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Optimization of pretreatment condition for ethanol production from oxalic acid pretreated biomass by response surface methodology

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ABSTRACT

The optimal pretreatment condition for ethanol production from yellow poplar by simultaneous saccharification and fermentation (SSF) was investigated using response surface methodology. The degradation rate of yellow poplar was gradually increased by increasing the pretreatment severity. The amount of xylan degradation was directly proportional to the degradation rate. The structural change in the pretreated biomass brought about oxalic acid pretreatment was studied by XRD, BET, and solid state CP/MAS ^{13}C NMR. The results suggested that hemicelluloses and amorphous cellulose were hydrolyzed by oxalic acid pretreatment. The crystallinity value of the pretreated biomass increased until the combined severity factor (CSF) became 1.52, while it decreased when the CSF became 1.92 due to degradation of some of the crystalline cellulose under severe pretreatment conditions. The surface area of the pretreated biomass increased slightly from 0.49 to 1.01 m^2/g due to the removal of hemicellulose during oxalic acid pretreatment. The highest ethanol yield obtained 95.21% when the pretreated biomass was used for SSF. Using response surface methodology, it was found that the optimal oxalic acid pretreatment condition: oxalic acid, 82 mM; temperature, 160 °C; and time, 58 min. This condition agreed well with that obtained by the model prediction.

1. Introduction

Concerns regarding global climate change have led to the development of sustainable energy sources. Lignocellulosic biomass has received special attention as a more appropriate feedstock and alternative energy source compared to other sources for replacing fossil fuels. It can be converted to alternative transportation fuels, including bioethanol or biodiesel (Campbell and Laherrere, 1998) In particular, bioethanol is the most dominant biofuel at the moment representing approximately 85% of global production of biofuel. Lignocellulosic biomass is the most abundant organic material on earth, and it has not driven up food prices or raised concerns of a food crisis compare to first generation feedstocks such as starch and sugar-based crops (Sun and Cheng, 2002).

Lignocellulosic biomass consists primarily of cellulose, hemicelluloses, and lignin. Carbohydrates make up about 65%–75% of the overall lignocellulosic biomass. Therefore, it can be converted to fermentable sugar by pretreatment and enzymatic hydrolysis, similar to first generation feedstock conversion to fermentable sugars. Four major steps are involved in bioethanol production from lignocellulosic biomass: pretreatment, enzymatic hydrolysis, fermentation, and ethanol recovery. Various pretreatment processes have been developed to improve the bioconversion of biomass due to its recalcitrant characteristics. The purpose of pretreatment is to remove hemicelluloses or lignin from the biomass to increase enzyme accessibility to cellulose. Many pretreatment techniques have been developed including physical, chemical, biological approaches and combinations thereof (Hendriks and Zeeman, 2009; Pan et al., 2005; Schilling et al., 2012; Wu et al., 2011). However, the effect of pretreatment for fermentable sugar production differs depending on the kind of biomass involved due to differences in the structure and chemical compositions. Therefore, appreciate pretreatment method for biomass is required, that is closely related to downstream processes such as enzymatic hydrolysis and fermentation.

As a classic pretreatment, dilute sulfuric acid has been used on biomass. This pretreatment does not require sophisticated equipment and it is a cost-effective technique with high a hydrolysis yield (Hendriks and Zeeman, 2009). However, there is a disadvantage in that a large amounts of gypsum and a high concentration of

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Table 1
The central composite design with three central points employed for two independent variables.

Sample no.	Variables		Coded levels		CSF[a]
	Time (min)	Acid concentration (mM)	Time χ_1	Acid concentration χ_2	
1	30	82	0	0	1.89
2	30	82	0	0	1.89
3	30	82	0	0	1.89
4	50	122	1	1	2.29
5	10	122	−1	1	1.59
6	50	41	1	−1	1.92
7	10	41	−1	−1	1.22
8	30	139	0	1.4	2.08
9	58	82	1.4	0	2.18
10	30	24	0	−1.4	1.52
11	2	82	−1.4	0	0.72

Reaction temperature fixed at 160 °C.

[a] Combined severity factor (CSF) = $\log\{t \times \exp[(T_H - T_R)/14.75]\} - \text{pH}$ (t is the reaction time for the pretreatment in minutes, T_H the reaction temperature in °C, and T_R the reference temperature, most often 100 °C (Scordia et al., 2013).

Table 2
Chemical compositions and degradation rate of biomass depending on pretreatment severity.

CSF	Glucan (%)	Xylan (%)	Lignin (%)	Degradation rate (%)
Raw material	41.33	20.90	24.36	–
0.72	58.53	2.46	23.19	24.18
1.22	59.68	2.55	24.74	21.07
1.52	59.16	2.58	23.72	27.41
1.59	64.40	N.A.	23.71	30.50
1.89	64.20	N.A.	22.90	30.11
1.92	61.86	N.A.	23.32	28.78
2.08	63.23	N.A.	25.13	34.36
2.18	64.09	N.A.	25.16	36.11
2.29	65.42	N.A.	26.46	35.47

fermentation inhibitors are generated compared to other acid catalysts. This can negatively affect the downstream process. Oxalic acid has been suggested as an alternative to sulfuric acid for pretreatment (Kootstra et al., 2009). It is strong enough to catalyze hemicellulose hydrolysis with a relatively low concentration of fermentation inhibitors; thus, it might be a suitable catalyst for pretreatment.

In a previous study, oxalic acid pretreatment was applied to various types of biomass to investigate changes in the structural properties and hydrolysis rate of the biomass (Lee et al., 2010; Jeong et al., 2014; Scordia et al., 2013; Kundu et al., 2015). The main purpose of the present study was to determine the optimal pretreatment condition for ethanol production from yellow poplar by simultaneous saccharification and fermentation (SSF). We evaluated the effect of the reaction time and acid concentration on ethanol production based on an analysis using response surface methodology.. The pore size of the biomass was related to the enzyme accessibility to the cellulose. The size of cellulase with a spherical diameter has been reported to be 240–740 Å (Cowing and Kirk, 1976). In this study, pores of above 300 Å comprised majority of the pretreated biomass. At high CSF, the pore size of the pretreated biomass increased from 160 Å. This implies that biomass pretreated at high CSF leads to effective enzymatic hydrolysis via an increase in the pore size and surface area.

CP/MAS ^{13}C NMR was used to investigate structural changes in the pretreated biomass. The main components of biomass contribute their characteristic shifts to the spectrum (Popescu et al., 2011; Li et al., 2010). The CP/MAS ^{13}C NMR spectra of raw material and pretreated biomass are shown in Fig. 2

2. Materials and methods

2.1. Biomass and pretreatment conditions

Yellow poplar (*Liriodendron tulipifera*L.) was obtained from the Korea Forest Research Institute (KFRI). The biomass was ground and then screened to a 20–80 mesh size. It was stored in plastic bags at 4 °C before pretreatment. The chemical composition of the biomass was glucan 41.33 ± 0.34%, xylan 16.28 ± 0.14%, total lignin 24.36 ± 0.07%, ash 0.68 ± 0.05% and acetyl group 4.10 ± 0.10% on a dry weight basis.

2.2. Oxalic acid pretreatment of yellow poplar

The oxalic acid pretreatment of the yellow poplar was carried out in an EMS reactor (Mode EMV-HT/HP 600, Gyeonggi-do, Korea). The reactor consisted of a heater, a stirrer, a stainless steel vessel, and controllers for speed and temperature. The ground biomass was treated with 200 mL of oxalic acid solution in a stainless steel vessel. The pretreatment was performed with 25 g of biomass (dry weight basis) and a total solid/liquid ratio of 1:8 (w/w) depending on the reaction time and pH (oxalic acid concentration). The reaction temperature was fixed at 160 °C, and stirring speed was 150 rpm to keep the acid solution in contact with the biomass during pretreatment. The reaction time and pH were the factors that affect pretreatment in this study. After pretreatment, the heater was turned off and the reactor was rapidly cooled in ice water

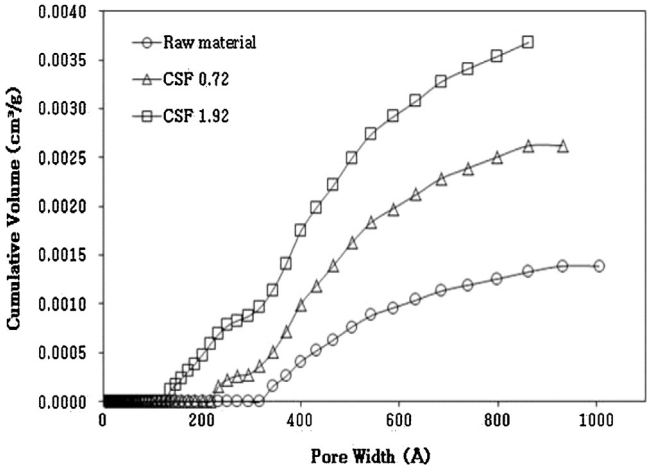

Fig. 1. Changes of pore sized distribution based on N_2 adsorption for untreated and pretreated biomass.