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Production of ethyl levulinate by direct conversion of wheat straw in ethanol media

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HIGHLIGHTS

- ▶ Ethyl levulinate can be produced from wheat straw by direct conversion in ethanol media.
- ▶ The higher yield of ethyl levulinate 17.91% can be obtained, representing a theoretical yield 51.0%.
- ▶ Wheat straw is a good material for ethyl levulinate production.

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ABSTRACT

The production of ethyl levulinate from wheat straw by direct conversion in ethanol media was investigated. Response surface methodology (RSM) was applied to optimize the effects of processing parameters, and the regression analysis was performed on the data obtained. A close agreement between the experimental results and the model predictions was achieved. The optimal conditions for ethyl levulinate production from wheat straw were acid concentration 2.5%, reaction temperature 183 °C, mass ratio of liquid to solid 19.8 and reaction time 36 min. Under the optimum conditions, the yield of ethyl levulinate 17.91% was obtained, representing a theoretical yield of 51.0%. The results suggest that wheat straw can be used as potential raw materials for the production of ethyl levulinate by direct conversion in ethanol media.

1. Introduction

In view of declining petroleum resources, conversion of cellulosic biomass has recently received great attention due to the possibility of becoming an alternative source for the sustainable production of chemicals and fuels. The cellulosic biomass is the most abundant renewable resources available, and it is currently viewed as the feedstock for the green chemistry of the future (Bozell, 2010). The cellulosic biomass can be converted to various chemicals (e.g. sugar, furfural, 5-hydroxymethyl furfural, levulinic acid) by hydrolysis reaction under various conditions (Sen et al., 2012). For example, Chareonlimkun et al. (2010) studied the catalytic conversion of cellulosic biomass (e.g. rice husk, sugarcane bagasse, corncob) in the presence of TiO_2, ZrO_2 and mixed-oxide TiO_2–ZrO_2 under hot compressed water (HCW) conditions, whereas Ya'aini et al. (2012) investigated the conversion of glucose, empty fruit bunch and kenaf to levulinic acid over a new hybrid catalyst. Among various chemicals that can be converted from cellulosic biomass, ethyl levulinate (EL) is a versatile chemical feedstock with numerous potential industrial applications (Pasquale et al., 2012). Ethyl levulinate has been applied in the flavoring and fragrance industries (Zhang et al., 2011). Moreover, it can be used up to 5 wt.% as the diesel miscible biofuel directly in regular diesel car engines. Adding ethyl levulinate to the diesel can result in a clean burning fuel with high lubricity, flashpoint stability, reduced sulphur content and improved viscosity (Joshi et al., 2011).

Two different routes have been reported for ethyl levulinate production from cellulosic biomass. The first route is through esterification of levulinic acid with ethanol in the presence of catalyst, such as mineral liquid acid, solid acid or immobilized lipases (Fernandes et al., 2012; Lee et al., 2010; Mao et al., 2011; Pasquale et al., 2012; Saravanamurugan et al., 2011; Saravanamurugan and Riisager, 2012). Thus, two reaction steps are needed from cellulosic biomass to ethyl levulinate. Firstly, levulinic acid is produced from cellulosic biomass by acid hydrolysis (Bozell and Petersen, 2010), then the esterification of the levulinic acid with ethanol. The second route is direct production of ethyl levulinate from cellulosic biomass by acid catalyzed reaction in ethanol media. This method provides a convenient one-step reaction to produce ethyl levulinate, compared with two-step reactions involving purification of levulinic acid. In addition, the latter route has several advantages, like minimized wastewater discharged and higher grade products

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easily isolated by fractionation. The direct conversion of cellulosic biomass into ethyl levulinate has been regarded as a promising method (Peng et al., 2011). Several studies have been reported on the ethyl levulinate production by direct conversion of cellulosic biomass. However, most yields reported were lower than 50% (based on theoretical yield). In detail, Garves (1988) investigated the degradation of cellulose by alcohols and strong acid-catalysts, and the yield of 44.0% was obtained. Mao et al. (2011) developed a new process for the acid-catalyzed conversion of cellulosic biomass into ethyl levulinate, and the highest yield of ethyl levulinate from wood chips was 44.4%. Therefore, it is necessary to optimize the process to improve the yield of ethyl levulinate.

Wheat straw is a kind of renewable, cheap and widely available cellulosic biomass. But, most of them are directly burned without any disposal in China, which pollutes the environment and wastes the biomass resource. For utilizing wheat straw effectively, researchers try to convert them into some important chemicals, like cellulosic ethanol (Badawi et al., 2012). However, to the best of our knowledge, little research has been reported on the ethyl levulinate production from wheat straw. To enhance the value of wheat straw, the direct conversion of wheat straw into ethyl levulinate in ethanol media might be a new alternative use for the abundant cellulosic biomass. Response surface methodology (RSM) is a statistical tool for designing experiments, building empirical models, and evaluating the effects of factors (Duarte et al., 2011). Several variables of the process, including reaction temperature, acid concentration, ratio of liquid to solid and reaction time were selected as the factors of experimental design by preliminary tests in this study. Thus, the aim of this work was to evaluate the effects of the variables on the production of ethyl levulinate and determine the process conditions to optimize the production.

2. Experimental

2.1. Materials

The raw material used in experiments was wheat straw collected in a local farm (Zhengzhou, China). The straw was air-dried, milled, screened to select the fraction of particles with a size 20–40 mesh. The main composition of wheat straw was: cellulose 39.5 ± 0.3%, hemicelluloses 17.7 ± 0.7% and lignin 15.9 ± 0.4%. Ethyl levulinate used as the standard with the purity of over 99% were 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 equipment

The experiments of direct conversion of wheat straw in ethanol media were carried out in a 200 ml cylindrical pressurized reactor, which was made of stainless steel (316L). Wheat straw, ethanol, and a given amount of concentrated sulfuric acid were mixed in the reactor, and the total reaction volume was 70 ml. The reactor was heated by placing it in a high temperature salt bath, which was controlled by an adjustable electric heater and thermostat. A K-type thermocouple was inserted into the reactor, and the temperature inside the reactor was measured to ensure the accuracy of the salt bath temperature setting. The reactions were conducted at a temperature range of 180–200 °C, sulfuric acid concentration range of 1.0–3.0 wt.%, reaction time range of 15–45 min and the ratio of liquid to solid range of 15–25, respectively. After running the reaction for a desired duration, the reactor was quenched by quickly immersing in a cool water bath to terminate the reaction. After quenching, the sample was filtered and analyzed. All experiments were performed in duplicated and average values were reported.

2.3. Analytical methods

Samples were filtered and washed with ethanol, and the filtrate made up to volume in a 100 mL volumetric flask. The concentration of ethyl levulinate was determined by a gas chromatography with a flame ionization detector (FID). Ethyl levulinate was separated on an FFAP capillary column (30 m × 0.32 mm × 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. The reaction products were also confirmed by GC–MS (Thermo Fisher Scientific). Physical changes in the native and the residues of wheat straw were observed by scanning electron microscopy (SEM). Images of the surfaces were taken at magnification 1000× using a scanning electron microscope (JSM-7500F). X-ray diffraction (XRD) profiles of wheat straw fibers before and after reaction were collected, and the samples were taken in powdered form and analyzed by using a Philips X'pert ProX-ray diffractometer system.

Eq. (1) was used to calculate the yield of ethyl levulinate from wheat straw (based on the weight), and Eq. (2) was used to calculate the theoretical yield of ethyl levulinate from wheat straw.

$$\text{Yield of ethyl levulinate } (\%) = \text{Ethyl levulinate content after reaction (g)}/\text{Wheat straw content before reaction (g)} \times 100\% \quad (1)$$

$$\text{Theoretical yield of ethyl levulinate } (\%) = \text{Cellulose content (g)} \times 0.89/\text{Wheat straw content before reaction (g)} \times 100\% \quad (2)$$

2.4. Response surface methodology

The Box–Behnken experimental design, with four variables, was used to study the response pattern and to determine the optimum combination of variables. The effects of the X_1 (acid concentration), X_2 (reaction temperature), X_3 (liquid:solid mass ratio) and X_4 (reaction time), at three variables levels (Table 1) in the reaction process are shown in Table 1. For statistical calculation, the variables are coded according to Eq. (3).

$$x_i = (X_i - X_0)/\Delta X \quad (3)$$

where x_i is the coded value of the independent variable, X_i is the real value of the independent variable, X_0 is the real value of the independent variable on the center point and ΔX_i is the step change value. The specific codes were:

$$x_1 = (X_1 - 2)/1 \quad (4)$$

$$x_2 = (X_2 - 190)/10 \quad (5)$$

$$x_3 = (X_3 - 20)/5 \quad (6)$$

$$x_4 = (X_4 - 30)/15 \quad (7)$$

Table 1
Independent variable values of the process and their corresponding levels.

Independent Variable	Symbol		Levels		
	Uncoded	Coded	−1	0	1
Acid concentration (wt.%)	X_1	x_1	1	2	3
Reaction temperature (°C)	X_2	x_2	180	190	200
Liquid:solid ratio (w/w)	X_3	x_3	15:1	20:1	25:1
Reaction time (min)	X_4	x_4	15	30	45