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Efficient microwave-assisted production of biofuel ethyl levulinate from corn stover in ethanol medium

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ABSTRACT

Levulinate esters are versatile chemicals that have been used in various fields. Herein, the production of ethyl levulinate (EL) from corn stover was investigated under microwave irradiation. Several reaction parameters, including acid concentration, reaction temperature, reaction time, and liquid-to-solid mass ratio, were investigated to evaluate the reaction conditions. Response surface methodology (RSM) was employed to optimize the reaction conditions for the production of EL. A quadratic polynomial model was fitted to the data with an R^2 value of 0.93. The model validation results reflected a good fit between the experimental and predicted values. A high conversion yield (58.1 mol%) was obtained at the optimum conditions of 190 °C, 30.4 min, 2.84 wt% acid, and 15 g/g liquid-to-solid mass ratio. Compared with conventional heating, microwave irradiation facilitated the conversion of corn stover to EL by dramatically shortening the reaction time from several hours to ~30 min. Thus, microwave-assisted conversion of corn stover to EL is an efficient way of utilizing a renewable biomass resource.

1. Introduction

Owing to the decrease in petroleum resources and gradual deprivation of the environment, the development of renewable resource has attracted increasing interest in recent years. As the only carbon-based renewable resource, biomass, with the advantage of abundant availability, is regarded as a promising alternative to nonrenewable resources for the sustainable production of biofuels and high-value-added chemicals [1–3]. In recent years, levulinate esters (e.g., methyl levulinate, ethyl levulinate, and butyl levulinate) have been deemed "second generation" biofuels and bio-additives in transportation fuels [4,5]. As stated by the U.S. Department of Energy and the Pacific Northwest National Laboratory, levulinate esters are important chemicals owing to their unique physicochemical properties, which contribute to plentiful potential applications in the flavoring, pharmaceutical, and fragrance industries [6–10]. Moreover, levulinate esters are promising substrates for conversion to numerous chemicals of industrial significance, such as γ-valerolactone and its derivatives [10,11].

Recently, an increasing number of reports have focused on the direct conversion of saccharides [6,12–14] or cellulose [15–17] into levulinate esters with 13–80 mol% yields varying with different reactants and catalysts. However, as plant material is cheap and readily available, it is more valuable to use lignocellulosic biomass instead of model compounds, such as pure cellulose and glucose, for the production of levulinate esters. In the last few years, wood chips, wheat straw, and bamboo have been catalyzed by sulfuric acid to produce alkyl levulinates with corresponding alcohols at a 22–83 mol% yield [18–21]. Furfural residues were also used in the EL production at 51 mol% using sulfuric acid and zeolite USY mixed acid system [22]. Corn stover is a cheap and abundant lignocellulosic feedstock in China; however, most of this material is wasted. In 2013, the output of corn stover in China was about 2.4×10^8 metric tons, ranking first in amount among all crop straws. Further, approximately 5.7×10^7 metric tons of corn stover was burned directly, resulting in serious environmental pollution and resource waste [23]. As the Chinese government has strictly prohibited stalk burning since 2014, it is imperative to find efficient uses for corn stover.

However, owing to the complexity of biomass, it generally takes several hours to reach the reaction equilibrium in the production of levulinate esters [18–22]. Microwave irradiation is an alternative method widely used in organic synthesis that offers considerable advantages, such as shorter reaction times and higher

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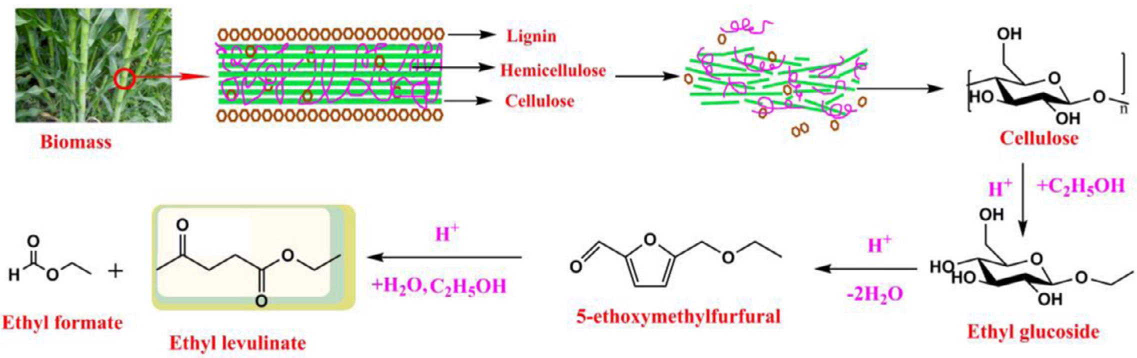

Scheme 1. Proposed reaction pathway for the microwave-assisted conversion of biomass to EL in ethanol, according to previous reports [16,21].

product yields, which cannot be achieved through conventional heating methods [24–26]. We previously reported that microwave heating could facilitate esterification reactions of lignocellulose [27].

Thus, microwave was applied for the efficient production of ethyl levulinate (EL) from corn stover in ethanol medium to enhance the added value of the agriculture wastes (Scheme 1). Ethanol was used as the solvent, as it can also be derived from biomass, making the process sustainable. In this study, we studied the effects of sulfuric acid catalyst concentration, reaction temperature, reaction time, and liquid-to-solid mass ratio on corn stover-derived EL production. Response surface methodology (RSM) was applied to evaluate the interactions of the parameters and determine the optimum conditions for the production of EL. In addition, the conversion of EL under different heating methods was compared to evaluate the influence of microwave heating on the reaction process.

2. Experimental

2.1. Materials

The corn stover raw material was collected from the Shangzhuang Experiment Station of China Agricultural University in Beijing, China. The corn stover used in the experiment was milled and screened through a 40-mesh screen and then dried at 105 °C for 48 h. The cellulose, hemicellulose, and lignin contents in the corn stover were 33.16%, 16.25%, and 16.61%, based on weight respectively, as determined using NREL standard laboratory analytical procedures [28]. EL (>98%; TCI, Shanghai, China) was used as a standard. All other chemicals were analytical reagents (Beijing Chemical Plant, Beijing, China) and used without further purification.

2.2. Microwave-assisted alcoholysis of corn stover

Microwave-assisted alcoholysis of corn stover was carried out in a microwave apparatus using 100 mL closed Teflon reaction vessels under pressure (ETHOS® RT microwave digestion–extraction system, Milestone Co., Sorisole, Italy). Given amounts of corn stover (1–5 g), ethanol (15 g), and concentrated sulfuric acid (1–4 wt%) were mixed in the Teflon reaction vessels and then heated to predefined temperatures (160–200 °C) within 1 min for specified reaction times (10–50 min) at an initial microwave power of 600 W. A magnetic stirrer was used during the reaction. After the reaction time elapsed, the reaction vessels were cooled to room temperature using the air-cooling device of the microwave apparatus before collecting the alcoholysis products. Aliquots of the samples were diluted with methanol in a 50 mL volumetric flask and then filtered through an organic membrane filter (0.22 μm pore size) before analysis. All experiments were conducted in duplicate.

2.3. Analytical methods

EL in the liquefaction products was analyzed using gas chromatography (Shimadzu GC-2014C, Kyoto, Japan) equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). Nitrogen was used as the carrier gas. The injection volume was 2 μL, and the temperature program was as follows: 50 °C for 2 min, increase at 6 °C/min to 180 °C for 3 min, then increase at 10 °C/min to 250 °C and hold for 8 min. The concentration of EL in the samples was determined using standard curves obtained by quantitative analysis of standard solutions of known concentration. The products in the reaction mixture were identified by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890A/5975C system (Santa Clara, CA, USA) equipped with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and helium as the carrier gas. The temperature program was the same as that used on GC. Mass spectra were scanned from m/z 30 to 600 at a rate of 1.5 scans/s and the electron impact ionization energy was 70 eV.

The yield (based on mole, mol%) of EL from corn stover was calculated according to the reaction stoichiometry using the following equations:

$$\text{Yield of EL (mol\%)} = \frac{\text{Mole of EL after reaction (mol)}}{\text{Theoretical yield of EL (mol)}} \times 100\% \quad (1)$$

$$\text{Theoretical yield of EL (mol)} = \frac{\text{Cellulose content of corn stover (g)}}{\text{Molecular weight of anhydroglucose (g/mol)}} \quad (2)$$

2.4. Response surface methodology

A rotatable central composite design (CCD) with four factors was applied to evaluate the interactions of the parameters and determine the optimum reaction conditions for microwave-assisted conversion of corn stover to EL. The design comprised 31 experimental runs, including seven replicates at the center point that were applied to obtain an estimate of the experimental error. The independent variables and the corresponding five variable levels selected for the synthesis of EL (reaction temperature (X_1, 160–200 °C), reaction time (X_2, 10–50 min), liquid-to-solid mass ratio (X_3, 5–25 g/g), and acid concentration (X_4, 1–5 wt%)) are shown in Table 1.

The SAS 9.0 software (SAS Institute, Cary, NC, USA) was used to design the CCD and analyze the experimental data. The