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Levulinic acid production from wheat straw

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Abstract

Studies were carried out on the effects of temperature, acid concentration, liquid:solid ratio and reaction time on levulinic acid production from wheat straw using response surface methodology. The *P*-value of the coefficient for acid concentration was 0.0002, suggesting that this was highly significant. The quadratic effects of temperature and liquid:solid ratio were also significant and their *P*-values were <0.0001 and 0.0027, respectively. The coefficient determination (R^2) was good for the second-order model. The optimal conditions for levulinic acid production from wheat straw were 209.3 °C, 3.5% acid concentration, 15.6 liquid:solid ratio and 37.6 min of reaction time resulted 19.86% yield.

Keywords: Levulinic acid; Wheat straw; Response surface methodology; Yield

1. Introduction

Levulinic acid is a short chain fatty acid having a ketone carbonyl group and an acidic carboxyl group. It is a versatile new platform chemical with numerous potential uses, which can be used as textile dye, antifreeze, animal feed, coating material, solvent, food flavoring agent, pharmaceutical compounds and resin (Bozell et al., 2000). Recently, the aggravation of energy crisis and the increasing petroleum oil prices are forcing the chemical industry to find alternative raw materials for the production of basic chemicals. Levulinic acid has the potential as an important basic chemical material.

Levulinic acid can be produced by heating hexose, or any carbohydrate containing hexose with a dilute mineral acid for an extended time (Harris, 1975). Many materials such as glucose, sucrose, fructose and biomass materials including wood, starch, cane sugar, grain sorghum and agricultural wastes have been used to produce levulinic acid (Moyer, 1942; Sassenrath and Shilling, 1966; Fang and Hanna, 2002). A US Patent (Fitzpatreck, 1995) described a continuous process for producing levulinic acid from carbohydrate-containing materials. The raw materials were supplied continuously to two consecutive reactors, and the materials were hydrolyzed into hydroxymethyl furfural (HMF) in the first reactor at between 210 °C and 230 °C for between 13 and 25 s in the presence of 1–5% mineral acid. HMF was hydrolyzed further in the second reactor at 195 and 215 °C for between 15 and 30 min to produce levulinic acid. Ghorpade and Hanna (1999) patented a continuous reactive extrusion technology for levulinic acid production. The slurry of starch mixed with mineral acid was extruded using a twin-screw extruder at 80–150 °C for between 80 and 100 s to produce levulinic acid. Farone and Cuzens (2000) described another method for the preparation of levulinic acid. The conversion from biomass to levulinic acid was achieved by hydrolyzed biomass at 40–240 °C for 1–96 h in the presence of 5–90% sulfuric acid.

Under acidic condition at elevated temperatures, carbohydrate decomposition can result in a variety of soluble and humiclike products, with levulinic acid and formic acid

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being the final soluble products from hexoses through an intermediate 5-hydroxymethyl-2-furfural (5-HMF). Horvat et al. (1985) proposed a mechanism of 5-HMF degradation, which two possible reaction routes may exist in the reaction process. One reaction route leads to the formation of 2,5-dioxo-3-hexenal, which undergoes the decomposition to levulinic acid and formic acid. The other reaction route results in the formation of polymers, thus reducing levulinic acid formation.

Wheat straw is a renewable, cheap and widely available biomass. Most of wheat straw is burnt directly in China, which results in sever environmental pollution. To enhance the value of wheat straw and decrease the pollution, new industrial uses of wheat straw need to be developed. The hydrolysis of wheat straw to produce levulinic acid can be a good alternative use for this abundant biomass. As a major source of carbohydrates, including cellulose, hemicellulose and lignin, if wheat straw can be directly used for levulinic acid production, the production cost of levulinic acid will be lower greatly.

Reaction temperature, acid concentration, liquid:solid ratio and reaction time were considered as four important variables which had much effect on levulinic acid production (Fang and Hanna, 2002). The objectives of this study were to investigate the possibility of utilizing wheat straw as the raw material for levulinic acid production, and to obtain the optimum conditions of the four variables under the experimental conditions applying response surface methodology.

2. Methods

2.1. Materials

Wheat straw collected from a local farm (Zhengzhou, China). The straw was air-dried, milled, screened to select the fraction of particles with a size lower than 0.5 mm and homogenized in a single let. The main composition of wheat straw was: cellulose 40.4%, hemicelluloses 25.6% and lignin 22.3%.

2.2. Experimental equipment

The experiments on the hydrolysis reactions were carried out in a cylindrical stainless steel (316L) pressurized reactor with inner diameter 35 mm, depth 130 mm and wall thickness 7.5 mm (volume about 125 ml). The temperature of the reactor contents was monitored by a thermocouple connected to the reactor, and a salt bath was used to heat the reactor. The salt bath temperature was controlled by an adjustable electric cooker and monitored using a thermal couple with digital readout. The reaction was stopped by quickly immersing the reactor in an ice water bath.

2.3. Levulinic acid yield analysis

Samples were filtered and washed with water and the filtrate was made up to 100 ml. The concentration of levulinic acid was determined by gas chromatography with a flame ionization detector (FID). Levulinic acid was separated on an FFAP capillary column (30 m × 0.32 mm × 0.33 μm) at a linear temperature program of 15 °C $\min^{-1}$ (initial 90 °C, final 210 °C, injector 240 °C, detector 250 °C). The butyric acid was used as internal standard. Levulinic acid yield based on the weight of raw material was calculated as: Yield of levulinic acid (%) = Levulinic acid content after reaction (g)/Wheat straw content before reaction (g) × 100%.

2.4. Experimental design of RSM

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

$$x_{ik} = (X_i - X_0)/\Delta X_i \tag{1}$$

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

$$x_1 = (T - 210)/20 \tag{2}$$

$$x_2 = (C - 3)/2 \tag{3}$$

$$x_3 = (R - 15)/5 \tag{4}$$

$$x_4 = (t - 30)/15 \tag{5}$$

The levulinic acid yield was taken as the dependent variables or response, Y_i. The model proposed for the response was given below:

$$Y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4$$

where Y_i was predicted response, β_0 was offset term, β_1, β_2 and β_3 were linear effect terms, β_{11}, β_{22}, β_{33} and β_{44} were squared effects and β_{12}, β_{13}, β_{14}, β_{23}, β_{24} and β_{34} were interaction effects. The significance of each coefficient of the above equations was determined by Student's t-test and

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

Independent variable	Symbol		Levels		
	Uncode	Coded	−1	0	1
Temperature (°C)	X_1	x_1	190	210	230
Acid concentration (%)	X_2	x_2	1	3	5
Liquid:solid ratio (w/w)	X_3	x_3	10:1	15:1	20:1
Reaction time (min)	X_4	x_4	15	30	45