Available online at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

Optimization design to study the effect of acid-catalyzed hydrolysis of corn stalk using severity and statistical model for high solid and liquid phase recovery

Yong-Gang Sun [a,b], Yu-Long Ma [a,b,*], Xuan Chang [b], Guan-Yu Pan [b], Yuan-Yuan Li [a]

[a] State Key Laboratory Cultivation Base of Energy Sources and Chemical Engineering, Ningxia University, Yinchuan 750021, China

[b] College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

ARTICLE INFO

Article history:
Received 18 June 2014
Received in revised form
15 March 2015
Accepted 31 March 2015
Available online 18 April 2015

Keywords:
Acid catalysis
Combined severity parameter
Total sugar recovery
Statistical model
Corn stalk

ABSTRACT

In this research, the effects of combined severity parameters (CSP), response surface methodology (RSM), and separation factor (SF) on the recovery and/or removal rate of main fraction for acid-catalyzed hydrolysis of corn stalk were defined and investigated. The results demonstrated that the maximum total sugar yield (44.31 wt%) was obtained from corn stalk after hydrolysis with 2.05 wt% of acid catalysis at 113.17 °C for 61.69 min ($CSP_0 = 1.80$) while the high glucan recovery (88.02%), de-pentosane rate (97.21%), and SF of solid phase fraction were obtained with CSP_0 range of 1.14–2.18 (CSP_1 range of 1.80–2.82). The findings suggest that CSP_1 can be used to more efficiently evaluate the separation degree of glucan with lignin ($SF_{G\text{-}L}$) than CSP_0. The acid-catalyzed hydrolysis of corn stalk has an advantage of high solid–liquid phase recovery and CSP can be used to describe the effect of acid hydrolysis.

1. Introduction

How to increase the utilization of cellulosic biomass has recently become an issue of great interest in the biorefinery area. Any effective pretreatment technology must provide an optimized utilization of cellulosic biomass toward isolated useful sugars for effective separation of lignin [1]. Pretreatment is one of the most expensive processing steps in biomass-to-reducing sugars conversion. Therefore, the rigorous optimization of the conditions should be investigated to reduce overall cost. Various physical or chemical, and both methods for pretreatment have been described [2,3]. Sulfuric acid catalyzed hydrolysis represents the most widely researched technology on different types of feedstock ranging from agricultural residues to woody and herbaceous crops [4,5]. This method can cause the hydrolysis of hemicellulose, increase portion of amorphous cellulose and result in high

* *Corresponding author*. State Key Laboratory Cultivation Base of Energy Sources and Chemical Engineering, Ningxia University, Helanshan Rd. 539, Yinchuan 750021, China. Tel.: +86 951 2062380; fax: +86 951 2062323.
E-mail address: yulongma796@sohu.com (Y.-L. Ma).
http://dx.doi.org/10.1016/j.biombioe.2015.03.033
0961-9534/

recovery of xylose in the liquid phase and high digestible cellulose and lignin in the solid fraction [6,7]. Additionally, the removal of pentosane weakens the carbohydrates - lignin matrix structure, thus increasing cellulose accessibility.

However, the interaction effects of process parameters make it complex and difficult to evaluate and optimize acid hydrolysis of corn stalk. Three major variables including hydrolysis temperature, time and acid loading were found to have significant effects [8]. Therefore, optimization of pretreatment conditions is important for efficient conversion of biomass material into fermentable sugars [9]. Statistical approaches are often employed to investigate the optimum conditions for pretreatment processes [10,11]. Central composite design (CCD) and response surface methodology (RSM) are usually used to design a systematic experimental method. RSM is able to map a response surface over a particular region of interest. CCD is well suited for fitting a quadratic surface which usually works well for process optimization [8,12]. Additionally, the effectiveness of acid-catalyzed hydrolysis is also evaluated using severity correlation which describes the severity of the hydrolysis as a function of reaction time, temperature, and acid loading through the combined severity parameters (CSP) [13]. It has been proved to provide a useful means of trading off the combined effects of these three variables on the acid-catalyzed performance. The use of CSP had been previously reported only for the dilute-acid hydrolysis of cellulosic biomass such as softwood and wheat straw [1]. The effect of the acid-catalyzed hydrolysis of corn stalk has not been deeply investigated using CSP and statistical model for high solid–liquid phase recovery. Moreover, it has seldom been reported about the trend between CSP and SF in other literature.

The objectives of this study were to investigate the effect of CSP on the conversion of corn stalk into total reducing sugars recovery and to obtain for high solid-phase component separation factor. The RSM statistical model was used to systematically evaluate the effects of acid catalysis conditions (temperature, acid loading and reaction time) on the hydrolysis responses of corn stalk. Meanwhile, the further identification of the most important variable parameter for the acid catalyzed hydrolysis of corn stalk was performed using CSP_0 and CSP_1. CSP_1 is used for correlation of the xylan solubilization and the lignin reduction by sulfuric acid. The effect of acid catalyst was taken into account by the pH of the liquor after hydrolysis, and the reaction severity described as CSP_0, which facilitates comparisons of different conditions.

2. Materials and methods

2.1. Substrate and composition

Corn stalk was obtained from the city of Yinchuan, China. The air-dried corn stalk was ground by a milling machine and then sieved to be less than 80 meshes. The composition of corn stalk was measured by National Renewable Energy Laboratory (NREL) analytical methods [14]. The results were as follows: 41.13 wt% glucan, 21.68 wt% xylan, 10.29 wt% acid soluble lignin (ASL), 15.83 wt% acid insoluble lignin (AIL), 2.75 wt% arabinan, 5.28 wt% benzene alcohol extractives, and 2.49 wt% ash on dry weight basis.

2.2. Acid-catalyzed hydrolysis process

The sulfuric acid-catalyzed hydrolysis of corn stalk was carried out in a zipper-clave autoclave. For acid-catalyzed hydrolysis process, 2 g of corn stalk with soaking in 2.0 wt% H_2SO_4 solution at solid–liquid ratio of 1:20 (wt/vol) was introduced, which was then heated to targeted temperature using steam. Hydrolysis time started to count upon the desired temperature inside the zipper-clave autoclave was reached. After the acid-catalyzed hydrolysis was completed, the pretreated sample was washed with distilled water and solid residues were collected by filtration. It was dried at 105 °C for 16 h for further composition analysis. The experimental design was summarized in Table 1. All experiments were performed in triplicate and the average values were reported.

2.3. Analytical methods

The total sugar yield (TSY) (pentose and hexose) in the liquid phase from the pretreated materials was quantified by ultraviolet spectrophotometer (UVS) according to 3, 5-dinitrosalicylic acid (DNS) colorimetric method [15] while ASL and other components in solid phase were determined using a NREL method [14]. Briefly, the sample was treated with 72 wt% H_2SO_4 at 30 °C for 60 min in a shaking water bath. The reaction mixture was then diluted to 4 wt% H_2SO_4 and autoclaved at 121 °C for 60 min. The hydrolysis solution was filtered and the solid part was dried at 105 °C overnight and further placed in the muffle furnace at 575 °C for 24 h for AIL and ash analysis. The amounts of glucose, xylose, and arabinose in the liquid fraction were determined using a HPLC method with a refraction index detector (Shimadzu, Japan) and an Aminex® HPX-87H lon Exclusion column at 65 °C. Sulfuric acid (0.005 M) at flow rate of 0.6 mL/min was used as mobile phase, all samples were filtered through 0.22 micron filters prior to analysis, and then 20 μL of sample was injected. The complete sample elution was accomplished within 20 min.

2.4. Calculation

The contents of glucan and pentosane (xylan and arabinan) were calculated as 0.9 × glucose, 0.88 × xylose + 0.88 × arabinose, respectively [14]. The amounts of ASL and AIL were calculated according to the following formulas:

$$ASL\ /\% = \left[\left(A_{280\ nm} \times V_f \times N\right)/\left(\varepsilon \times M_{sample} \times d\right)\right] \times 100 \quad (1)$$

$$AIL\ /\% = \left[\left(M_{AIR} - M_{ash}\right)/M_{sample}\right] \times 100 \quad (2)$$

where *ASL* (%) and *AIL* (%) are the acid-soluble lignin and acid-insoluble lignin, respectively, A_{280nm} is the average absorbance for corn stalk at 280 nm, V_f (mL) is the volume of filtrate liquor after acid-catalyzed hydrolysis, the value is 86.73 mL, M_{sample} (g) is the oven-dry weight of corn stalk, *N* is the sample diluted factor, ε (L/g·cm) is the absorptivity of corn stalk at