

Electronic Supplementary Information:

Oxidative conversion of glucose to gluconic acid by iron (III) chloride in water at mild conditions

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1. Materials and Methods

1.1 Materials

D-Glucose (>99%) was purchased from Acros Organics (Morris Plains, NJ, USA). Iron (III)

chloride (98%) was from Alfa Aesar (Ward Hill, MA USA). Sodium gluconate (>99%) was bought from TCI America (Portland, OR, USA). Formic acid (99.9%) and acetic acid (99.9%) were purchased from Fisher Scientific (Pittsburgh, PA, USA).

1.2 Reaction procedure

The conversion of glucose was carried out using a 40-mL glass vessel with a magnetic stirrer. Glucose (0.25 g) and concentrated (30-60%) FeCl₃ solution (5mL) were loaded into the vessel and heated up in a temperature-controlled oil bath. When desired temperature was reached in 1~2 min, reaction time was recorded. When the reaction finished, the reactor was immediately removed from oil bath and cooled down in icy water to stop the reaction. The reaction mixture was separated by filtration. The filtrate was analyzed by High Performance Ion Chromatography (HPIC) and High Performance Liquid Chromatography (HPLC) to determine the concentrations of reactant (glucose) and products (gluconic acid, formic acid, and acetic acid), respectively, as described below.

1.3 Analytical methods

Glucose was quantitated using a HPIC system (Dionex ICS-3000) with an integrated amperometric detector and a CarboPac PA1 column at 30 °C using pure water as eluent at a flow rate of 0.7 mL/min, as described previously (Shuai et al., 2010). Gluconic acid, formic acid, and acetic acid generated in the conversion process were analyzed by a HPLC system equipped with a Supelcogel C-610H column at temperature 20 °C and a UV detector at 210 nm. Phosphoric acid (0.1%) was used as eluent at a flow rate of 0.7 mL/min. The concentrations of products were determined by comparison to the calibration curves created by external standards. The glucose

conversion and product yield were calculated using the following equations:

$$\text{Conversion (\%)} = \frac{\text{Moles of carbon in feedstock consumed}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

$$\text{Product yield (\%)} = \frac{\text{Moles of carbon in organic acid}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

2. Effect of FeCl₃ Concentration, Temperature, and Time on the Yield of Gluconic Acid

As shown in Figure 1, gluconic acid yield from glucose was greatly affected by FeCl₃ concentration, reaction temperature, and reaction time. TableCurve 3D was used to determine the best fit for gluconic acid yield in relation to FeCl₃ concentration and reaction time, reaction temperature, and time. A surface representing those data points is presented in Figure S1 with R² = 1. As shown in Figure S1, the yield of gluconic acid increased with the increment of FeCl₃ concentration, elevation of reaction temperature, and extension of time in a certain extent. The maximal yield of gluconic acid (52.3%) was obtained with 40% FeCl₃ at 110 °C and 4 h. Higher concentration of FeCl₃ and reaction temperature and longer reaction time could accelerate the glucose conversion, as shown in Figure 1, but severe reaction conditions could cause undesired oxidation of gluconic acid, leading to reduction of gluconic acid yield.

Reference:

Shuai, L., Q. Yang, J.Y. Zhu, F.C. Lu, P.J. Weimer, J. Ralph, and X.J. Pan. Comparative study of SPORL and dilute acid pretreatments of spruce for cellulosic ethanol production. *Bioresource Technology*, 2010, 101, 3106-3114.

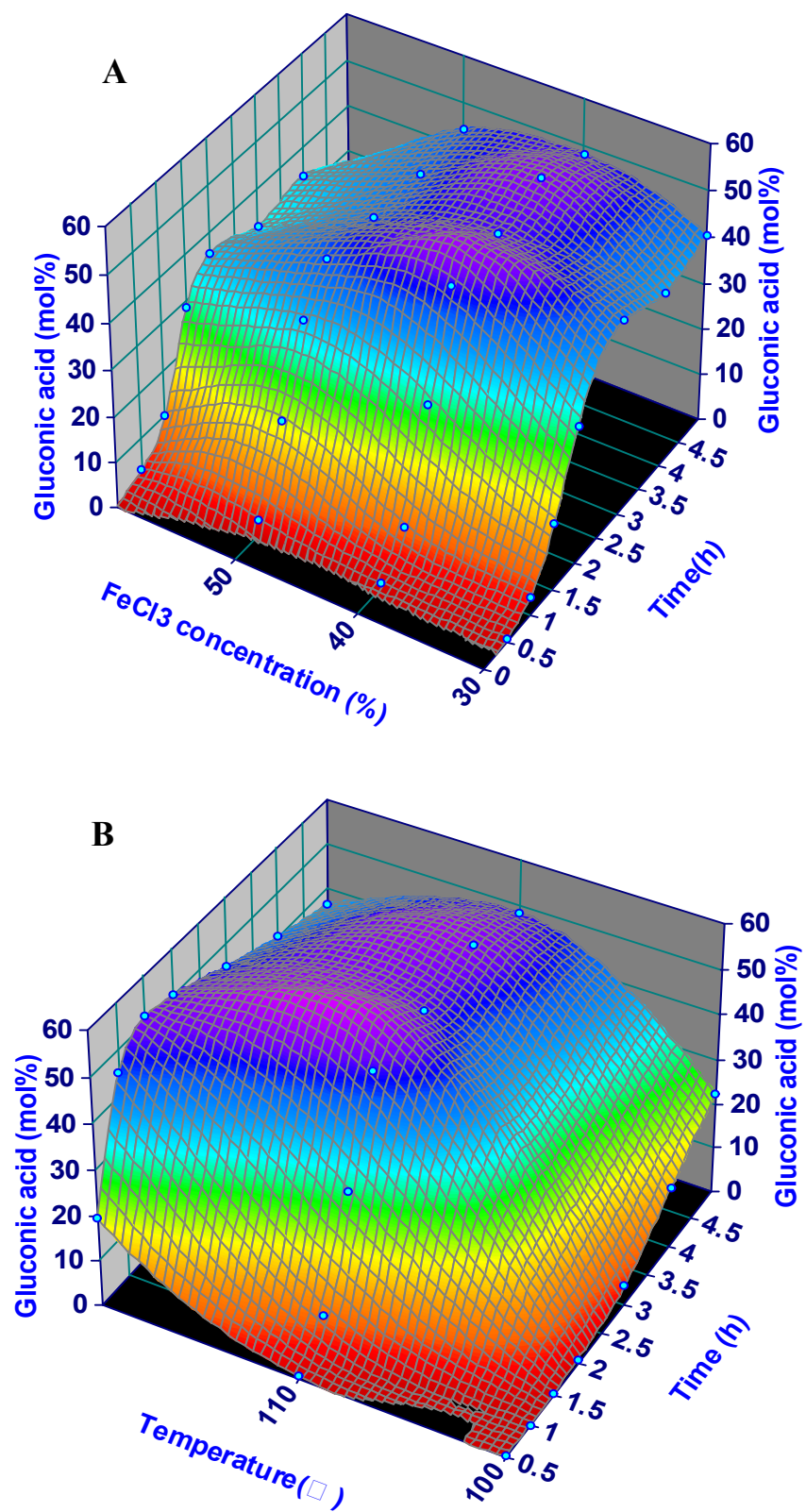


Figure S1 Effect of FeCl₃ concentration, reaction time, and temperature on gluconic acid yield.

Table S1. Oxidation of acetic acid, lactic acid, HMF, and fructose in 40% FeCl₃ at 110 °C for 2h

Reactant	Conversion (%)	Product yield (%)				
		Formic acid	Acetic acid	Lactic acid	CO ₂	CH ₄
Acetic acid	3.1	n.d. ^a	--	n.d.	Trace ^b	Trace ^b
Lactic acid	5.8	n.d.	n.d.	--	--	--
HMF ^c	92.0	6.4	2.1	7.0	--	--
Fructose	100.0	5.4	12.8	2.8	--	--

Note: a. n.b. – not detected; b. Trace amounts of CO₂ and CH₄ were detected in the gas phase by GC after acetic acid was treated in 40% FeCl₃ at 110 °C for 2 h under nitrogen atmosphere; c. HMF was oxidized in 60% FeCl₃ at 110 °C for 1h.