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# One-pot production of a liquid biofuel candidate—Ethyl levulinate from glucose and furfural residues using a combination of extremely low sulfuric acid and zeolite USY

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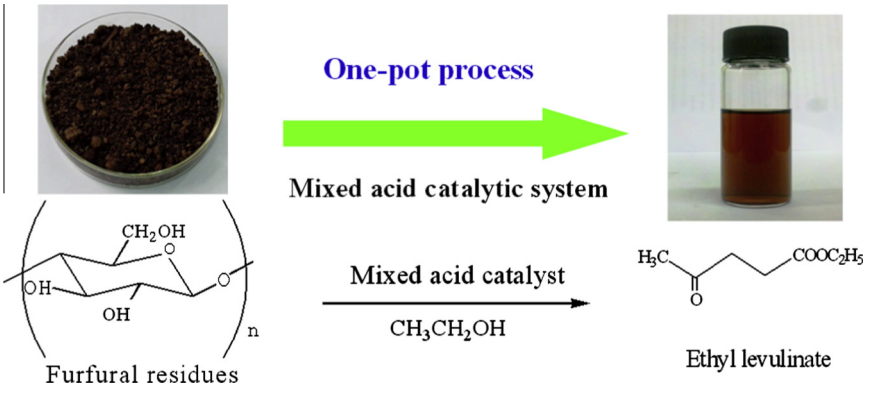
## HIGHLIGHTS

- Combination of extremely low sulfuric acid and USY is efficient for EL production.
- Higher EL yield of 51.47% from glucose can be obtained in the mixed acid system.
- Higher EL yield of 18.68% from FRs can be obtained in the mixed acid system.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Ethyl levulinate has been considered as a potential liquid biofuel candidate for the future. The conversion of glucose to ethyl levulinate in ethanol medium was firstly investigated in this study. Experimental results showed that the combination of extremely low sulfuric acid and zeolite USY can be used as an effective catalytic system for one-pot EL production from glucose. The ethyl levulinate yield of 51.47% from glucose can be obtained at 180 °C and 120 min in the mixed acid system comprising of 0.1% sulfuric acid and 2.0% USY. Furfural residues were further taken as substrates for ethyl levulinate production in the mixed acid system. Artificial neural network coupled with genetic algorithm was employed to optimize the process. The optimum conditions were reaction temperature 219 °C, USY loading 2.3%, mass ratio of liquid to solid 40 and reaction time 107 min. Under the optimum conditions, higher ethyl levulinate yield of 18.68% was obtained, representing a theoretical yield of 51.22%.



## 1. Introduction

Nowadays, extensive research is being undertaken worldwide to convert cellulosic biomass into biofuel, and latest efforts have focused on direct converting cellulosic biomass into biofuel via one-pot process [1]. Recently, ethyl levulinate (EL) has drawn

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much attention due to its numerous potential industrial applications. EL can not only be used as flavoring, solvent and plasticizer, but also be suitable for the use as additives for gasoline and diesel transportation fuels due to its unique properties, such as non-toxicity, high lubricity, flashpoint stability and superior flow properties under cold conditions [2].

EL can be produced directly from cellulosic biomass in ethanol. The conversion can take place in the presence of mineral acid catalysts. But, when the mineral acid is in higher concentrations, it has serious drawbacks in separation and recycling, as well as equipment corrosion. One of the promising methods for one-pot EL production is the usage of extremely low acid, which has minimal impact on the environment, and the corrosion is close to that in a neutral reaction [3]. However, little research focusing on one-pot EL production from cellulosic biomass catalyzed by extremely low acid has been reported.

The use of solid catalysts for one-pot EL production is increasingly important since they provide green alternative to homogeneous catalysts. There have been several reports about one-pot EL production from levulinic acid or furfuryl alcohol catalyzed by different solid catalysts [4–6]. However, levulinic acid and furfuryl alcohol as raw materials are of high costs with their present production technology. Recently, Peng presented a catalytic process for the direct EL production from glucose in the presence of solid acid catalyst $SO_4^{2-}/ZrO_2$, an EL yield of above 30 mol% was obtained at 200 °C for 3 h [7]. Zeolite USY can also be used as an efficient solid catalyst for one-pot EL production from glucose [8]. However, to our knowledge, most EL yields from glucose were lower than 50% (mole yield), and cellulosic biomass has rarely been used as a feedstock for EL production. The main reason is due to the lower catalytic activity and stability of solid acid catalysts in the process of EL production from cellulosic biomass. Therefore, it is necessary to develop an environmentally benign catalyst system with high activity and stability for one-pot EL production from cellulosic biomass.

Furfural residues (FRs) are industrial byproducts that are produced during the production of furfural from corncobs. Hemicelluloses of corncobs can be converted to furfural under acidic conditions, and the wasted residues are mainly composed of cellulose and lignin, with about 45% of the component being cellulose [9]. Generally, most of residues are burned as waste, which not only increases the release of greenhouse gases but also result in loss of a valuable biomass resource. Thus, it is worthwhile to use such cellulose-rich wastes for one-pot production of EL. In this study, a mixed catalytic system comprising of extremely low acid and zeolite USY was firstly explored for catalytic conversion of glucose to EL, then followed by optimization of the process of EL production from FRs. The objective is to develop an efficient one-pot process for EL production from renewable biomass.

## 2. Experimental

### 2.1. Material

Glucose, ethanol and sulfuric acid were analytical grade from Kermel Chemical Reagent (Tianjin, China). EL, ethyl glucoside (EG) and 5-ethoxymethylfurfural (EMF) used as the standard with the purity of over 99% were purchased from Sigma-aldrich. Wasted FRs were provided by local furfural factory (Anyang, China), and screened with 40 meshes after being dried at 100 °C for 6 h. The average contents of cellulose, hemicellulose and lignin were 40.98 ± 0.4%, 0.37 ± 0.03% and 34.97 ± 0.3%, respectively. Zeolite solid catalyst USY (NKF-7) is a commercial material (Tianjin, China). USY was calcined at 400 °C for 4 h before use. Other chemicals were all of analytical grade from Sinopharm Chemical Reagent Company (Shanghai, China) and used without further purification. Deionized water was used for all experiments.

### 2.2. Experimental equipment

All the experiments were carried out in a 0.2 L cylindrical pressurised reactor made of stainless steel (316 L). The reactor was equipped with an electrical heating jacket and a magnetic stirrer. For each experiment, glucose or FRs, ethanol, and a given amount of acid catalysts were added into the reactor, and the total reaction volume was 80 mL. Then, the reactor was sealed and heated to the desired temperature by the adjustable heating jacket, and the stirring rate of the magnetic stirrer was set to 500 rpm. The reaction temperature was monitored by a thermocouple with the accuracy of ±0.5 °C connected to the reactor, and the reaction performed at an elevated temperature range of 170–210 °C. After desired reaction duration, the reactor was quenched in an ice cool water bath to terminate the reaction. The reaction liquid was filtered and collected for analysis.

### 2.3. Analytical methods

The EL concentration was determined by gas chromatography using a flame ionisation detector. The amounts of EG and EMF in the liquid were analyzed on an Agilent 1260 HPLC system equipped with a RID detector (Bio-Rad Aminex HPX-87H columns, 60 °C, $H_2SO_4$ 0.005 mol/L, 0.6 mL/min), and the liquid products were also confirmed by GC-MS (Thermo Fisher Scientific Trace GC ULTRA-DSQIIMS, USA) [10]. X-ray diffraction (XRD) pattern of USY was carried out using a Philips X' pert ProX-ray diffractometer system with the Cu Ka radiation ($\lambda = 0.154$ nm) operated at 40 kV and 40 mA over a $2\theta$ range of 5–60° at a scanning speed of $4° \text{ min}^{-1}$. The KBr pellet technique was applied for determining IR spectra of USY. Spectra were recorded on a Nicolet-IR 200 FT-IR spectrometer with 4 $\text{cm}^{-1}$ resolution, and the scanning range was from 400 to 4000 $\text{cm}^{-1}$. The EL yield (in mole %) from glucose was calculated using Eq. (1), where $C_{G0}$ and $C_{EL}$ are the initial mole concentrations of glucose and EL, respectively.

$$\text{EL yield}(\text{mole }\%) = C_{EL}/C_{G0} \times 100\% \quad (1)$$

Eq. (2) was used to calculate the EL yield from FRs (based on the weight), and Eq. (3) was used to calculate the theoretical EL yield from FRs.

$$\text{EL yield}(\%) = M_{EL}/M_{FRs} \times 100\% \quad (2)$$

$$\text{Theoretical EL yield}(\%) = M_{Cellulose} \times 0.89/M_{FRs} \times 100\% \quad (3)$$

where $M_{EL}$, $M_{Cellulose}$ and $M_{FRs}$ are the EL content after reaction (g), the cellulose content (g) and FRs content before reaction (g), respectively.

### 2.4. Experimental design and modeling

A Box-Behnken design was used to design the experiments for optimizing one-pot EL production from FRs. According to the preliminary tests, the sulfuric acid concentration was fixed to 0.1%, and the USY loading was chosen as one of the variables. Moreover, EL yield was chosen as the response variable, while reaction temperature ($X_1$), USY loading ($X_2$), mass ratio of liquid to FRs ($X_3$) and reaction time ($X_4$) were chosen as four independent variables. The levels of independent variables in the reaction are shown in Table 1. Then, artificial neural network (ANN) was introduced to obtain a model that can be used to predict the EL yield. A back propagation network was designed with Levenberg–Marquardt training algorithm by using MATLAB 7.0 Neural Network Toolbox. Genetic algorithm (GA) was further be used to optimize the EL