Supporting information for

Quantitative chemocatalytic production of lactic acid from glucose under anaerobic conditions at room temperature

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1. Experimental section

1.1 Materials

Glucose (99%), fructose (99%) and cellobiose (>99%) were purchased from Guangfu fine chemicals research institute (Tianjin). Sucrose (>99%) was obtained from Jinke fine chemicals research institute (Tianjin). Microcrystalline cellulose (pharmaceutical grade, particle size 50 μm, DP_V 219) was provided by the Boya company (Tianjin). NaOH, KOH, $Ba(OH)_2{\cdot}8H_2O$ and $Mg(OH)_2$ were analytical grade and provided by J&K Scientific Ltd. Lactic acid (>98%), 1,3-dihydroxyacetone dimer (>97%), pyruvaldehyde (30% solution in water) were purchased from Ark pharm, Inc. Formic acid, glycolic acid, glyceraldehyde and oxalic acid, tartronic acid and malonic acid (purity > 98%) were provided by Sinopharm.

1.2 Catalytic reaction and products analysis

The catalytic reaction was conducted in a teflon-liner fitted 50 mL stainless steel autoclave, which had an attached pressure gauge and inlet and outlet valves. Boiled

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ultra-pure water was used in the reaction to remove the dissolved gases. In a typical experiment, 0.36 g of glucose was dissolved into 20 mL 0.25 M $Ba(OH)_2$ aqueous solution, and the mixture was loaded into the autoclave, which was then sealed and purged with N_2 or O_2 for three times. After introduction of N_2 or O_2 at a certain pressure (1-20 bar), the sealed autoclave was placed in a thermostated shaker bath (DSHZ-300A, Jiangsu) at 25 ^oC ($\pm$1 ^oC) and shaken at 100 rpm for 48 h. After reaction, the reaction mixture was acidified with 20 mL of 0.5 M sulfuric acid aqueous solution. By this procedure, various salts formed in the reaction were converted to their respective free acids. Thus, all of the acid products in this work are given and discussed as free organic acids instead of organic salts such as lactate. The analysis of the products was performed with HPLC (Waters Acquity UPLC H-Class) equipped with RI and UV detectors and a Shodex SUGAR SH1011 column. The temperature of column and the RI detector was set to 50 and 35 ^oC, respectively. A wavelength of 210 nm was used for the UV detector. Dilute sulfuric acid aqueous solution (5 mM) was used as mobile phase at a flow rate of 0.5 mL/min. The total organic carbon (TOC) of the reaction solution was determined with a Shimadzu TOC-V analyzer.

All experiments were conducted in triplicate as a minimum, and the results provided are mean values of the repeated trials that had relative deviations below 3%. In most cases, the carbon balance under anaerobic and aerobic conditions was higher than 90% and 80%, respectively. The lost carbon mainly originates from the formation of oligo- and polymerization products that cannot be reliably quantified.

Substrate conversion, product yield and selectivity were calculated on a carbon basis as follows:

$$\text{Substrate conversion (\%)} = \left\{1 - \left(\frac{molar\ concentration\ of\ remained\ substrate}{molar\ concentration\ of\ introduced\ substrate}\right) \times 100\%\right\}$$

$$\text{Product yield (\%)} = \left\{\left(\frac{moles\ of\ the\ product}{moles\ of\ \ the\ introduced\ substrate} \times \frac{carbon\ numbers\ in\ 1\ mol\ product}{carbon\ numbers\ in\ 1\ mol\ \ substrate}\right) \times 100\%\right\}$$

$$\text{Product selectivity (\%)} = \left\{\left(\frac{product\ yield}{substrate\ conversion}\right) \times 100\%\right\}$$

2. HPLC spectra (RI detector) of glucose conversion at different reaction times catalyzed by $Ba(OH)_2$ under anaerobic conditions at ambient pressure

After the reaction mixtures obtained at different reaction times were acidified with 20 mL of 0.5 M sulfuric acid aqueous solution, they were analyzed with HPLC, and the HPLC spectra were shown in Figure S1, showing a simple product distribution with fructose, glyceraldehyde and lactic acid as main products. The other C2 and C4 aldoses such as glycolaldehyde and erythrose that could be observed in the degradation of glucose under hydrothermal conditions was not found in this work [1, 2].

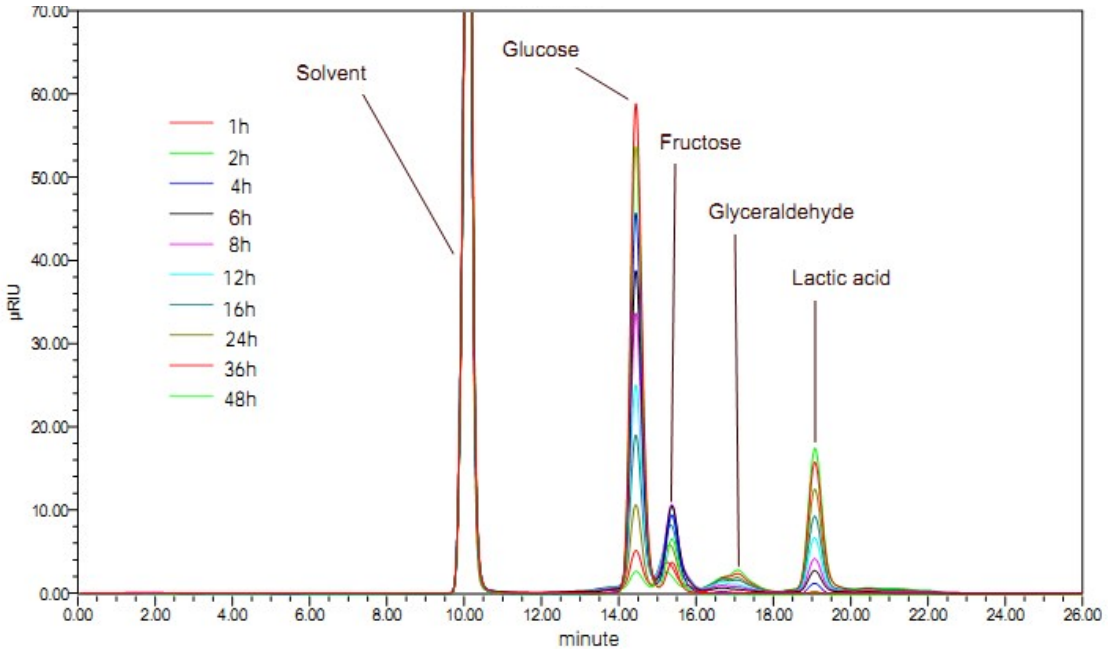

Figure S1. HPLC spectra (RI detector) of glucose conversion as a function of reaction time catalyzed by $Ba(OH)_2$ under a N_2 atmosphere. Reaction conditions: 0.1 M glucose, 0.25 M $Ba(OH)_2$, 25 ^oC, 1 bar total pressure.

3. Catalytic conversion of glucose to lactic acid under different temperatures

To shorten the required reaction time for the transformation of glucose into lactic acid catalyzed by $Ba(OH)_2$, the effect of reaction temperature on the reaction was studied (Figure S2). It can be seen that when the temperature was increased to 45 and 55 ^oC, respectively, lactic acid yield of 82.4% and 76.0% could be obtained for 8 h and 2 h, respectively.

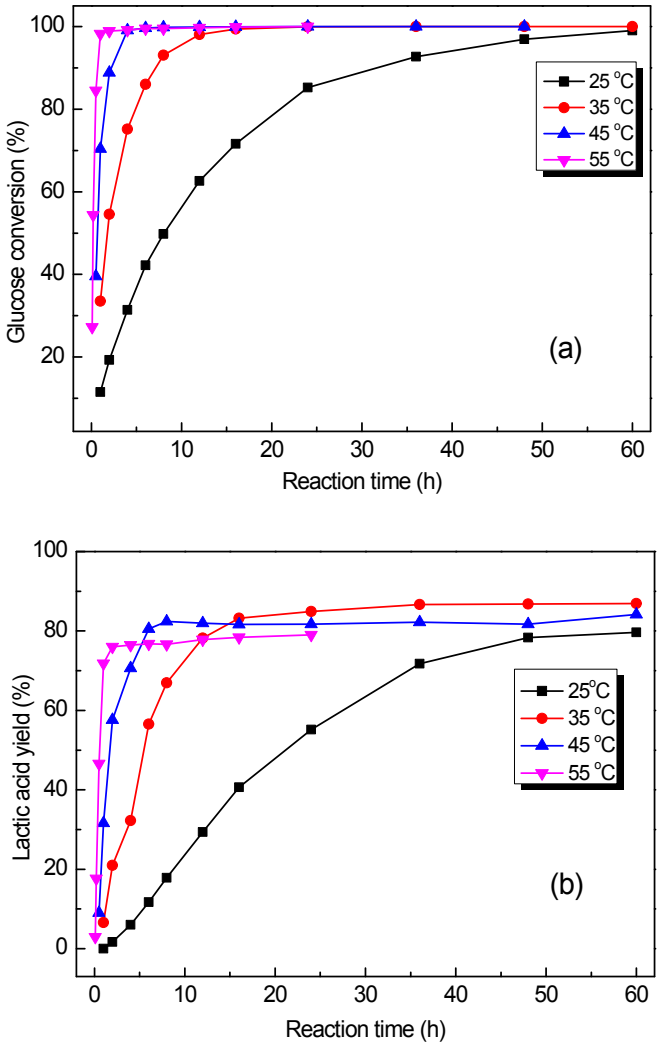

Figure S2. Catalytic conversion of glucose to lactic acid under different reaction temperatures. Reaction conditions: glucose, 0.1 M; $Ba(OH)_2$, 0.25 M; nitrogen atmosphere, 1 bar total pressure.

4. Effect of $Ba(OH)_2$ dosage on lactic acid production from glucose

The effect of $Ba(OH)_2$ concentration on the production of lactic acid from glucose at room temperature under a nitrogen atmosphere at 1 bar total pressure was investigated (Figure S2). The results showed that at low $Ba(OH)_2$ concentrations (0.0625 M), fructose was the main product (36.0% yield) and the yield of lactic acid was 10.5%. With increasing $Ba(OH)_2$ concentration, the fructose yield remarkably decreased, accompanied by a significant increase in lactic acid yield. When 0.25 M $Ba(OH)_2$ was used, a lactic acid yield of 78.3% was obtained with the final (remaining) fructose yield being 3.3%. Low $Ba(OH)_2$ concentrations promoted the isomerization of glucose to fructose, while relatively high $Ba(OH)_2$ concentrations promoted lactic acid formation from glucose via fructose. Similar results were obtained for glucose conversion catalyzed by NaOH, in which fructose yields of up to 48.8% were obtained with only a small quantity of lactic acid being formed (<3% yield) for NaOH concentrations being below 0.125 M, after which the lactic acid yield increased to 62.8% with fructose yield correspondingly decreasing to 16.2% in the 1 M NaOH aqueous solution (Figures S3 and S4).

Further increase of $Ba(OH)_2$ concentration to 0.5 M had a limited effect on the lactic acid yield, which should be ascribed to 0.25 M concentration being close to the solubility of $Ba(OH)_2$ in water at 25 ^oC (0.27 M, 46.8 g/L), and the additional $Ba(OH)_2$ being above the saturation conditions that would have had little effect on the formation of lactic acid.

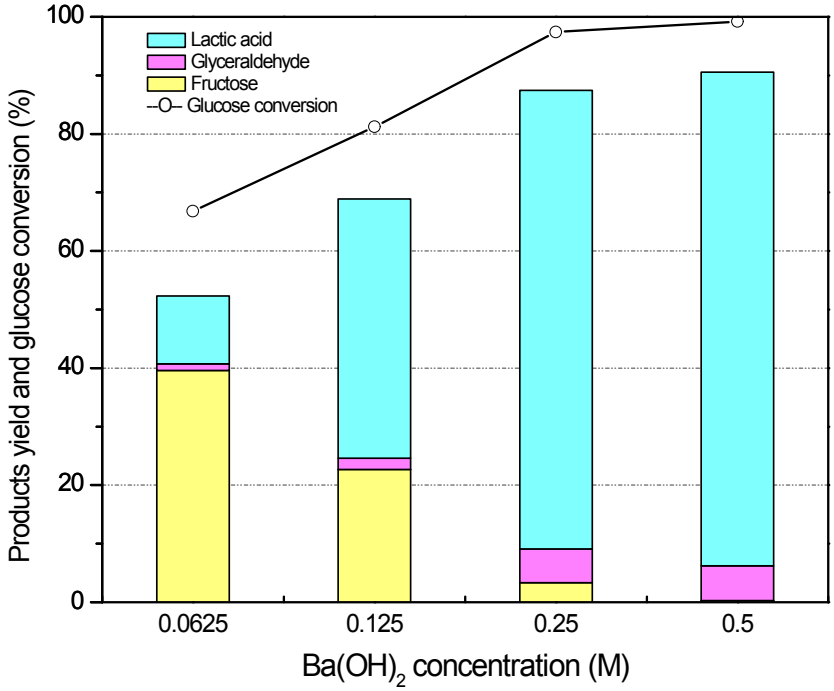

Figure S3. Effect of $Ba(OH)_2$ dosage on lactic acid production from glucose at 25 °C under anaerobic conditions. Reaction conditions: glucose, 0.1 M; reaction time, 48 h; nitrogen atmosphere, 1 bar total pressure.

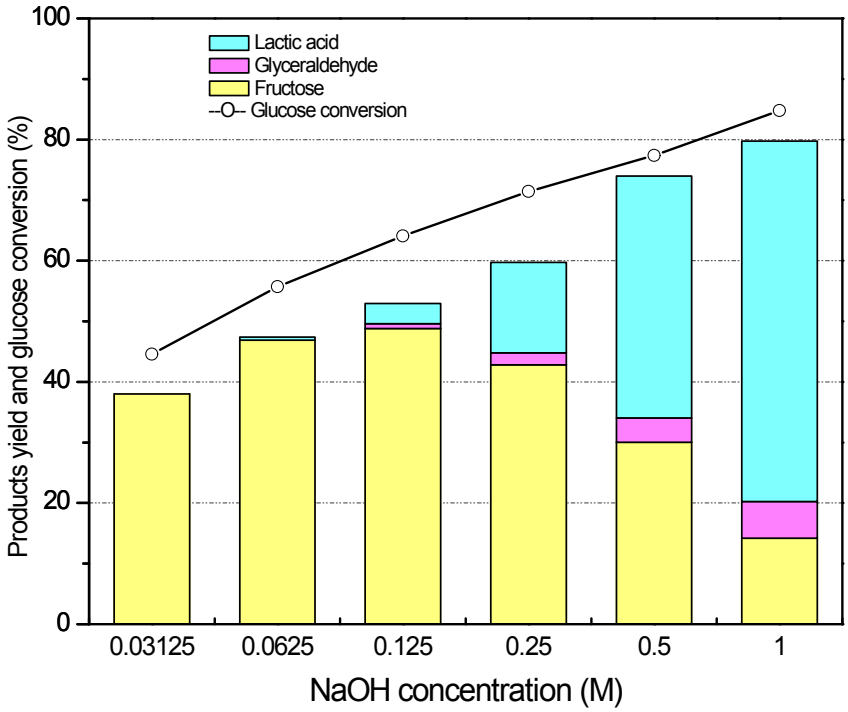

Figure S4. Effect of NaOH concentration on the glucose conversion at 25 °C under anaerobic conditions. Reaction conditions: 0.1 M glucose, 48 h reaction time, nitrogen atmosphere, 1 bar total pressure.

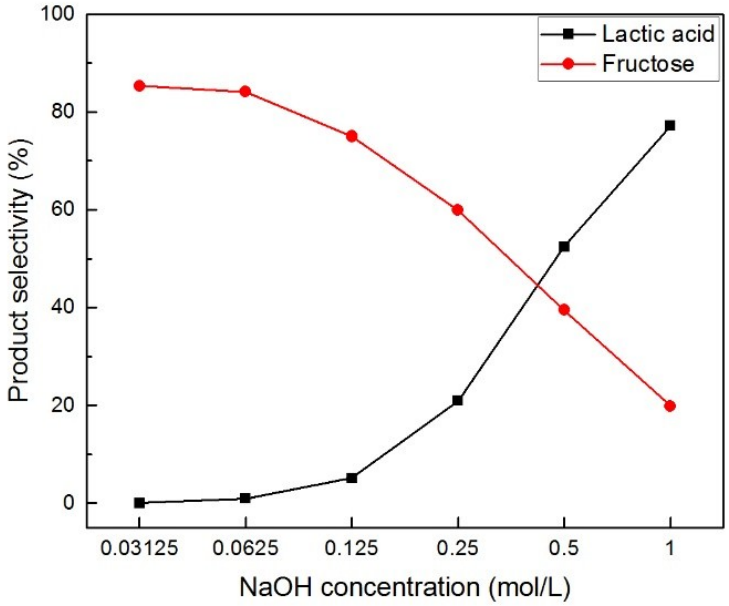

Figure S5. Variation of lactic acid and fructose selectivity from glucose catalyzed by various concentrations of NaOH at 25 °C under anaerobic conditions. Reaction conditions: 0.1 M glucose, 25 °C, 48 h reaction time, nitrogen atmosphere, 1 bar total pressure.

5. Effect of reaction atmosphere on glucose conversion into lactic acid at room temperature and 1 bar pressure

The effect of the reaction atmosphere on glucose conversion in $Ba(OH)_2$ catalyzed system at room temperature was examined.

Table S1. Catalytic conversion of glucose by $Ba(OH)_2$ under different atmospheres at 25 ^oC and at 1 bar total pressure [a]

Atmosphere	Glucose conversion (%)	Products yield (%)							
		Fructose	Glyceraldehyde	Lactic acid	Glyceric acid	Glycolic acid	Formic acid	Malonic acid	CO_2
N_2	97.4	3.4	5.8	79.4	0	0	0	0	0
N_2 [b]	97.3	3.5	5.7	79.3	0	0	0	0	0
Ar	97.6	3.3	5.9	79.5	0	0	0	0	0
Air[c]	98.2	3.2	4.9	61.3	1.3	1.1	3.1	2.2	1.2

[a] Reaction conditions: glucose, 0.1M; $Ba(OH)_2$, 0.25M, temperature, 25^oC; reaction time, 48h.

[b] Reaction was conducted in sealed glass flasks.

[c] Besides these products, trace amount of tartronic acid and oxalic acid were detected.

6. Effect of reaction time on glucose conversion in the presence of $Ba(OH)_2$ under aerobic conditions

The time course for glucose conversion in the presence of $Ba(OH)_2$ at room temperature under 20 bar O_2 partial pressure was studied (Figure S6). The formed fructose firstly increased and then decreased with increasing reaction time, similar to that which occurs under anaerobic conditions, demonstrating that fructose formation through glucose isomerization is the initial reaction step. By prolonging the reaction time to 48 h, the yield of glyceric, glycolic, formic, malonic, lactic and other acids as well as CO_2 increased (Figures. S6 and S7). It should be noticed that as one of the products in glucose oxidation under hydrothermal conditions, the production of acetic acid was negligible. It seems that the presence of O_2 in the reaction system as dissolved oxygen determined by its Henry's constant leads to the production of a variety of organic acids and inhibits the formation of lactic acid. Thus, to achieve high yields of lactic acid from glucose, anaerobic conditions must be strictly controlled in the chemocatalytic reaction system. When experiments that used glucose, glyceraldehyde and dihydroxyacetone as substrates were conducted in the absence of $Ba(OH)_2$ under O_2 atmosphere at 25 ^oC, these species were shown to be stable even after 48 h reaction time, indicating the catalyst $Ba(OH)_2$ was responsible for the oxidation of lactic acid precursors. The detailed mechanism will be investigated in future work.

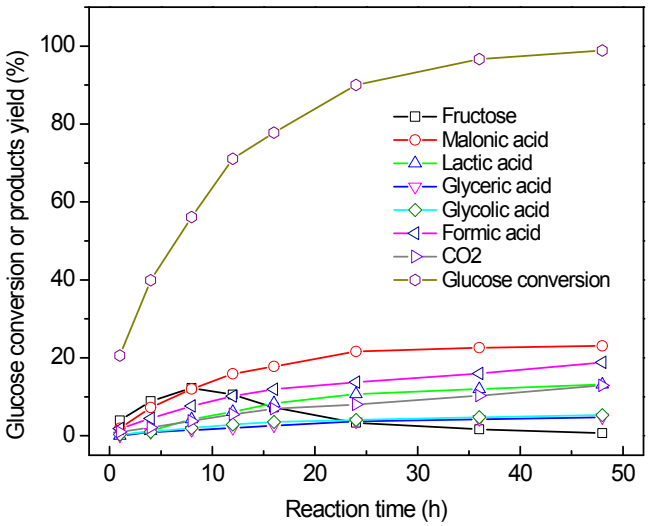

Figure S6. Time course for glucose conversion in the presence of $Ba(OH)_2$ under aerobic conditions. Reaction conditions: glucose, 0.1M; $Ba(OH)_2$, 0.25 M, temperature, 25 ^oC; reaction time, 48 h; 20 bar O_2 partial pressure.

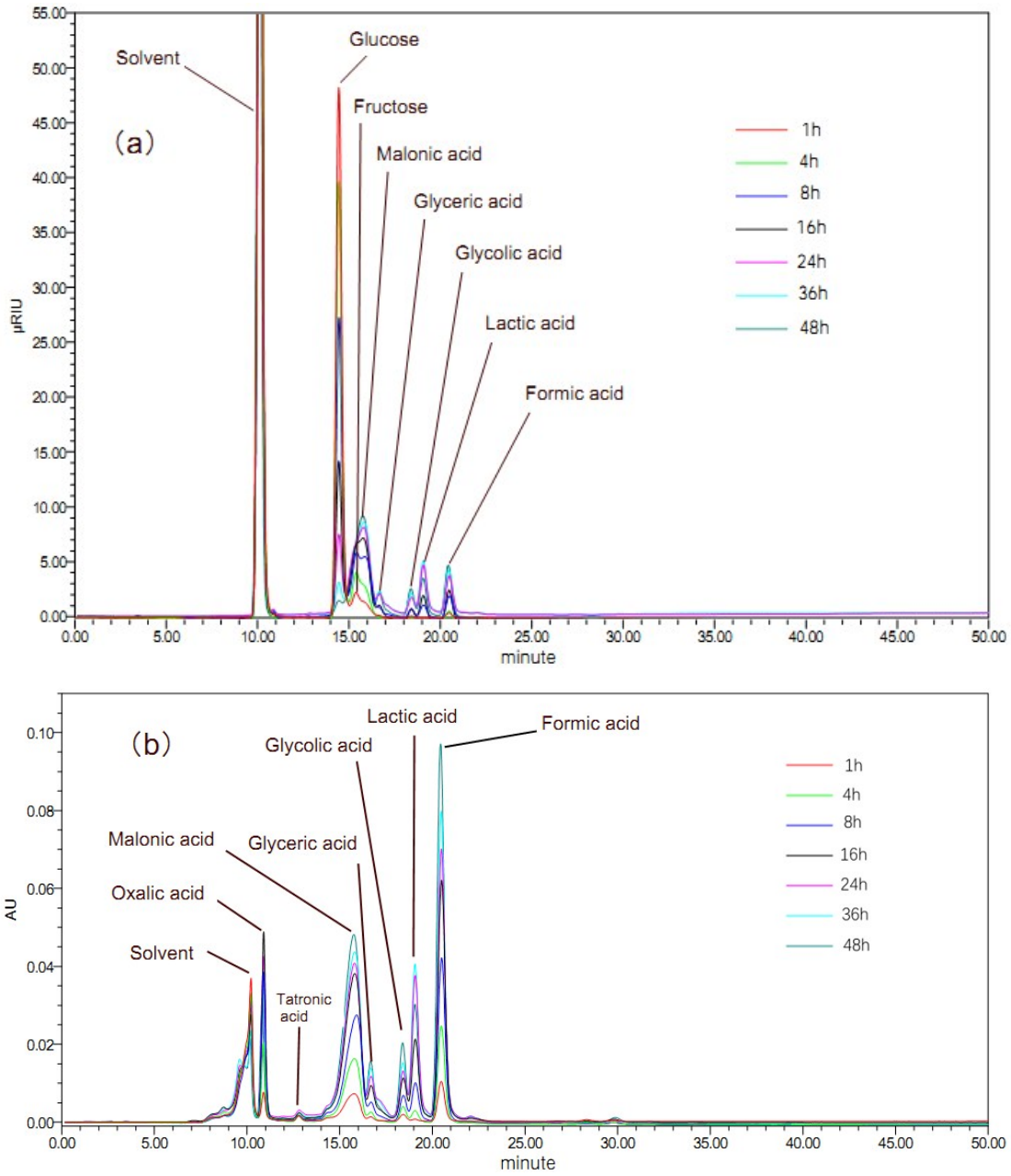

Figure S7. HPLC spectra (a-RI detector, b-UV detector) of glucose conversion as a function of reaction time catalyzed by $Ba(OH)_2$ under aerobic conditions. Reaction conditions: 0.1 M glucose, 0.25 M $Ba(OH)_2$, temperature, 25 ^oC, 20 bar O_2 partial pressure.

References:

[S1] H. Kishida, F. M. Jin, X. Y. Yan, T. Moriya, H. Enomoto, *Carbohyd Res*. **2006**, 341, 2619.
[S2] F. Jin, H. Enomoto, *Energy Environ. Sci.* **2011**, 4, 382.