

Article

Production of Acrylic Acid from Biomass-Derived Fumaric Acid under Hydrothermal Conditions

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Abstract: Production of energy and chemicals from biomass resources has been regarded as one promising method to address the challenge of global warming. In this research, production of acrylic acid from fumaric acid, one of the biomass-derived building blocks, is proposed. CuO was employed as a solid oxidant, which showed excellent activity and selectivity for the production of acrylic acid, and water played an essential role in acting as not only a solvent but also a catalyst in this process. An optimum acrylic acid yield of 76.4% was successfully obtained after the reaction of fumaric acid with CuO at 300 °C for only 60 s. This research provides a green and highly efficient way to produce value-added chemicals from biomass-derived building blocks, and thus is promising for practical application.

Keywords: acrylic acid; fumaric acid; biomass resource; biomass-derived chemical; hydrothermal reaction



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1. Introduction

To produce energy and chemicals from sustainable biomass is of vital importance for avoiding CO₂ emissions and global warming [1]. Acrylic acid (AA) is an essential chemical with broad applications in polymers and plastics [2–4]. Currently, acrylic acid is produced mainly from petroleum-derived products [5–7]. However, the objective of minimizing the environmental impact throughout products' lifecycles is motivating the production of chemicals, including acrylic acid from renewable sources, such as biomass or biomass-derived building blocks [3,8]. Recently, various methods of acrylic acid production from biomass-derived products have been developed. A typical example is the production of acrylic acid from sugar via fermentation. In addition, different processes as well as biomass-derived feedstocks were employed to improve efficiency in acrylic acid production research [9–13].

Hydrothermal reactions have demonstrated many advantages in biomass conversion reactions, such as quick reaction rate and compatibility, producing a wide range of renewable chemicals [14–16]. Compared to ambient liquid water, the high-temperature water (HTW) has higher ionic product (K_w), weaker hydrogen bonds, and other unique properties, which makes the HTW act as not only an environment-friendly solvent but also acid/basic catalysts in reactions [17]. Previous research has successfully demonstrated that lactic acid could be oxidized to acrylic acid under hydrothermal conditions [10].

Fumaric acid is not only a natural carboxylic acid, being isolated from the plant *Fumaria officinalis* for the first time, but also a sugar-derived chemical listed in the top twelve biomass-derived building blocks reported by the US Department of Energy [18,19]. Owing to its diversity, the worldwide demand for fumaric acid was estimated to be over 300 kt in

2020 [20]. Fortunately, various studies have been carried out to develop new methods, such as microbial fermentation, to enhance fumaric acid production and sustainability. Usually, a mixture of carboxylic acids and sugars are obtained in fermentation broth when fumaric acid is produced by fermentation [21]. The traditional downstream process of fumaric is composed of a rather complex sequence of steps involving acidification, heating, filtration, and drying [22,23]. If the fermentation broth can be used directly to produce acrylic acid, it will reduce the high operational costs. However, not only can glucose in the fermentation broth react with CuO to produce complex carboxylic acids, but carboxylic acids can also react with CuO [24,25]. Therefore, fairly high-purity fumaric acid is used in this study. Recently, many works have demonstrated that lignin models could also be oxidized into fumaric acid under hydrothermal conditions [26–30]. As a building block, fumaric acid has been widely studied [31]. It was reported that maleic and fumaric acid can degrade to acrylic [32,33]. Our previous studies showed that lignin model compounds can be oxidized to fumaric more than maleic acid under hydrothermal conditions [28].

In this paper, the potential of fumaric acid as a feedstock for the production of acrylic acid under hydrothermal conditions is studied. CuO is employed as an oxidant due to it being more affordable than synthetic H₂O₂ and more convenient than gaseous O₂.

2. Material and Methods

2.1. Materials

Fumaric acid (99%), acrylic acid (98%), NaOH (96%), and CuO (99%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Malic acid (99%) was purchased from Wako Pure Chemicals Industries Co., Ltd. (Tokyo, Japan).

2.2. Experimental Procedure

All experiments were conducted in a tubular reactor made of a SUS-316 stainless-steel tube (3/8 inches, 1 mm wall thickness, and 120 mm long) with two end fittings, providing an inner volume of 5.7 mL. A typical experimental procedure is as follows: A desired amount of fumaric acid, CuO, and 2 mL of deionized water were loaded into the tubular reactor, with a water filling of approximately 35%. Then, the reactor was purged with nitrogen gas to replace the remaining air. Subsequently, the reactor was sealed and immersed into a salt bath which had been preheated to the desired reaction temperature. During the reaction, the reactor was shaken automatically to improve mass transfer. After the desired reaction time, the reactor was removed from the salt bath and immediately cooled with cold water to room temperature. Details of this method are described in our previous reports [34–36]. The reaction time was defined as the time that the reactor was kept in the salt bath. The actual reaction time is shorter than the defined reaction time because it will require approximately 15 s for reactants to rise from 20 to 300 °C [37,38]. The reaction pressure is about 9 MPa. All experiments were performed at 300 °C because it was the optimum reaction temperature according to our previous research [27].

2.3. Product Analysis

After the reaction, liquid samples were collected, diluted, and analyzed using a high-performance liquid chromatograph (HPLC, Agilent 1200, Agilent Technologies Co., Ltd., Santa Clara, CA, USA), equipped with two RspakKC-811 (SHODEX) columns, a tunable absorbance detector (UV/vis detector), and a differential refractometer (RI detector). A gas chromatograph (GC-FID, Agilent 6890N, Agilent Technologies Co., Ltd., Santa Clara, CA, USA) equipped with an HP-INNOWAX capillary column (30 m × 0.53 mm ID) was also used for the liquid sample analysis. The temperature program of the GC system was initially set at 50 °C for 2 min and was increased at a rate of 7 °C/min to 230 °C, and held for 5 min. Peak identification was accomplished by comparison of sample peak retention times with those of standard solutions of pure compounds. Quantitative estimations of carboxylic acids reported in this study were based on the average value of the analytical results of at least three samples, with the relative errors always less than 5% for all experiments.

Aqueous products were also prepared for total organic carbon (TOC) analysis. For TOC analysis, the aqueous phase after reaction was filtered through a 0.22 μm syringe filter then diluted with water. TOC was measured by a Shimadzu total organic carbon analyzer (model TOC-VCSH, Shimadzu, Corp., Kyoto, Japan). The TC standard was prepared by reagent-grade potassium hydrogen phthalate, and the IC standard was prepared by reagent-grade sodium bicarbonate and sodium carbonate.

Gas samples were analyzed by a Hewlett-Packard model 5890 Series II Plus gas chromatograph (GC-TCD, Agilent Technologies Co., Ltd., Santa Clara, CA, USA). Solid samples were examined by a Bruker D8 Advance X-ray diffractometer (XRD, Bruker Co., Ltd., Karlsruhe, Germany).

2.4. Definition

In this study, the product yield and the TOC yield (total organic carbon yield) are calculated using the following equations:

$$\text{Product yield} = \frac{\text{mole of product}}{\text{mole of feedstock}} 100\% \quad (1)$$

$$\text{TOC yield} = \frac{\text{total carbon weight of organic products in aqueous solution}}{\text{carbon weight of feedstock}} 100\% \quad (2)$$

3. Results and Discussion

3.1. Effects of Different Copper Oxides on the Yield of Acrylic Acid

In our previous works, copper oxides (CuO and Cu_2O) were used as excellent oxidants for the synthesis of carboxylic acids from glucose or cellulose under hydrothermal conditions [25,39]. To examine whether copper oxides can be effective in the oxidation of fumaric acid into acrylic acid, experiments of fumaric acid reacting in the presence and absence of copper oxides (CuO and Cu_2O) were conducted at 300 $^\circ\text{C}$ for 60 s. From the HPLC-VWD analysis of the aqueous products (Figure 1), acrylic acid was formed when copper oxides were added. The yields of acrylic were 8.2% and 15.2% in the presence of Cu_2O and CuO , respectively (Supplementary Figure S1). These results suggest that copper oxides had a clear promotion effect on the production of acrylic acid from fumaric acid, and the effect of CuO was better compared with Cu_2O . Consequently, CuO was used in the following studies. Aqueous products after the reaction of fumaric acid with CuO were also analyzed by HPLC-RID and GC-FID to further investigate other possible products. HPLC-RID analysis results revealed that malic and formic acids were also produced as well as the maleic and acrylic acids (Supplementary Figure S2). However, only a strong peak of acrylic acid was shown in the spectrum of GC-FID analysis, which means acrylic acid has a strong and clear response with GC-FID analysis. Thus, quantification of acrylic acid was performed by GC-FID in this research.

Solid products after the reaction of fumaric acid with CuO were subjected to XRD analysis, and the result is depicted in Supplementary Figure S3. Peaks of both CuO and Cu_2O were observed in the solid product, indicating that CuO acted as an oxidant and was reduced to Cu_2O during the reaction. In addition, some other peaks belonging to neither CuO nor Cu_2O were probably attributed to the copper fumarate.

3.2. Reaction Characteristics and Optimization of the Acrylic Acid Yield

To optimize the yield of acrylic acid, fumaric acid was converted at different process conditions, including reaction time, NaOH concentration, and CuO amount. As shown in Figure 2, the conversion of fumaric acid and the acrylic acid yield increased quickly with the reaction time in 90 s, and then slowed down. The yield of acrylic acid ascended sharply from 27.0% to 37.9% from 60 to 90 s, then reached 51.4% when the reaction time extended to 300 s. The conversion of fumaric acid increased from 83.2% to 93.1% from 60 to 120 s, and then reached 97.3% as the reaction time extended to 300 s. These results suggest that

the oxidation of fumaric acid with CuO was rather effective and a reaction time of no more than 90 s could obtain a relatively high efficiency of acrylic acid production.

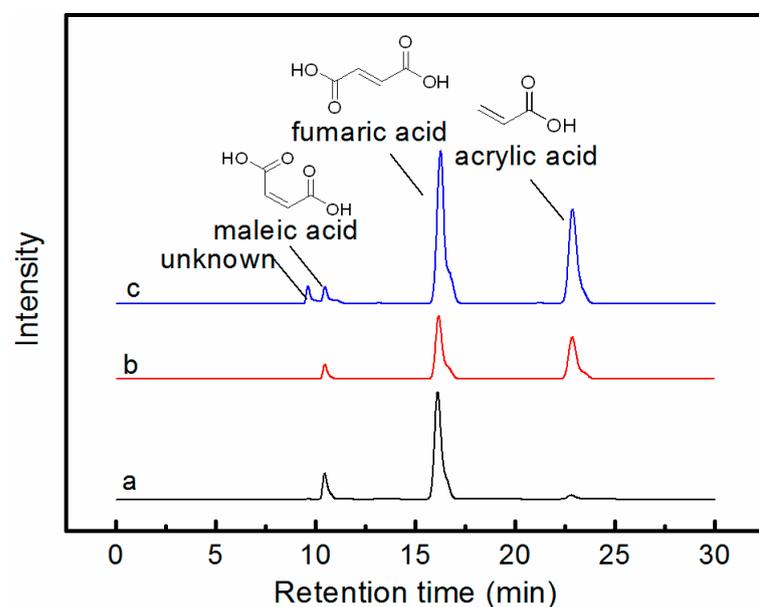


Figure 1. HPLC-VWD chromatograms of aqueous products after the reaction of fumaric acid without copper oxides (a), with 3.2 mmol of Cu_2O (b), or with 3.2 mmol of CuO (c) (reaction conditions: 1.0 mmol of fumaric acid, 2 mL of H_2O , 300 °C, 120 s).

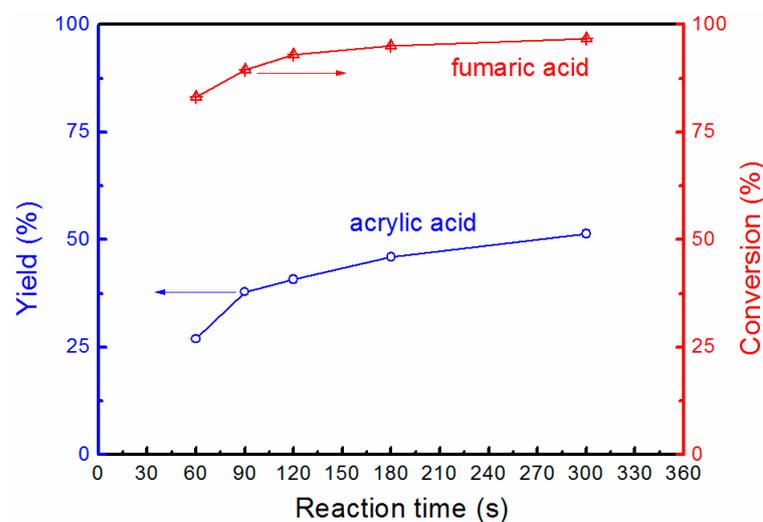


Figure 2. Yield of acrylic acid and conversion rate of fumaric acid obtained at different reaction times (reaction conditions: 1.0 mmol of fumaric acid, 2 mL of H_2O , 3.2 mmol of CuO, 300 °C).

Moreover, our previous studies have demonstrated that alkali has a significant influence on the conversion of carbon hydrate biomass to carboxylic acids under hydrothermal conditions [27,35]. Thus, the effect of alkali on the acrylic yield from fumaric acid was investigated. As illustrated in Figure 3, when NaOH was added to the reaction to increase the alkalinity of the solution, both the conversion rate of fumaric acid and the yield of acrylic acid declined significantly. The conversion rate of fumaric acid and the yield of acrylic acid dropped to 54.0% and 4.2% respectively, when 1 mol/L of NaOH was added. Although the conversion rate of fumaric acid had a slight increase when the NaOH concentration further increased beyond 1.0 mol/L, the yield of acrylic acid kept decreasing. As a result, the conversion rate of fumaric acid and the yield of acrylic acid decreased with the

addition of NaOH. The results indicate that a low NaOH concentration can prevent the decomposition of fumaric and acrylic acid, while a high NaOH concentration can cause further degradation of fumaric and acrylic acids, resulting in an increase of the conversion of fumaric acid and a decrease of the yield of acrylic acid. Similar results were obtained in our previous studies [25,28,40]. The reason may probably be attributed to the fact that the addition of NaOH led to a conversion of fumaric acid to sodium fumarate, which is more difficult to be oxidized by CuO. As alkali had an adverse effect on the acrylic acid yield, no alkali was used in the following studies.

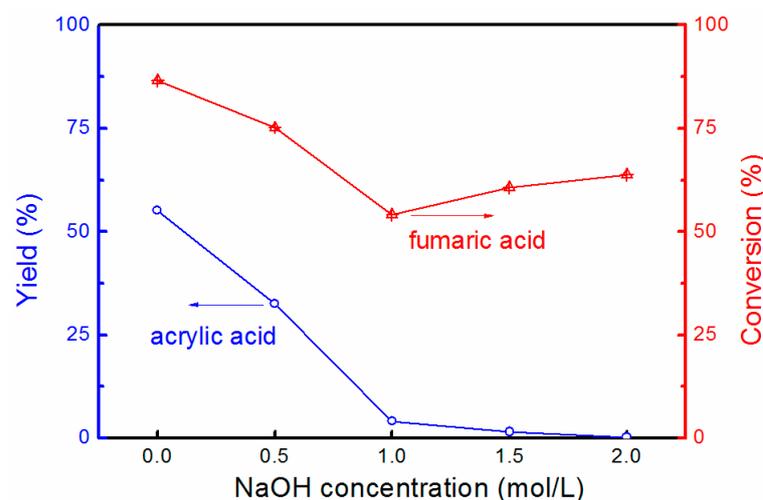


Figure 3. Effect of NaOH concentration on the yield of acrylic acid and the conversion rate of fumaric acid (reaction conditions: 1.0 mmol of fumaric acid, 0.6 mmol of CuO, 2 mL of H₂O, 300 °C, 120 s).

Furthermore, the effect of CuO amount on the conversion rate of fumaric acid and the yield of acrylic acid was studied. As depicted in Figure 4, the conversion rate of fumaric acid gradually increased from 84.6% to 92.7% when the CuO amount increased from 0.3 to 4.5 mmol. However, the yield of acrylic acid increased greatly when the CuO amount increased from 0.3 to 0.6 mmol, and then decreased gradually with the CuO amount increasing to 4.5 mmol. The highest yield of acrylic acid reached 76.4% with 0.6 mmol of CuO. As the conversion of fumaric acid increased with the CuO amount, the decrease in the yield of acrylic acid suggests that other side reactions must have occurred in the presence of large amounts of CuO. Thus, TOC analysis of the liquid sample after the reaction was performed accordingly. Results showed that the TOC yield of organic carbons decreased dramatically with the increasing amount of CuO (Supplementary Figure S4), suggesting that extra CuO promoted the further oxidation of produced carboxylic acids to CO₂. To further confirm the oxidation of acrylic acid by CuO, a reaction of acrylic acid with CuO was conducted. Within 60 and 180 s, the acrylic acid decomposed by 14.5% and 32.6%, respectively (Supplementary Figure S5). These results evidenced that acrylic acid was prone to decompose by CuO under hydrothermal conditions. In addition, overloaded CuO may react with fumaric acid to generate fumarate sediment, as minor fumarate was detected in solid residues (Supplementary Figure S3). Thus, a relatively small amount of CuO as well as a short reaction time is preferred to obtain a high yield of acrylic acid.

3.3. Possible Reaction Pathways of the Fumaric Acid Oxidation to Acrylic Acid

As shown in Supplementary Figure S2, malic acid, maleic acid, and formic acid were generated as well as acrylic acid after the reaction of fumaric acid with CuO. To reveal the reaction pathway of acrylic acid production from fumaric acid, the conversion of these products was traced. However, the yields of maleic and formic acid were less than 1.0% in all reactions in this research. Thus, only the yields of fumaric, malic, and acrylic acid were considered, and the results are shown in Figure 5.

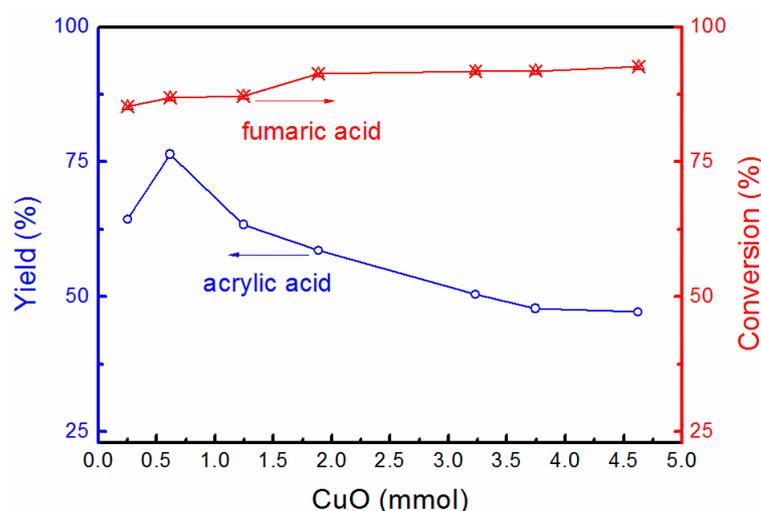


Figure 4. Effect of CuO amount on the yield of acrylic acid and the conversion rate of fumaric acid (reaction conditions: 1.0 mmol of fumaric acid, 2 mL of H₂O, 300 °C, 60 s).

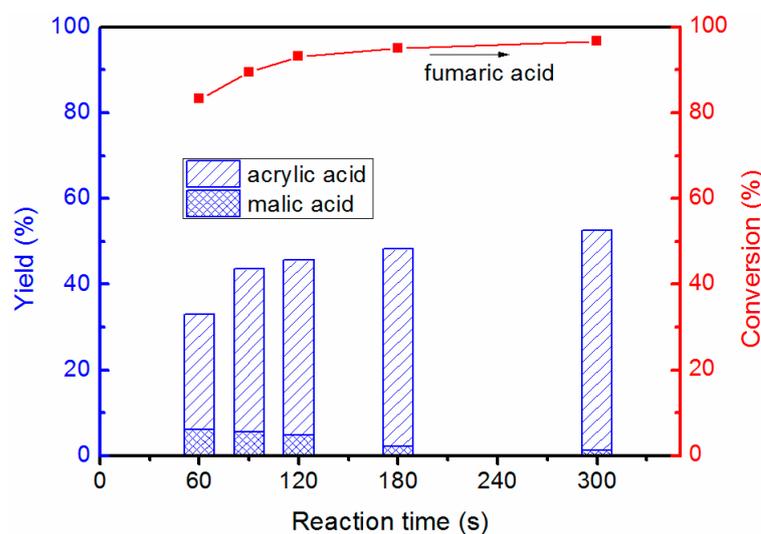
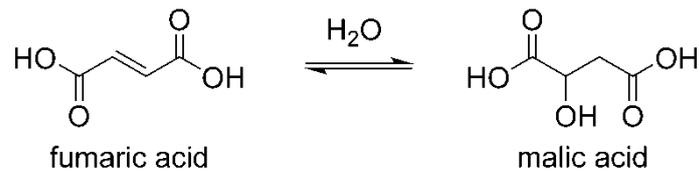


Figure 5. Yield of major products and conversion rate of fumaric acid obtained at different reaction times (reaction conditions: 1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of H₂O, 300 °C).

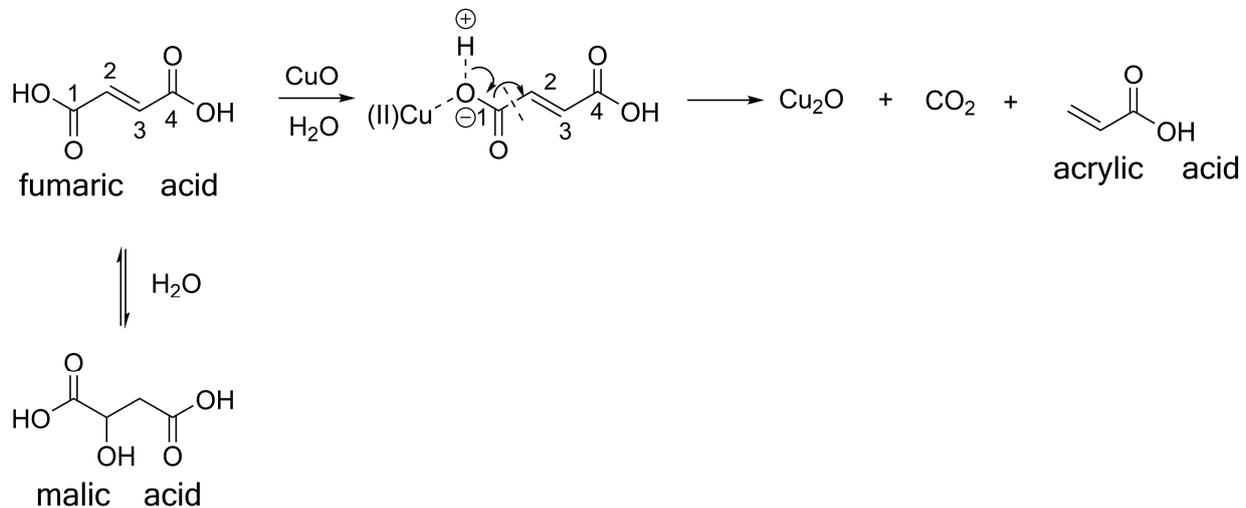
As malic acid was detected as a major product, except for acrylic acid, in the aqueous products and decreased with the increase of the yield of acrylic acid (Figure 5), malic acid was probably a by-product of the fumaric acid. The experiment of fumaric acid under hydrothermal conditions at 300 °C for 60 s without CuO showed that the major product was malic acid (yield of 11.3%), while only trace amounts of acrylic acid (yield of 1.4%) were detected. Interestingly, when malic acid was reacted under the same hydrothermal conditions without CuO for 60 s, fumaric acid was generated with a yield of 12.0%. Then, the reaction of malic acid with CuO was studied, and the results showed that not only fumaric acid, but also acrylic acid was produced (Supplementary Figure S6). However, the yield of acrylic acid obtained with malic acid was much lower than that obtained with fumaric acid. These results suggest that the conversion of fumaric acid to malic acid is reversible under hydrothermal conditions (Scheme 1), and it was reported that the hydration of fumarate and the dehydration of malate reactions are both first-order reactions [41].



Scheme 1. Reversible conversion of fumaric acid to malic acid.

To further understand the role of water in the production of acrylic acid, experiments of 1.0 mmol of fumaric acid or malic acid reacting with 0.6 mmol of CuO in 2 mL of anhydrous diethyl ether were conducted. Results showed that no acrylic acid was obtained in either case, indicating that H₂O plays as an essential role in the conversion of fumaric acid to acrylic acid. Interestingly, in the reaction of 1.0 mmol of malic acid with 0.6 mmol of CuO in 2 mL of anhydrous diethyl ether at 300 °C for 60 s, fumaric acid was produced. This result suggests that the fumaric acid is probably produced from the dehydration of malic acid in the absence of water.

Based on these results, a possible reaction pathway of the production of acrylic acid from the oxidation of fumaric acid with CuO under a hydrothermal condition is proposed in Scheme 2. Fumaric acid is prone to ionize in the presence of water. When fumaric acid is oxidized by CuO, Cu(II) bonds to the oxygen atom of the hydroxyl group, which linked to C₁, resulting in the π-bond between C₂ and C₃ showing a negative valence, and the H of the hydroxyl group will transfer to the π-bond. Cu(II) is prone to take the electron away to produce Cu₂O or Cu [29,42]. In this research, Cu(II) took the electron away, producing Cu₂O, and led to the formation of a double bond between O of the hydroxyl group and C₁, as well as a cleavage of the bond between C₁ and C₂, producing acrylic acid and CO₂. During the reaction, fumaric acid can also react with water to produce malic acid, which is a side reaction.



Scheme 2. The possible reaction mechanism of acrylic acid production.

4. Conclusions

In summary, acrylic acid was successfully produced from fumaric acid, a renewable feedstock, with CuO as an oxidant under a hydrothermal condition. CuO exhibited excellent activity and selectivity in the conversion of fumaric acid to acrylic acid, and a yield of 76.4% was obtained. The reaction mechanism of hydrothermal conversion of fumaric acid into acrylic acid showed that CuO can oxidize fumaric acid in aqueous solution to CO₂ and acrylic acid, by reducing to Cu₂O. This research is meaningful to facilitate studies for developing green and sustainable processes to produce value-added acrylic acid from renewable fumaric acid.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/en14175456/s1>, Figure S1: Yields of acrylic acid obtained with different additives (reaction conditions: 1.0 mmol of fumaric acid, 2.5 mmol of CuO or Cu₂O, 2 mL of H₂O, 300 °C, 60 s), Figure S2: HPLC-RID chromatogram (A) and GC-FID chromatogram (B) of aqueous products after the reaction (1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of H₂O, 300 °C, 120 s), Figure S3: XRD pattern of the solid product after the reaction of fumaric acid with CuO (reaction conditions: 1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of H₂O, 300 °C, 120 s), Figure S4: TOC yield of carboxylic acids after the reaction of fumaric acid with different amount of CuO (reaction conditions: 1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of H₂O, 300 °C, 120 s), Figure S5: Acrylic decomposition with CuO at different time (1.0 mmol of acrylic acid, 0.6 mmol of CuO, 2 mL of H₂O, 300 °C), Figure S6: Aqueous products obtained after the reaction of malic with CuO at different time (1.0 mmol of malic acid, 0.6 mmol of CuO, 2 mL of H₂O, 300 °C).

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