



Effects of pretreatment factors on fermentable sugar production and enzymatic hydrolysis of mixed hardwood



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HIGHLIGHTS

- ▶ The pretreatment factors for fermentable sugar production differed by acid catalyst.
- ▶ pH was important to produce fermentable sugar in dicarboxylic acid pretreatment.
- ▶ Sulfuric acid pretreatment demanded a high reaction temperature than time or pH.

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ABSTRACT

The aim of this study was to investigate the effects of different acid catalysts and pretreatment factors on the hydrolysis of biomass compounds over a range of thermochemical pretreatments; maleic, oxalic, and sulfuric acids were each used under different pretreatment conditions. The most influential factor for fermentable sugar production in the dicarboxylic acid-pretreated mixed hardwood was pH. Reaction time was the next significant factor followed by reaction temperature. However, fermentable sugar production was more dependent on reaction temperature than time during sulfuric acid pretreatment, whereas the effect of acid concentration was considerably lower. Maleic acid pretreatment was very effective for attaining high glucose yields after enzymatic hydrolysis. The highest enzymatic hydrolysis yield was found following maleic acid pretreatment, which reached 95.56%. The trend in enzymatic hydrolysis yields that were detected concomitantly with pretreatment condition or type of acid catalyst was closely related to xylose production in the hydrolysate.

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1. Introduction

The increase in energy consumption and consequent environmental problems has accelerated the development of alternative energy. Thus, much of the growth in bioethanol production is expected to come from next generation energy in the near future. Lignocellulosic biomass for ethanol production is advantageous because it is a renewable resource that consists of abundant carbohydrates. However, it is difficult to apply carbohydrate hydrolysis to produce fermentable sugars with a lignocellulosic biomass, because the biomass is highly recalcitrant (Yang and Wyman, 2008). Therefore, a pretreatment step is needed to make the cellulose more accessible to enzymes.

Various pretreatment methods have been used to overcome these restrictions such as dilute acids, steam explosion, organosolvent extraction, and biological treatment with white rot fungi

(Ferraz et al., 2001; Lloyd and Wyman, 2005; Pan et al., 2005). In addition, supercritical water and ionic liquid treatments have been gaining interest because of their potential to effectively remove lignin and hemicellulose and decrease cellulose crystallinity (Uju et al., 2012; Weerachanchai et al., 2012). Among the pretreatment methods, a dilute acid pretreatment with sulfuric acid has been commonly used to hydrolyze hemicellulose. However, this method has several disadvantages, such as production of inhibitory products that can negatively affect the downstream process, corrosion of equipment, and difficulties recovering the sulfuric acid after pretreatment. Dicarboxylic acids such as oxalic, fumaric and maleic acids have been suggested as alternatives for sulfuric acid pretreatment to overcome these disadvantages (Mosier et al., 2002; Kootstra et al., 2009; Lee and Jeffries, 2011).

Dicarboxylic acids are sufficiently strong to catalyze hemicellulose hydrolysis, they are selective enough to avoid extensive cellulose degradation under mild conditions. These acids exhibit a higher catalytic efficiency for hydrolysis than sulfuric acid when applied under the same severity conditions (Mosier et al., 2001; Lee and Jeffries, 2011). In addition, xylose degradation is much

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slower in the presence of dicarboxylic acids compared with that of sulfuric acid (Lu and Mosier, 2007). However, pretreatment parameters such as reaction time, temperature, and pH affecting pretreatment based on acid catalysts have not been compared.

In this study, we examined degradation of a mixed hardwood using sulfuric, maleic, and oxalic acid during pretreatment at different combinations of reaction temperature, time, and pH while maintaining the combined severity factor (CSF) constant. We hypothesized that the catalytic rates and product yields would reveal properties specifically attributable to the dicarboxylic acid properties and pretreatment parameters (Chum et al., 1990; Pedersen and Meyer, 2010). The findings showed highly significant differences among the three acids and pretreatment parameters, and the dicarboxylic acids exhibited much higher hydrolytic efficiencies than other pretreatment. Furthermore, the effect of enzymatic hydrolysis on the pretreated biomass was examined to compare the effectiveness of various acid catalysis systems and pretreatment parameters.

2. Methods

2.1. Biomass and pretreatment conditions

Mixed hardwood (*Quercus mongolica*, *Robinia pseudoacacia* L., and *Castanea crenata*) chips were purchased from Poong Lim Inc. (Daejeon, Korea). The mixed hardwood was milled and screened to a 40–60 mesh size using a J-NCM Wiley mill (JISICO, Seoul, Korea) and stored at 4 °C with less than 10% moisture content.

The pretreatment was conducted in 500 ml cylindrical stainless steel reaction vessels. Mixed hardwood and acid solutions were placed in the stainless steel vessels which were in turn placed into a larger tumbling digester, heated to the reaction temperature, and then rotated to keep the liquor in contact with the material during pretreatment. Each vessel was loaded with 50 g (dry weight basis) of biomass and sufficient acid/water mixture to give a total solid/liquid ratio of 1:4 (w/w). The reaction temperature, time, and pH were the factors affecting pretreatment in this study. The pretreatment conditions are shown in Table 1.

2.2. Sugar, inhibitors, and oligomer analysis of the hydrolysate

The glucose, xylose, arabinose, and fermentation inhibitors concentrations such as acetic acid, furfural, and 5-hydroxymethylfurfural (HMF) in the hydrolysate were determined using HPLC (Waters 2695 system; Alliance, MA, USA) outfitted with an Aminex HPX-87H column (300 × 7.8 mm, Bio-Rad, Hercules, CA, USA) and a refractive index detector (Waters 2414 system; Alliance, MA,

USA). The analysis was performed with 5 mM H₂SO₄ as the mobile phase at an isocratic flow rate of 0.3 ml/min for 55 min. All samples were properly diluted and filtered through a 0.45 μm spin-filter before analysis to remove particles. Total phenolic compounds (TPCs) were estimated colorimetrically by the Folin-Ciocalteu method via a standard curve related to absorbance at 760 nm (Scalbert et al., 1989). All analyses were carried out in triplicate.

2.3. Chemical analysis of the pretreated biomass

The chemical composition of the pretreated waste mushroom medium was determined using a NREL Laboratory Analytical Procedure (Determination of structural carbohydrates and lignin in biomass). The pretreated biomass was hydrolyzed with 3 ml (w/w) H₂SO₄ for 1 h at 30 °C. Hydrolysates were diluted to 4% (w/w) H₂SO₄ with distilled water and then heated at 120 °C for 1 h. After hydrolysis, 2 ml supernatant samples were centrifuged and filtered through a 0.45 μm filter, and the solution was analyzed for monosaccharides by HPLC, as described in Section 2.2.

2.4. Enzymatic hydrolysis of the pretreated biomass

Enzymatic saccharification was performed using Accellerase 1000 (Genencor, NY, USA) which is a commercial cellulose enzyme complex. The pretreated material of 5 g dry weight was transferred to a 125 ml Erlenmeyer flask, and 50 ml of 50 mM sodium citrate buffer (pH 6.0) was added. Appropriate amounts of cellulase (500 CMC U/g) and β-glucosidase (80 pNPG U/g) were added. The flask was placed in a shaking incubator at 50 °C and 150 rpm and incubated for 72 h. Samples were taken at 24, 48, and 72 h and the released monosaccharide was analyzed by HPLC. Each determination was conducted in triplicate.

3. Results and discussion

3.1. The roles of pretreatment factors on hydrolysis of mixed hardwood during pretreatment

Pretreatment was performed at the same CSF of 2.50 to investigate different catalytic properties and pretreatment factors on degradation of the biomass compounds. The compositional analysis of the hydrolysate under different pretreatment conditions is shown in Tables 2 and 3. Xylose was the most abundant sugar in the hydrolysate under the pretreatment conditions studied, whereas glucose released from cellulose was relatively low. The effects of pretreatment factors were analyzed based on the yield of fermentable sugar generated during pretreatment. When all three acid catalysts and pretreatment factors were compared at the same CSF, the xylose concentrations differed significantly, which agreed with a report by Guo et al. (2008).

At the same reaction temperature (pretreatment nos. 1, 2, and 3 in Table 1), pH shows strongly influenced xylose production compared to reaction time when dicarboxylic acids such as oxalic and maleic acid were used as the pretreatment catalyst. The glucose production trend using the dicarboxylic acid catalysts was similar to xylose production. However, the xylose concentration in the sulfuric acid hydrolysate increased as reaction time increased suggesting that reaction time is a more significant factor than pH to produce xylose using a sulfuric acid catalyst.

The high concentration of dicarboxylic acids seemed to favor the production of fermentable sugars in the hydrolysate during pretreatment at the same reaction time (pretreatment nos. 4, 5, and 6 in Table 1), indicating that pH is more important than reaction temperature during fermentable sugar production. In contrast,

Table 1
Pretreatment condition for acid catalyst^a pretreatment on mixed hardwood.

No.	Temperature (°C)	pH ^b	Time (min)	CSF ^c
1	170	1.04	30	2.50
2	170	1.34	60	2.50
3	170	1.52	90	2.50
4	160	1.04	60	2.50
5	170	1.34	60	2.50
6	180	1.63	60	2.50
7	160	1.34	118	2.50
8	170	1.34	60	2.50
9	180	1.34	30	2.49

^a Sulfuric, oxalic and maleic acid were used as acid catalyst.

^b pH was adjusted based on 200 ml of distilled water with each acid catalyst.

^c Combined Severity Factor (CSF) was calculated by " $\log\{t \cdot \exp[(T_H - T_R)/14.75]\} - \text{pH}$ " (t is reaction time, T_H the reaction temperature in °C, T_R the reference temperature, most often 100 °C, and pH is the acidity of the aqueous solution in terms of acid concentration, Lloyd and Wyman, 2005)

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