Corn stover saccharification with concentrated sulfuric acid: Effects of saccharification conditions on sugar recovery and by-product generation

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HIGHLIGHTS

► Saccharification conditions affected sugar recovery significantly.
► Glucose recovery and xylose recovery were affected differently.
► By-product generation during concentrated sulfuric acid saccharification was low.

GRAPHICAL ABSTRACT
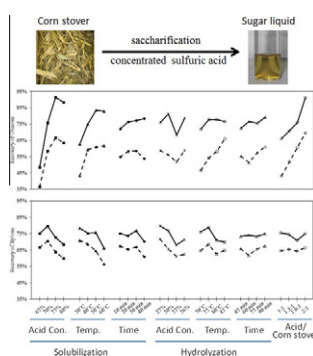
ABSTRACT

Although concentrated sulfuric acid saccharification is not a novel method for breaking down lignocellulosic biomass, the process by which saccharification affects biomass decomposition, sugar recovery, and by-product generation is not well studied. The present study employed Taguchi experimental design to study the effects of seven parameters on corn stover concentrated sulfuric acid saccharification. The concentration of sulfuric acid and the temperature of solubilization significantly affect corn stover decomposition. They also have significant effects on glucose and xylose recoveries. Low generation of furfural and 5-hydroxymethyl-2-furfural (5HMF) was noted and organic acids were the main by-products detected in the hydrolysate. Temperature also significantly affected the generation of levulinic acid and formic acid; however, acetic acid generation was not significantly influenced by all seven parameters. The ratio of acid to feedstock significantly affected glucose recovery, but not total sugar recovery. The corn stover hydrolysate was well fermented by both glucose- and xylose-fermenting yeast strains.

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1. Introduction

Use of second-generation bioethanol, produced from lignocellulosic biomass, is a promising alternative to the use of fossil fuels in powering vehicles (Ragauskas et al., 2006). The benefits of bioethanol include, but are not limited to, value-added utilization of agricultural and forest residues, reduced emission of greenhouse gases, improved independence and security of national energy, and enhancement of the rural economy. However, hydrolyzing cellulose and hemicellulose to monosaccharides (hexose and pentose) is still one of the bottlenecks in the production of ethanol from lignocellulosic biomass, and therefore, hinders its industrial application.

Generally, pretreatment followed by enzymatic hydrolysis, dilute acid hydrolysis, and concentrated acid hydrolysis is utilized in lignocellulosic biomass saccharification. However, these methods are not developed enough to be technically or economically feasible for large-scale production (Balat, 2011; Demirbas, 2005).

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Pretreatment followed by enzymatic hydrolysis is considered the most feasible environment-friendly process, provided the cost can be reduced to an acceptable level. However, currently, pretreatment techniques are performed under relatively high temperature and pressure, which are costly not only because of operation but also because of equipments (Balat, 2011; Demirbas, 2005; Eggeman and Elander, 2005). Dilute acid hydrolysis is a two-stage process that requires hemicellulose hydrolysis and cellulose hydrolysis. Although, both the stages are carried out under high temperature and pressure, the efficiency of glucose recovery is relatively low, only approximately 50% (Balat, 2011; Demirbas, 2005; Hayes, 2009). Furthermore, toxic inhibitors are generated in abundance as by-products during the pretreatment and hydrolysis processes, which are performed under high temperature and pressure; this phenomenon is observed especially when dilute acids are used simultaneously. Detoxification is generally needed before fermentation, but it increases the cost of the process and the sugar loss incurs (Purwadi et al., 2004).

Cellulosic biomass saccharification using concentrated sulfuric acid is an old process. Abundant literature has summarized the advantages and disadvantages of this method (Balat, 2011; Demirbas, 2005; Yu et al., 2008). Saccharification with concentrated sulfuric acid (H_2SO_4) consists of two steps: solubilization and hydrolyzation. The solubilization step is mainly responsible for decrystallizing the lignocellulose structure, while the hydrolyzation step hydrolyzes the fragments of cellulose and hemicellulose (Hayes, 2009). Concentrated acid saccharification leads to decreased degradation of sugar and generates much higher sugar yields compared to dilute acid saccharification. However, corrosion problems, acid consumption, and recovery are major barriers to the economic success of this method (Yu et al., 2008). Fortunately, in the last 50 years, acid recovery has significantly improved from 80% to 97% (Hamelinck et al., 2005), which could enhance the feasibility of this technology. In addition, saccharification with concentrated acid is performed at relatively mild temperatures, and the only pressures involved are those generated by pumping materials from vessel to vessel. This allows the use of relatively low-cost materials such as fiberglass tanks and piping (Demirbas, 2005). Concentrated acid saccharification is still a reliable and feasible method for the saccharification of lignocellulosic biomass, at least for the short term. Although limited reports are available on this method, concentrated H_2SO_4 saccharification of wood chip and bamboo has been reported (Cho et al., 2011; Iranmahboob et al., 2002; Sun et al., 2011). Hydrolysates obtained by using concentrated H_2SO_4 saccharification show excellent fermentability (Cho et al., 2011; Sun et al., 2011; Tang et al., 2006). Furfural, 5HMF, and weak acids are generated as by-products during concentrated H_2SO_4 saccharification (Cho et al., 2011). However, the ways in which saccharification conditions affect saccharification efficiency, sugar recovery and degradation, as well as the formation of toxic by-products are still unclear, and need to be studied further.

This work mainly aimed to study the effects of solubilization and hydrolyzation conditions, including the concentration of H_2SO_4, the treatment temperature and time, the ratio of acid and biomass, on the efficiency of hydrolysis, the sugar recovery, as well as the formation of toxic materials during concentrated H_2SO_4 saccharification. Taguchi experimental design comprising of seven parameters and four levels was employed. Corn stover, which is the most abundant agricultural residual in China, was used as the lignocellulosic biomass. Thirteen responses, including biomass decomposition, sugar recovery, and generation of toxic by-products, were used to evaluate the effects of the seven parameters on hydrolysis. The fermentability of the hydrolysates was tested using Saccharomyces cerevisiae strains KF-7 (Tang et al., 2006) and NAPX37.

2. Materials and methods

2.1. Taguchi experimental design

Design of experiments (DOE) was performed based on the Taguchi method (Rao et al., 2008) to study the effects of the seven parameters on the production of sugars and by-products from corn stover during concentrated H_2SO_4 hydrolysis. Seven operational parameters, each with four levels, which included the ratio of acid to feedstock (A/F, 1:1–2:1 (w/w)), concentration of H_2SO_4 (S-CSA, 65–80% (w/w)), temperature (S-T, 30–60 °C), and reaction time (S-RT, 10–40 min) in the solubilization step; as well as the concentration of H_2SO_4 (H-CSA, 27–36% (w/w)), temperature (H-T, 70–85 °C), and reaction time (H-RT, 45–90 min) in the hydrolyzation step, were chosen on the basis of our previous experiments (data not shown). The L_{32} (4^9) orthogonal array was selected; the layout of the parameters and levels is shown in Table S1. The variation of results can be induced by parameters or error when performing the analysis of variance (ANOVA). To identify them, the "Error" column was saved and compared to the parameter column for calculating the F value.

The experimental data were processed using the "Solver" function of Microsoft Excel. The significance of the calculated parameters was investigated using ANOVA (Castorena-Cortes et al., 2009; Xu and Liu, 2009).

2.2. Experiments

2.2.1. Saccharification

Corn stover was collected from the Changping District of Beijing, China. It was crushed using a pulverizer (GS121GN; Ohashi, Japan), equipped with a screen stencil of 8-mm pore diameter. The crushed chips were then sun-dried and stored at room temperature. Before use, the chips were dried overnight at 60 °C to ensure that moisture content was <5%. The components of the corn stover (dry weight%) were as follows: glucan, 37.95%; xylan, 22.37%; galactan, 1.12%; arabinan, 3.22%; lignin, 19.58%; and ash, 5.21%.

Saccharification was carried out in a 2-L beaker. Two hundred grams of H_2SO_4 solution (65–80%) was thoroughly mixed with the corn stover at the start of the solubilization step. The temperature was controlled using a thermostat water bath (variability, ±2 °C). After solubilization, 10 g of slurry was sampled for determining the decomposition ratio (S-DR). Deionized water was then added to the slurry to dilute the acid to the desired concentration. Hydrolyzation was then carried out at the preset temperature by using a stirrer (SMT-104; Tornado, Japan) at an agitation rate of 150 rpm.

Ten grams of slurry was collected post hydrolyzation to determine sugar recovery and by-product generation. Forty grams of slurry was collected for post hydrolyzation analysis of the decomposition ratio (T-DR). The residual slurry was then filtered using a sand core funnel (G3, 30–50-μm mesh) and then used for color analysis and for determination of the concentration of sugar and by-products. Samples for all tests were analyzed in triplicate.

2.2.2. Fermentation of hydrolysate

The corn stover hydrolysate was fermented by batch fermentation according to methods previously reported by Tang et al. (2006). Following acid and sugar separation by ion exchange, the hydrolysate pH was adjusted to 3.0 with Ca(OH)$_2$ and the hydrolysate was stored overnight. The following day, the sediment was removed, and the hydrolysate pH was adjusted to 4.0 with NaOH. Then, 0.5 g of KH_2PO_4, 0.5 g of $MgSO_4·7H_2O$, 0.1 g of $CaCl_2·2H_2O$, 0.5 g of $(NH_4)_2SO_4$, and 2.5 g of dried corn steep were added per liter of the hydrolysate. The composition of the hydrolysate used for