entry 12), which indicated that xylose might be a key intermediate for formic acid production.

Table 1. Oxidation of different model compounds with Ag$_2$O under hydrothermal conditions$^a$

| Entry | Substrate | Conversion % | Formic acid % | Acetic acid % | Lactic acid % | Glycolic acid % |
|-------|-----------|--------------|---------------|--------------|--------------|----------------|
| 1     | Gluconic acid | 100          | 34.4          | 0            | 0            | 2.4            |
| 2     | Sodium oxalate | 0           | 0             | 0            | 0            | 0              |
| 3     | Glycolic acid | 0            | 0             | 0            | 0            | 100            |
| 4     | Acetic acid | 0            | 0             | 100          | 0            | 0              |
| 5     | Lactic acid | 3.3          | 0             | 0            | 96.7         | 0              |
| 6     | Methanol   | 100          | 0             | 0            | 0            | 0              |
| 7     | Sorbitol   | 100          | 0             | 0            | 0            | 0              |
| 8     | Glycolaldehyde (dimer) | 100   | 24.1          | 0            | 0            | 16.5           |
| 9     | Pyruvaldehyde | 100         | 3.2           | 21.4         | 53.6         | 0              |
| 10    | Glyceraldehyde | 100        | 1.1           | 0            | 2.2          | 2.8            |
| 11    | 1,3-dihydroxyacetone | 100   | 24.7          | 7.1          | 14.6         | 47.4           |
| 12    | Xylose     | 100          | 30.9          | 0.4          | 0            | 7.5            |

$^a$Reaction conditions: 0.5 mmol substrate, 0.75 mol/L NaOH, 100% Ag$_2$O, 135 °C, 30 min.

Based on the tested results, Scheme 1 shows the proposed reaction pathway for glucose conversion into formic acid with the oxidation of Ag$_2$O under mild conditions.
hydrothermal conditions. Glucose first transforms into its open-chain form, and
the aldehyde group is oxidized by Ag$_2$O and then gives the gluconic acid.
Subsequently, formic acid and xylose are formed by the breakage of C1-C2
bond of gluconic acid. Finally, xylose transforms into formaldehyde and
glycolaldehyde that are further oxidized into formic acid and glycolic acid,
respectively.

Scheme 1. Proposed reaction pathway of the oxidation of glucose into formic acid.

4. Conclusions

We developed a new method of one-step conversion of glucose into formic acid
with a simultaneous reduction of Ag$_2$O to Ag under mild hydrothermal conditions. At
optimum reaction conditions, a 40.7% yield of formic acid from glucose and a 100%
conversion of Ag$_2$O to Ag were obtained. This study not only developed a new way
for value-added chemical production from renewable biomass resource but also
proposed an alternative low-carbon and energy-saving route for silver extraction and
recovery.

Conflicts of interest
There are no conflicts to declare.

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