



Cellulose reactivity in ethanol at elevated temperature and the kinetics of one-pot preparation of ethyl levulinate from cellulose



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ABSTRACT

Cellulose reactivity in ethanol at elevated temperature (170–210 °C) was investigated in this study. Water and acid catalyst can improve the solubilization and the conversion of cellulose in ethanol. In ethanol/water medium, more humic solids will be formed, but the amounts of diethyl ether decreased greatly. In ethanol medium, the ethanolysis reaction of cellulose played a dominant role, with ethyl levulinate (EL) as the main liquid product. In addition, organic esters and furan derivatives were the main small molecules in the liquid, and diethoxymethane and diethyl sulfate were considered as the main liquid by-products. On the basis, the kinetics of one-pot preparation of EL from cellulose was further investigated at a temperature range of 170–210 °C and an acid concentration range of 0.5–2.0 wt%. Artificial Neural Network (ANN) was employed to develop an approach for the evaluation of the process. A good agreement of the ANN model results and the experimental data was obtained, and the optimum reaction conditions for one-pot preparation of EL were temperature 188 °C, reaction time 30 min, acid concentration 1.2 wt%. Under the conditions, higher EL yield can be obtained, which was close to the ANN model result.

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1. Introduction

With the depletion of fossil carbon resources like crude oil, coal and natural gas, researchers are keen to find substitutes for the non-renewable resources [1,2]. As a kind of biomass-derived carbohydrates, cellulose can be a source of sugar and sugar-based molecules. Latest efforts have focused on converting cellulosic biomass into new platform chemicals and biofuels in one-pot procedure [3,4]. Many studies have been contributed to the one-pot production of glucose, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) from cellulose [5–7]. Different solvents, like water, alcohol, acetone and ionic liquids were used in these processes [8–10]. Among these, ethanol is regarded as a new kind of green solvent for the conversion of cellulosic biomass. Ethanol can be produced from the renewable biomass, and some new platform chemicals with potential industrial applications, like 5-ethoxymethylfurfural (EMF) and ethyl levulinate (EL), can be obtained from cellulosic biomass in ethanol medium [11–13].

EL is a kind of important platform chemicals, which not only can be used in flavoring and fragrance industries, but also can be used as octane booster for gasoline and fuel extender for diesel [14,15]. Several studies have been reported on the production of EL from cellulosic biomass. For example, Mascall [16] commented on the processes for one-pot conversion of cellulose into EL, and the EL yield is on the order of 20%. Garves [17] investigated the degradation of cellulose by alcohols and liquid acid-catalysts and obtained the yield of EL was 44%. Mao et al. [18] developed a new process for the acid-catalyzed conversion of cellulosic biomass into EL, and the EL yield from wood chips was 44.4%. Our group reported the process for one-pot production of EL from wheat straw, and the results suggested that wheat straw can be used as potential raw materials for the one-pot production of EL [19]. Meanwhile, we also investigated the conversion of furfural residues to EL catalyzed by a combination of different acid catalysts [20].

Although such reports showed that direct conversion of cellulosic biomass in ethanol medium allows for the conventional multi-steps process to such platform chemicals in one-pot process, they mainly focused on the feasibility of EL production from cellulosic biomass. To our knowledge, little research on the cellulosic biomass reactivity in ethanol has been reported, and little information about

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the kinetics of one-pot production of EL has ever been proposed. Cellulose is a polysaccharide which usually is chosen as the mode material for the conversion of cellulosic biomass. Thus, the objective of this study is to investigate the cellulose reactivity in ethanol at elevated temperature. Moreover, the kinetics study on one-pot production of EL from cellulose was also investigated. In this study, the kinetics modeling was proposed by using artificial neural network (ANN) method, and the kinetics of one-pot preparation of EL was also evaluated. These results will be helpful to get insight into the conversion process of cellulose in ethanol, and also can provide important references for one-pot production of EL from cellulosic biomass.

2. Experimental

2.1. Materials

Microcrystalline cellulose (90 μm) was used as received from Aladdin Reagent (Shanghai, China). Ethyl levulinate, glucose and levulinic acid with the purity of over 99% were also obtained from Aladdin Reagent (Shanghai, China). Ethanol and sulfuric acid were all of analytical grade from Kermel Chemical Reagent (Tianjin, China). Deionized water was used for all experiments.

2.2. Experimental

All the experiments were carried out in a 200 mL cylindrical pressurized reactor, which was made of stainless steel (316L) to resist corrosion. 5.33 g Cellulose substrate, 80 mL pure ethanol (100%) or 80 mL ethanol solution in the absence of acid catalyst were mixed and poured into the reactor according to experimental design. Thus, the ratio of liquid to solid was 15 (volume: mass). For comparison, cellulose substrate and pure ethanol or ethanol solution in the presence of acid catalyst were also reacted under the same reaction conditions. Sulfuric acid was used as the acid catalyst due to its lower price and high activity, and the acid concentration was at the range of 0.5–2.0 wt%. The reactor was heated in a salt bath with the temperature of 300 °C to achieve the desired temperature of the reaction medium in 3 min. Then, the reactor was transferred into another salt bath with lower temperature to keep the temperature of the reactor contents constant. Both salt baths were controlled by an adjustable electric heater with a digital readout. The temperature of reactor contents was monitored by a calibrated thermocouple with the accuracy of ± 0.5 °C, and the reactions were performed at an elevated temperature range of 170–210 °C. Each run of tests started with the medium in the reactor heated to the desired temperature. After running the reaction for a desired duration, the reactor was quenched by immersing in a cool ice water bath to terminate the reaction. When the temperature of the medium was lower than 40 °C in 15 min, a reserve tank containing ice-cold ethanol was connected to the reactor. Then, the gas phase was slowly transferred from the reactor, and the amount of diethyl ether (DEE) in ethanol was calculated considering the mass changes of the reserve tank before and after the reaction. After that, samples were filtered with a 0.2 μm syringe filter, and the filtrate was collected and stored in a 4 °C refrigerator prior to analysis.

2.3. ANN modeling

To develop a modeling of one-pot preparation of EL from cellulose, ANN method was introduced in this study. ANN is a collection of interconnecting computational elements, which function like neurons in biological brain. It has the ability to model processes by learning from input and output data, without

mathematical knowledge of the process [21]. Therefore, ANN may be an effective way to emulate the complicate ethanolysis process.

ANN was used as models associating the process parameters to the EL yield. The topology of the ANN was fixed to three layers, including input layer, output layer and hidden layer. A back propagation network was designed with Levenberg–Marquardt training algorithm by using MATLAB 7.0 Neural Network Toolbox. The tangent sigmoid and pure linear functions were used as the transfer functions in the hidden and output layers of the ANN, respectively. The system adjusts the weights of the internal connections to minimize errors between the network output and target output, and the performance of the ANN model was statistically measured by Mean Squared Error (MSE) and regression coefficient obtained as follows:

$$\text{MSE} = \frac{1}{N} \sum_{i=1}^N (y_i - y_{di})^2 \quad (1)$$

$$r^2 = 1 - \frac{\sum_{i=1}^N (y_i - y_{di})^2}{\sum_{i=1}^N (y_{di} - y_m)^2} \quad (2)$$

where N is the number of data, y_i is the predicted yield of ethyl levulinate by ANNs, y_{di} is the experimental yield of ethyl levulinate, y_m is the average of actual yield of ethyl levulinate, and r^2 is regression coefficient. The network having minimum MSE and maximum r^2 was selected as the best ANN model.

2.4. Analytical methods

The amount of EL was determined by a gas chromatography (Shimadzu GC-14C, Japan) with a flame ionization detector. EL was separated on a FFAP capillary column (30 m \times 0.32 mm \times 0.33 μm) and programmed temperature range of 90–210 °C with nitrogen as the carrier gas. The 1-octanol was used as internal standard [16]. The amounts of glucose and LA 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). In addition, the reaction products were also confirmed by GC-MS (Thermo Fisher Scientific Trace GC ULTRA-DSQIIMS, USA) using a capillary column DB-624 (60 m \times 0.32 mm \times 1.8 μm) qualitatively. The temperature of the injection was 240 °C. The temperature of the column was maintained at 40 °C for 2 min and then raised to 220 °C with a ramp rate of 10 °C/min. The amount of diethyl ether (DEE) form ethanol was calculated according to weight changes of reserve tank before and after the reaction [22]. X-ray diffraction (XRD) profiles of untreated cellulose and residues after reaction were collected, and the samples were taken in powdered form and analyzed by using a Philips X'pert Pro X-ray diffractometer system with the Cu K α radiation ($\lambda = 0.154$ nm). The measurements were conducted at 40 kV and 40 mA over a 2θ range of 5–60° at a scanning speed of 4° min⁻¹. The KBr pellet technique was applied for determining IR spectra. Spectra were recorded on a Nicolet-IR 200 FT-IR spectrometer with 4 cm⁻¹ resolution. The scanning range was from 400 to 4000 cm⁻¹.

The following equation (3) and equation (4) were used to calculate the mass change ratio of solids and the mole yield of liquid products, respectively, where m_0 is the initial amount of untreated cellulose (g), m_1 is the amount of recovered solids after reaction (g).

$$\text{Mass change ratio (\%)} = (m_0 - m_1)/m_0 \times 100\% \quad (3)$$

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