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# Catalytic pyrolysis of corn straw with magnetic solid acid catalyst to prepare levulinic acid by response surface methodology

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ABSTRACT

This study investigated methods to optimize the process conditions for preparing levulinic acid (LA) using magnetic ferric oxide/$SO_4^{2-}$ biomass-based solid acid, to catalyze pyrolysis of corn straw using response surface methodology (RSM). The measured parameters were quality of liquid-solid ratio (QLSR), catalyst dosage (CDe), hydrolysis temperature (HT) and hydrolyzation duration (HD). The mathematical model of the quadratic polynomial of LA had a P-value less than 0.005, and the loss of quasi P-value was less than 0.01; the $R^2$ value of 0.9969 indicates that the model was highly significant. The coefficient of variation was 3.02% (< 10%), indicating that the model had high reliability. The optimal process conditions for preparing LA were determined by analyzing the three-dimensional surface and contour plots with a regression model equation. Using the Box-Behnken design to optimize the process conditions, the most favorable values of QLSR, CDe, HT and HD were 17.2:1 (V/W, mL:g), 3 g, 249.66 °C, and 67.3 min, respectively. Under optimized conditions, the maximum yield of LA was 23.17%, compared to the predicted value of 23.05%; the relative deviation between the two methods was 0.12%, indicating good repeatability. This study demonstrates that using RSM to optimize the conditions of LA preparation is feasible and has a very good application value.

## 1. Introduction

With the depletion of fossil fuel resources, the transformation and utilization of renewable resources has gained greater international attention (Zhao et al., 2014). Agriculture and forestry biomass is an important alternative to fossil fuel resources. The use of agricultural and forestry biomass as a raw material in the preparation of platform compounds and high value-added chemicals has been researched extensively (Xin et al., 2013). Aqsha et al. used a thermogravimetric analyzer and a bench-scale horizontal fixed-bed reactor to pyrolize straw biomass to better understand the devolatilization process, and to investigate product yields (Aqsha et al., 2017). Yang et al. optimized operating conditions to produce hydrogen-enriched syngas from the catalytic pyrolysis of biomass with Fe/CaO catalyst derived from a layered double hydroxide precursor (Yang et al., 2017). Barnés et al. studied the chemistry of the liquefaction process of wood and various model components to produce bio-oil at high temperatures (Barnés et al., 2017). Agarwal et al. evaluated the liquefaction/depolymerization of humins by catalytic pyrolysis to convert C-6 sugars to platform chemicals, such as hydroxymethylfurfural and levulinic acid (LA) (Agarwal et al., 2017). LA, a transformant that has been extensively studied (Van de Vyver et al., 2012), is a multi-functional platform compound (Omari et al., 2012) formed from the pyrolysis of lignocellulose by catalysts. LA has very good reactivity and is used widely for esterification, redox, and substitution reactions (Rackemann and Doherty, 2011). The formation mechanism is shown in Fig. 1. The preparation method is based on the raw materials used and is divided into furfuryl alcohol catalytic pyrolysis and biomass pyrolysis. Systems to produce LA and furfural from lignocellulosic polysaccharides using cellulose and xylan as model compounds (Sweygers et al., 2017), and catalyzed conversion of lignocellulosic biomass to LA in ionic liquid (Ya'aini and Saidina Amin, 2013), have been investigated. There are a number of issues associated with the production of LA, including low yield, complex products, numerous by-products, difficult separation and environmental pollution. In the United States, the Biofine process produces high yields of LA, but requires high temperature, high

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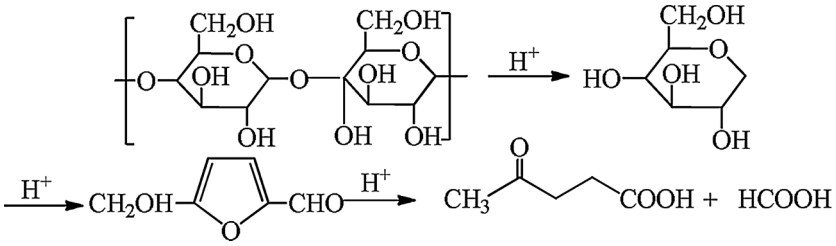


**Fig. 1.** Mechanism of levulinic acid (LA) formation.

pressure and acid equipment as a reactor, which represents a significant investment cost. A new method for LA preparation is needed to address these issues. At present, the research direction of most of the solid acid catalysts used to catalyze the pyrolysis of biomass has become a key technology for biomass conversion. In 2015, Zhang et al. used corn straw as carbon materials to optimize the condition of biomass-based solid acid catalyst preparations (Zhang et al., 2015). Lou et al., studied a solid acid catalyst containing a high density of $-SO_3H$ group that was prepared from cheap cellulose by incomplete carbonization and sulfonation (Lou et al., 2014); but biomass is comprised of many oxygen-containing functional groups that would fall off in the form of water during the carbonization process, which will reduce the carbon carrier yield (Keiluweit et al., 2010) and the catalytic activity of catalysts is also influenced by many factors; therefore, the study of magnetic solid acid catalysts has gradually become a trend of development in the catalyst industry. Li et al. used response surface method to prepare the optimal technological conditions of biomass-based precursor and using the sol-gel method to prepare magnetic $Fe_3O_4$ particles, and magnetic $Fe_3O_4$ particles were loaded on the surface and internal channel of biomass-based precursor to prepare a magnetic biomass-based solid acid catalyst (Li et al., 2015); the performance of four kinds of carbon-based magnetic solid acid catalysts were studied and all the catalysts have good catalytic activity (Li et al., 2017).

In this study, response surface methodology (RSM) was used to investigate the optimal process conditions to prepare LA using magnetic iron oxide/$SO_4^{2-}$-biomass-based solid acid (MIO/$SO_4^{2-}$ B-BSACs) as a catalyst and biomass raw material as a carbon precursor. Utilization of biomass resources addresses several environmental and energy problems, laying a solid foundation for the future use of biomass-based chemicals.

## 2. Experimental design

### 2.1. Raw materials and pretreatment

Corn straw was obtained from the Henan biomass energy key lab. Crushing, screening and pretreatment produced biomass-based precursors with a particle size < 0.15 mm (100 mesh).

Corn straw powder was mixed with 2% sodium hydroxide solution, and placed in a smart microwave chemical reactor (80 °C, 500 W microwave power) for 15 min. Separation, purification, filtration, and residue-filtering with repeated washing with distilled water produced a neutral, dry, grinding product.

### 2.2. Elemental and composition analysis of corn straw

The moisture, ash and volatiles of corn straw and coal were determined using a GYFX-610 automatic industrial analyzer, Calorific value was measured using fully automatic rapid heating (0R2012). The ash and volatile contents of coal are 20.10% and 28.41%, respectively, while the values for corn straw are 5.00% and 50.18%, respectively (Table 1). As corn straw has low ash content and high volatility, it is an ideal raw material for pyrolysis and gasification. The calorific value of coal is 34.20 MJ $kg^{-1}$, which is much higher than that of biomass, primarily due to the high energy of C—C bonds compared to C—O and C—H bonds. Compared to coal, corn straw contains less nitrogen and sulfur, and produces less air pollution during combustion. Thus, corn straw is a low-pollution and high-calorie renewable energy source.

### 2.3. Magnetic catalyst preparation

#### 2.3.1. Preparation of biomass-based precursors

Corn straw biomass was carbonized at 549 °C for 13 h to obtain a black solid. Sulfuric acid ($H_2SO_4$) was used as the solvent to sulfonate the black solid at 121 °C for 6 h. After the mixture cooled, deionized water was added and the preparation was left to stand until the solid-liquid separation was complete. The preparation was filtered and repeatedly washed with boiling water, then dried in a constant temperature oven at 80 °C to obtain biomass-based precursor (Li et al., 2015).

#### 2.3.2. Preparation of magnetic iron oxide particles

A three-necked flask with 200 mL distilled water was heated in a water bath to 60 °C; 0.2 g sodium sulfite ($Na_2SO_3$) was then added to the flask and exposed to ultrasound for 30 min. Next, 16.68 g ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) and 28.35 g ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were added sequentially and stirred. $NH_3{\cdot}H_2O$ was added to maintain a pH of 10, and the ultrasound reaction continued for 60 min. The reaction temperature was adjusted to 80 °C and aged for 30 min. After cooling, the process was repeated with distilled water until the washing solution was neutral. A constant temperature vacuum box at 50 °C was used to dry the preparation and obtain magnetic iron oxide (MIO) particles.

The biomass-based precursor and MIO were mixed uniformly at a mass ratio of 1:2, added to a 1 mol/L $H_2SO_4$ solution, soaked for 24 h, and dried. The preparation was calcined in a muffle furnace at 500 °C for 3 h to obtain MIO/$SO_4^{2-}$ B-BSACs (Fig. 2).

#### 2.3.3. Preparation of levulinic acid

Pre-treated corn straw and MIO/$SO_4^{2-}$ B-BSACs were combined in a high pressure reactor with distilled water according to the mass ratio. The program temperature was set to a heating rate of 10 °C/min. The response surface software was used to adjust the quality of liquid-solid ratio (QLSR), hydrolyzation duration (HD), hydrolysis temperature (HT) and catalyst dosage (CDe) to optimize the process conditions for LA yield. The preparation flow chart is shown in Fig. 3.

Yield of LA was measured using high performance liquid chromatography (Agilent 1200LC, Santa Clara, CA, USA) with distilled water as the mobile phase (Li et al., 2016; Rackemann et al., 2016). The flow rate was 1.0 mL/min, the column temperature was 75 °C, the injection volume was 10 μL, and a Sugar Park 16.53 mm column model was used. LA yield was calculated using the following equation:

$$\text{Yield of LA}(R_l) = \frac{\text{Actual quality of LA(g)}}{\text{Theoretical quality of LA(g)}} \times 100\%$$

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