Electronic Supplementary Information

Catalytic Deep Eutectic Solvents for Highly Efficient Conversion of Cellulose to Gluconic Acid with Gluconic Acid Self-Precipitation Separation

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Experimental Section

Materials and Reagents

Hydrogen bond acceptor (HBA) ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (≥ 99%) and hydrogen bond donor (HBDs) urea, ethylene glycol, glycerol, malonic acid, glycine, xylitol, and pentaerythritol with purities higher than 99% were purchased from Sinopharm Chemical Reagent Co., Ltd. L-Alanine, L-Serine (> 99%) were provided by J&K. Glucose (> 98.0%) and Gluconic acid (contains Gluconolactone, 45%-50% in water) were obtained from TCI. All chemicals were used directly without further purification.

Instruments and Analytical methods

The IR spectra were obtained by coupling of the attenuated total reflection (ATR) equipment with the FTIR spectrometer (Prestige 21, Shimadzu) in the range of 400 to 4000 cm^{-1}. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments, USA) system at a heating rate of 10 °C min^{-1}. All CDESs were run in aluminium pans in a sealed furnace and were cooled to -100 °C before heating up to room temperature. The viscosity (η) of CDESs was measured using an Anton Paar DMA 5000 M five times and the average value was reported. The conductivity of the CEDSs was measured by using a conductivity meter (DDS-307A, Shanghai INESA Scientific Instrument Co., Ltd, China) five times at 298.15 K. The deviation of the equipment was less than ±0.5%. After obtaining the product, we used ethyl acetate to wash product. And the residual Fe present in the washed gluconic acid was analysed by Agilent Technologies 700 Series ICP-OES. The yield and conversion were measured by high-performance liquid chromatography (HPLC) as described below.

The concentration of glucose in the reaction system was quantitatively analysed by a HPLC with

$$\text{Conversion} = \frac{\text{moles of carbon in substrate consumed}}{\text{inital moles of carbon in substrate}}$$

$$\text{Product yield} = \frac{\text{moles of carban in gluconic acid}}{\text{intial moles carban in substrate}}$$

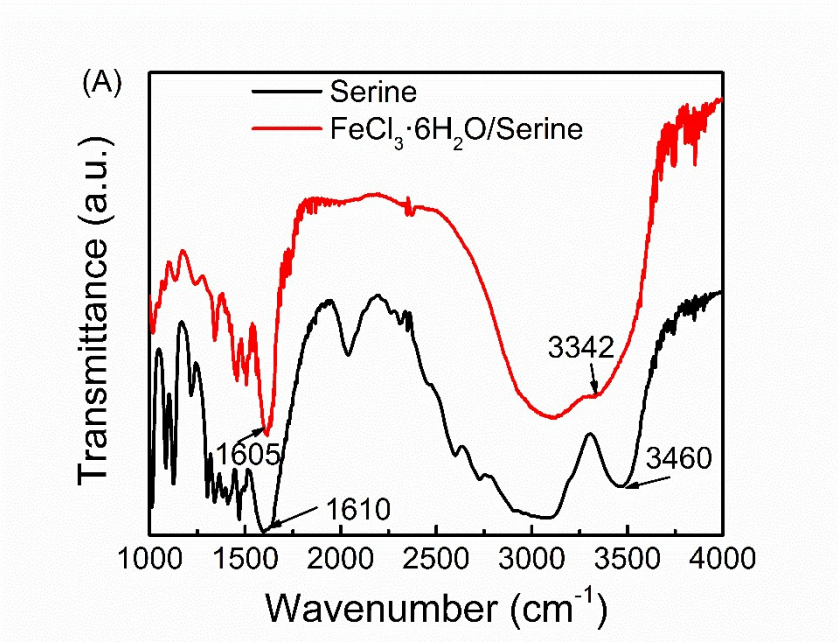
Hypersil NH_2 5 μm column at 30 ºC, Shimadzu LC-20AT pump, Shimadzu RID-10A detectors at room temperature, and water was used as flowing phase at 0.6 mL·min^{-1}. The product gluconic acid was quantitatively analyzed by using a HPLC system with a SB-C18 column (4.6 × 250 mm) and detected using a UV detector at a wavelength of 210 nm at 25 ℃. Methanol and 0.1% acetic acid (5:5) were used as eluent at a flow rate of 1 mL/min. The concentration of product was determined by comparison to the calibration curves created by external standards. The conversion of substrate and product yield were calculated using the following formula:

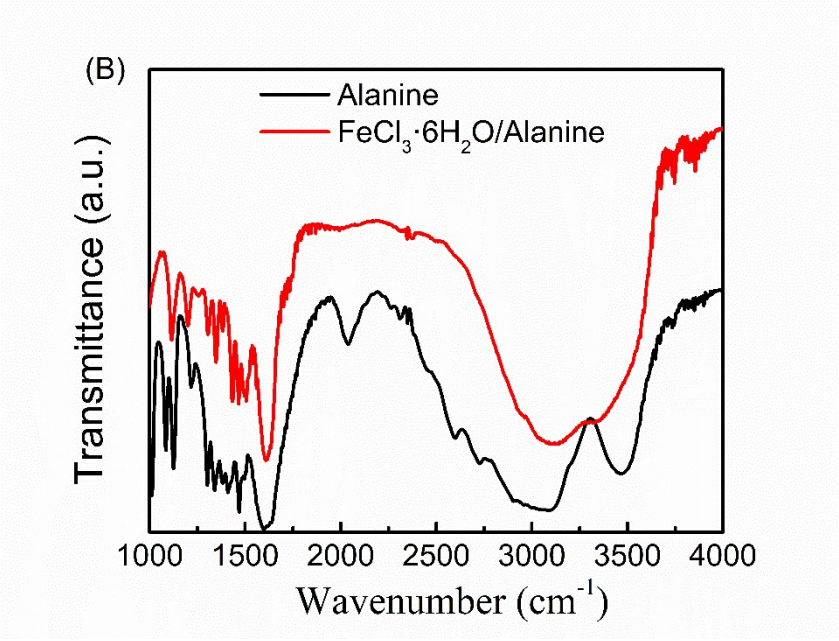
CDESs preparation

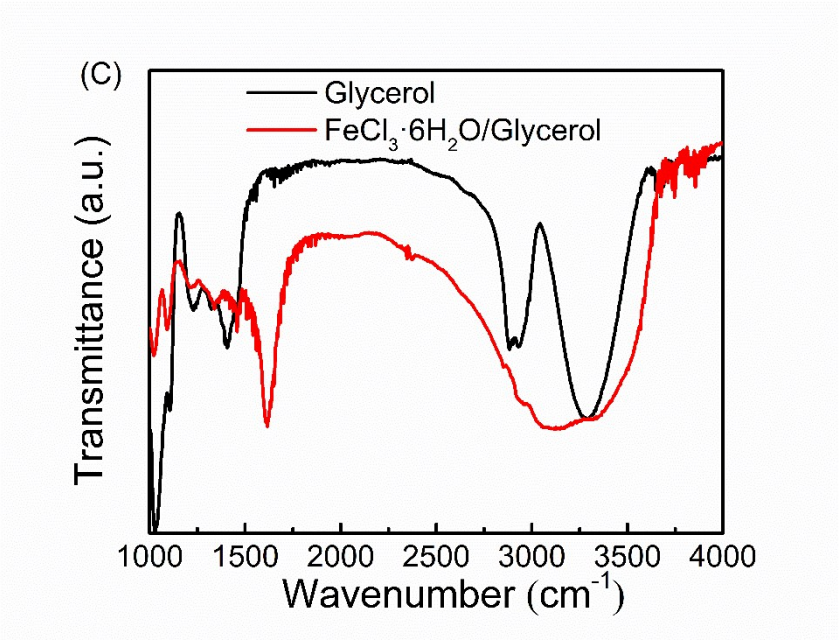
The Fe-based CDESs were prepared by simply mixing $FeCl_3 \cdot 6H_2O$ and nine HBDs in different molar ratio under mild heating (40 ℃). After a while, clear dark-brown homogenous liquids can be observed. All these DESs are stable at room temperature and reaction conditions.

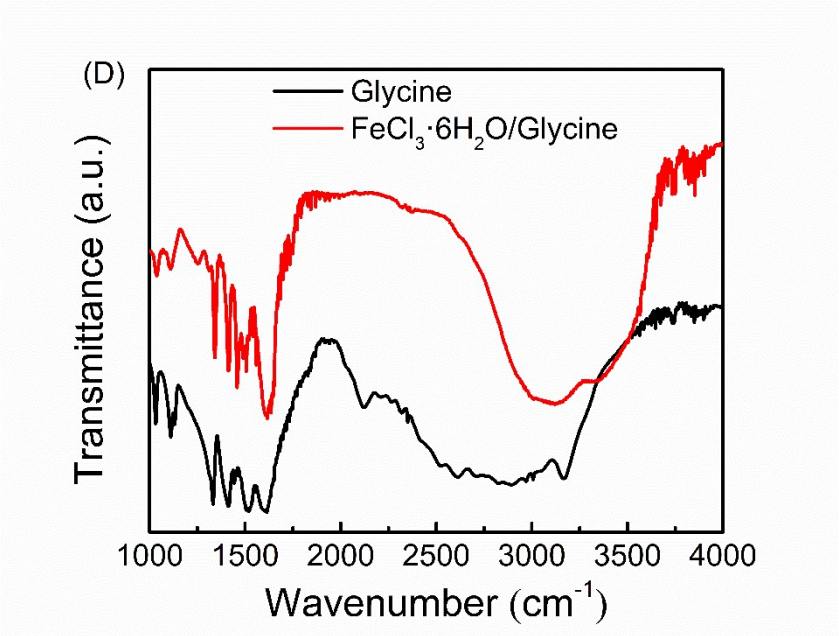
Catalytic conversion glucose and cellulose

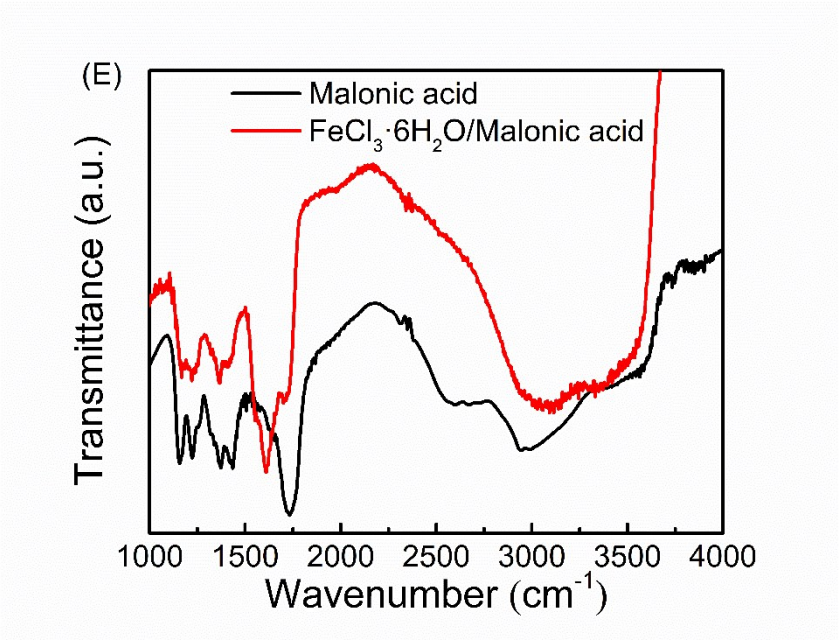
In a typical experiment, known quality of glucose or cellulose and 10 mL CDESs were loaded into a glass vial and heated in an oil with controlled temperature for a certain time. Then the vial was immediately placed in an ice-water bath to stop the reaction. The solid precipitation (products) could be found at the bottom of the glass vial, while the unreacted glucose could be found in CDESs. The solid product was washed with ethyl acetate and then dried in the oven. In final washing step of the solid, we used about 20 mL ethyl acetate to wash 9-10 times in total. Each time we use about 2 ml of ethyl acetate to clean by ultrasound followed with centrifuging. The final amount of residual Fe present in the washed gluconic acid was analysed by ICP-OES. For example, the residual Fe was about 1% (w/w) in $FeCl_3 \cdot 6H_2O$/ethylene glycol reaction system. The solid product and upper solvent were analyzed by high-performance liquid chromatography (HPLC) to calculate the yield and conversion rate respectively.

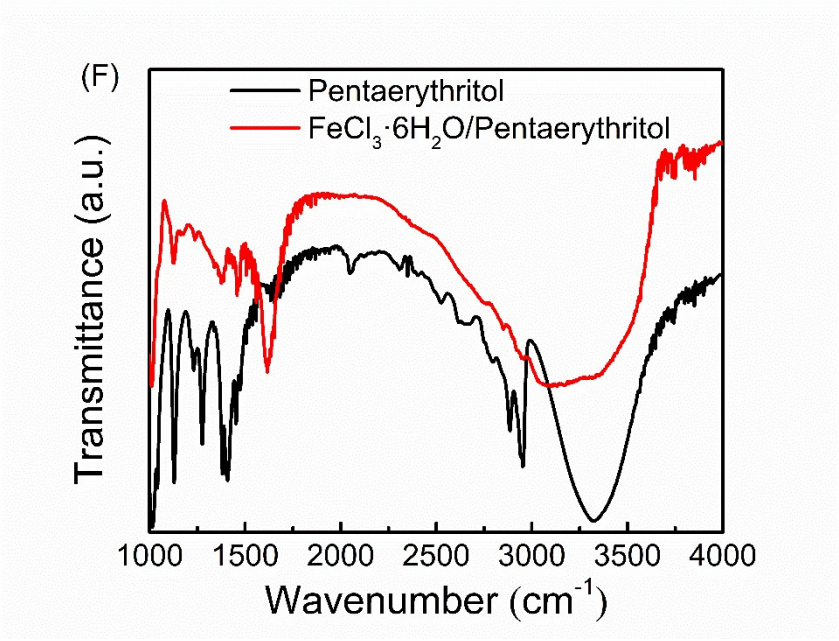

(A)
Serine
FeCl3·6H2O/Serine
Transmittance (a.u.)
3342
1605
3460
1610
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)


(B)
Alanine
FeCl3·6H2O/Alanine
Transmittance (a.u.)
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)


(C)
Glycerol
FeCl3·6H2O/Glycerol
Transmittance (a.u.)
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)


(D)
Glycine
FeCl3·6H2O/Glycine
Transmittance (a.u.)
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)


(E)
Malonic acid
FeCl3·6H2O/Malonic acid
Transmittance (a.u.)
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)


(F)
Pentaerythritol
FeCl3·6H2O/Pentaerythritol
Transmittance (a.u.)
1000 1500 2000 2500 3000 3500 4000
Wavenumber (cm-1)

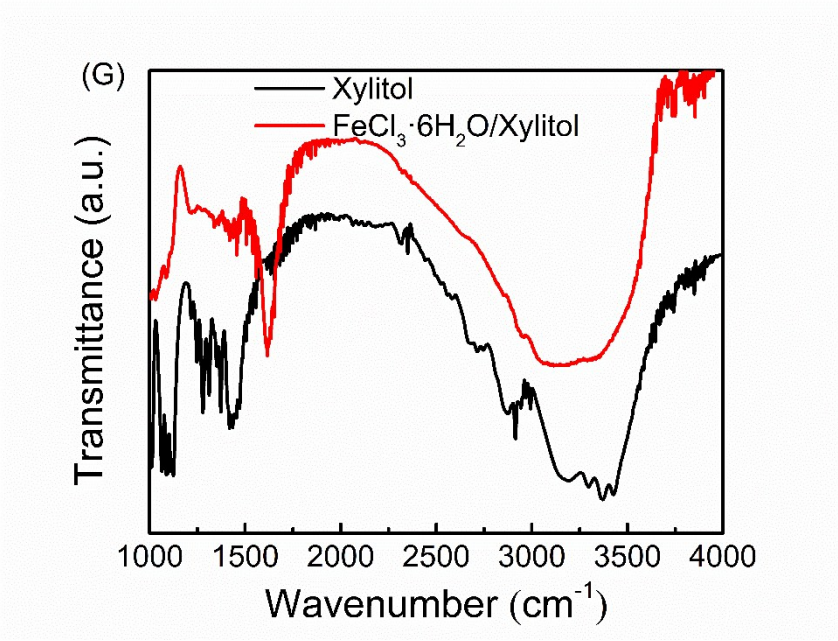


Fig. S1. FTIR of $FeCl_3 \cdot 6H_2O$ and different HBDs. (A) FTIR spectra of $FeCl_3 \cdot 6H_2O$/serine; (B)$FeCl_3 \cdot 6H_2O$/alanine; (C)$FeCl_3 \cdot 6H_2O$/glycerol; (D) $FeCl_3 \cdot 6H_2O$/glycine; (E) $FeCl_3 \cdot 6H_2O$/malonic acid; (F) $FeCl_3 \cdot 6H_2O$/pentaerythritol; (G) $FeCl_3 \cdot 6H_2O$/xylitol

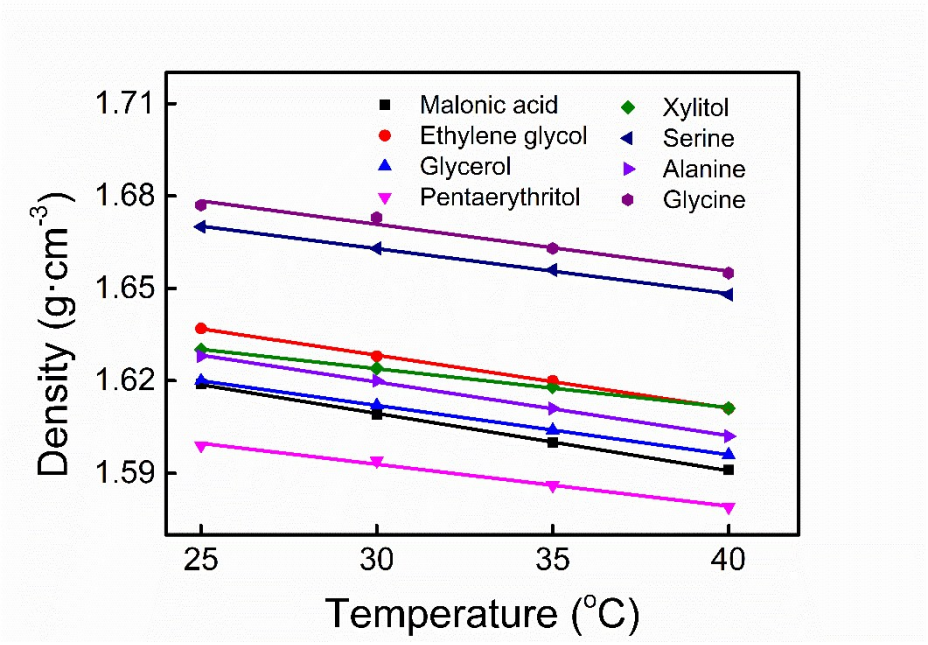


Fig. S2. The densities of all CDESs ($FeCl_3 \cdot 6H_2O$/HBDs) as a function of temperature.

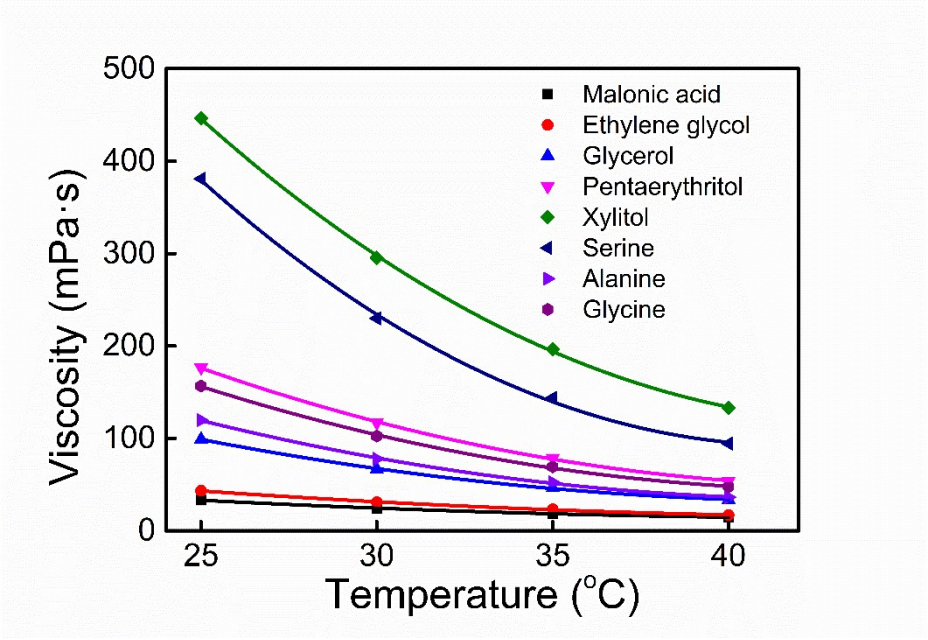


Fig. S3. The viscosities of all CDESs ($FeCl_3 \cdot 6H_2O$/HBDs) as a function of temperature.

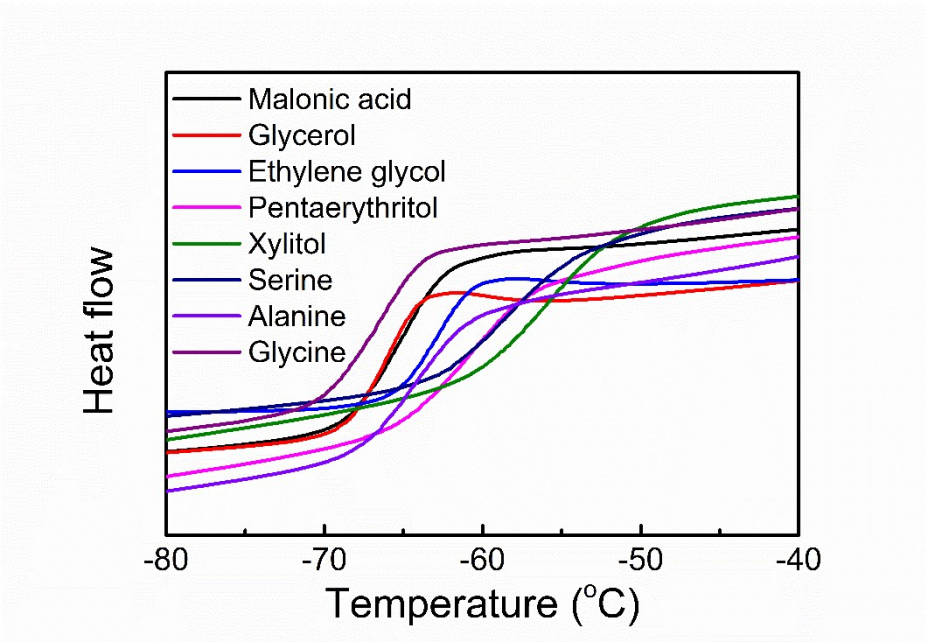


Fig. S4. Glass transition temperature (T_g) of all CDESs ($FeCl_3 \cdot 6H_2O$/HBDs) analyzed by differential scanning calorimetry (DSC).

Table S1. Physicochemical properties (viscosity, density, conductivity) of DESs at 25°C.

Entry	HBD	$FeCl_3 \cdot 6H_2O$/HBD molar ratio	Viscosity (mPa·s)	Density ($g \cdot cm^{-3}$)	Conductivity ($mS \cdot cm^{-1}$)	T_g (°C)
1	ethylene glycol	2:1	43.37	1.605	45.4	-64
2	glycerol	3:1	99.16	1.637	26.8	-66
3	malonic acid	2:1	33.16	1.619	108.3	-63
4	pentaerythritol	2:1	176.49	1.599	24.5	-60
5	xylitol	2:1	446.54	1.630	10.1	-55
6	serine	2:1	380.89	1.670	19.4	-56
7	alanine	2:1	119.75	1.628	37.4	-63
8	glycine	2:1	156.62	1.677	43.9	-65

Table S2. The pH of CDESs.

HBDs	pH	HBDs	pH
Ethylene glycol	-1.09	Serine	-1.62
Glycerol	-1.17	Alanine	-1.59
Malnoic acid	-1.78	Glycine	-1.50
Pentaerythritol	-1.14	Xylitol	-1.22

Table S3. The effect of temperature on product yield in the conversion of cellulose.

Cellulose conc. (w/v, %)	Time (minutes)	Temperature (°C)	Gluconic acid Yield (%)
5.0	60	90	12.8
5.0	60	100	19.6
5.0	60	110	35.4
5.0	60	120	52.7
5.0	60	130	39.5

Table S4. Conversion of cellulose in $FeCl_3 \cdot 6H_2O$/ethylene glycol at 120^oCin 60 minutes with different concentrations of cellulose.

Cellulose conc. (w/v, %)	Time (minutes)	Temperature (^oC)	Cellulose conversion (%)	Gluconic acid Yield (%)
2.5	60	120	100	24.5
5.0	60	120	100	52.7
7.5	60	120	100	30.7
10.0	60	120	100	21.6