

## Supplementary Material

### Production of acrylic acid from biomass-based fumaric acid under hydrothermal conditions

Guodong Yin<sup>a,1</sup>, Heng Zhong<sup>b,1</sup>, Guodong Yao<sup>a</sup>, Xu Zeng<sup>a</sup>, Fangming Jin<sup>b,c,\*</sup>

*<sup>a</sup>State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China.*

*<sup>b</sup>School of Environmental Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan RD, Shanghai 200240, China.*

*<sup>c</sup>Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China.*

\* Corresponding author: Fangming Jin

E-mail address: fmjin@sjtu.edu.cn;

Tel/Fax: +86-21-54742283

## 1. Experimental Section

### 1.1 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).

### 1.2 Experimental procedure

All experiments were conducted in a tubular reactor made of a SUS-316 stainless steel tube (3/8 inch, 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 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 remained air. Subsequently, the reactor was sealed and immersed into a salt bath that 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. (Jin et al., 2007; Jin et al., 2005; Shen et al., 2011) The reaction time was defined as the time that the reactor was kept in the salt bath. All experiments were performed at 300 °C because it was the optimum reaction temperature according to our previous research. (Jin and Enomoto, 2011)

### 1.3 Product analysis

After the reaction, liquid samples were collected, diluted and analyzed using a high-performance liquid chromatography (HPLC, Agilent 1200, Agilent Technologies Co., Ltd., USA) equipped with two RspakKC-811 (SHODEX) columns, a tunable absorbance detector (UV/vis detector) and a differential refractometer (RI detector). A gas chromatography (GC-FID, Agilent 6890N, Agilent Technologies Co., Ltd., 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 estimation 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. Japan). The TC standard was prepared by reagent grade potassium hydrogen phthalate, the IC standard was prepared by reagent grade sodium bicarbonate and sodium carbonate.

Gas samples were analyzed by a Hewlett-Packard model 5890 SeriesII Plus gas chromatograph (GC-TCD, Agilent Technologies Co., Ltd., USA). Solid samples were

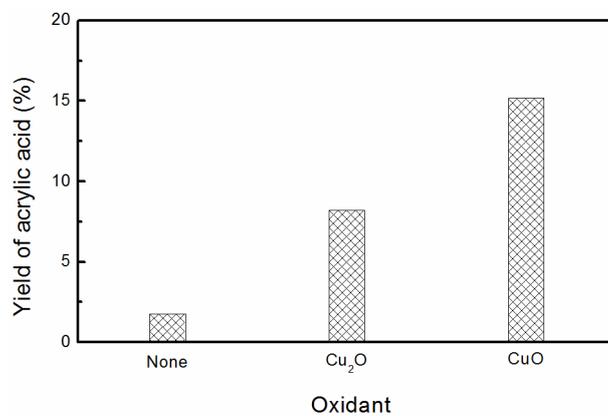
examined by a Bruker D8 Advance X-ray Diffractometer (XRD, Bruker Co., Ltd., Germany).

#### 1.4 Definition

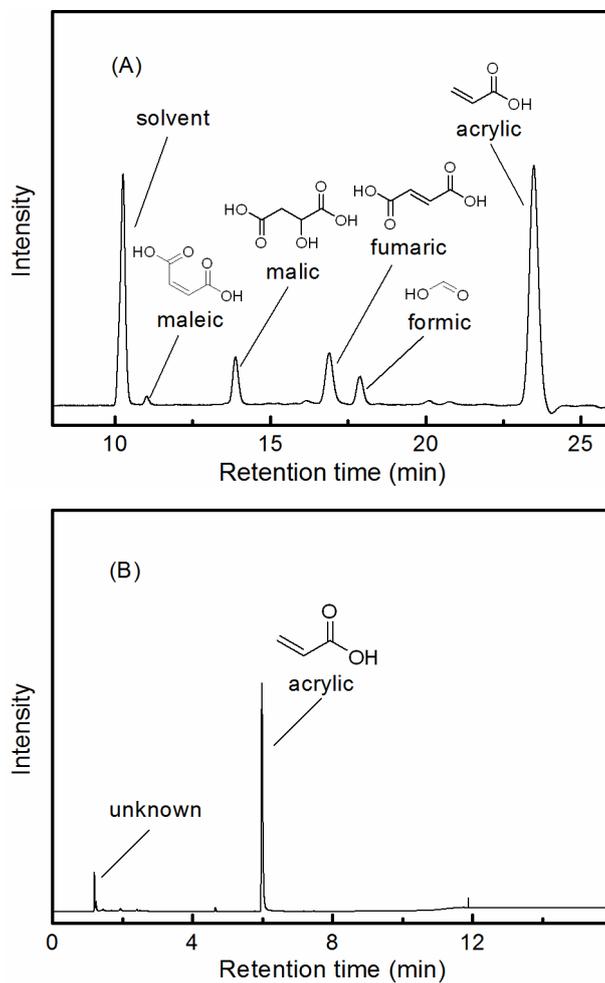
In this study, the product yield and the TOC yield (total organic carbon yield) are calculated using the following equations:

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

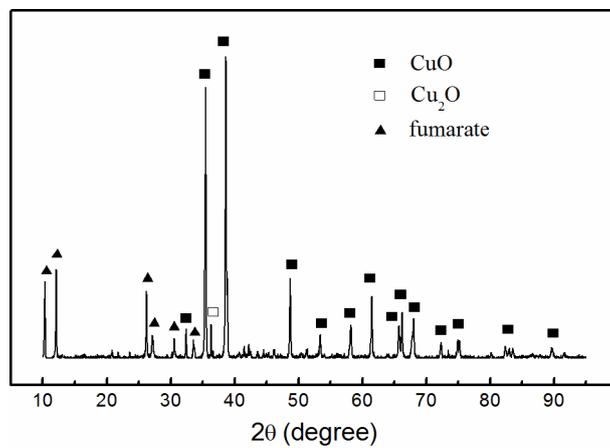
$$\text{TOC yield} = \frac{\text{total carbon weight of organic products in aqueous solution}}{\text{carbon weight of feedstock}} 100\% \quad (2)$$



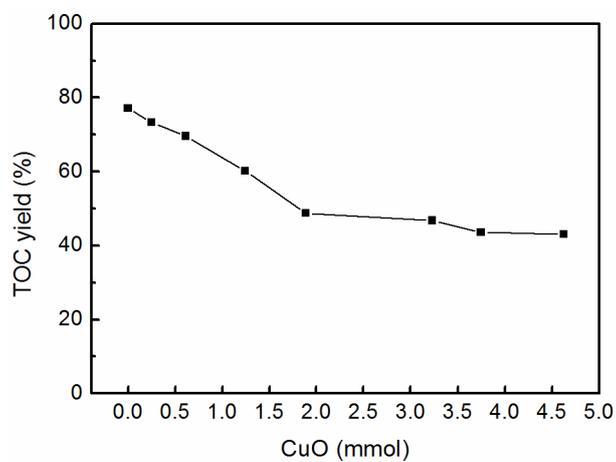
**Figure S1.** Yields of acrylic acid obtained with different additives (reaction conditions: 1.0 mmol of fumaric acid, 2.5 mmol of CuO or Cu<sub>2</sub>O, 2 mL of H<sub>2</sub>O, 300 °C, 60 s).



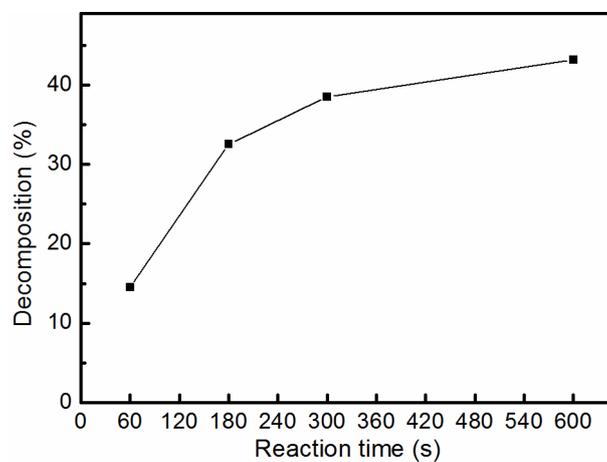
**Figure S2.** HPLC-RID chromatogram (A) and GC-FID chromatogram (B) of aqueous products after the reaction (1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of H<sub>2</sub>O, 300 °C, 120 s).



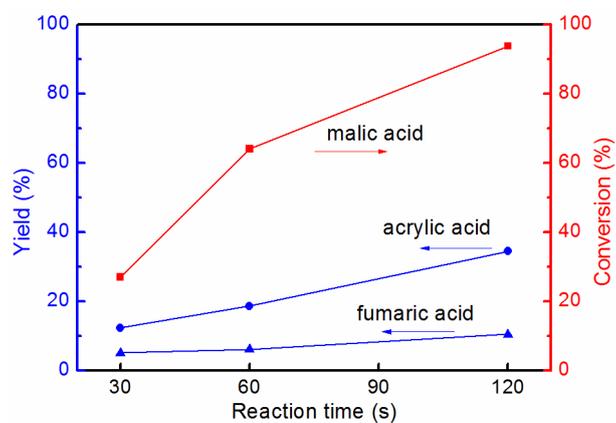
**Figure S3.** XRD pattern of the solid product after the reaction of fumaric acid with CuO (reaction conditions: 1.0 mmol of fumaric acid, 3.2 mmol of CuO, 2 mL of  $\text{H}_2\text{O}$ , 300 °C, 120 s).



**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 H<sub>2</sub>O, 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 H<sub>2</sub>O, 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 H<sub>2</sub>O, 300 °C).

## Reference:

Jin, F.M., Cao, J.X., Kishida, H., Moriya, T., Enomoto, H., 2007. Impact of phenolic compounds on hydrothermal oxidation of cellulose. *Carbohydr Res* 342, 1129-1132.

Jin, F.M., Enomoto, H., 2011. Rapid and highly selective conversion of biomass into value-added products in hydrothermal conditions: chemistry of acid/base-catalysed and oxidation reactions. *Energy Environ Sci* 4, 382-397.

Jin, F.M., Zhou, Z.Y., Moriya, T., Kishida, H., Higashijima, H., Enomoto, H., 2005. Controlling hydrothermal reaction pathways to improve acetic acid production from carbohydrate biomass. *Environ Sci Technol* 39, 1893-1902.

Shen, Z., Zhou, J.F., Zhou, X.F., Zhang, Y.L., 2011. The production of acetic acid from microalgae under hydrothermal conditions. *Appl Energy* 88, 3444-3447.