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Bioethanol production from oxalic acid-pretreated biomass and hemicellulose-rich hydrolysates via a combined detoxification process

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HIGHLIGHTS

- The combined detoxification processes removed fermentation inhibitors more efficiently.
- Ferulic acid was the major component in the detoxified hydrolysate.
- Ferulic acid concentration was high in the XAD-ED treated hydrolysate.
- ED-XAD process was most effective for ethanol production in the hydrolysate.
- The theoretical ethanol yields of ED-XAD treated hydrolysate (yellow poplar) was 91.22%.

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ABSTRACT

A combined detoxification process was investigated for ethanol fermentation with hemicellulose rich hydrolysates obtained from mixed hardwood and yellow poplar. Acetic acid was the most abundant compound in the hydrolysates, which also contained inhibitors such as 5-hydroxymethylfurfural (HMF), furfural, and total phenolic compounds (TPC). Electrodialysis (ED) efficiently removed 100% of the acetic acid, whereas most of the HMF, furfural, and TPC remained in the hydrolysates. However, XAD-4 resin removed non-ionizable compounds such as HMF, furfural and TPC. Compared with the single detoxification processes (ED or XAD), the combined detoxification processes (ED-XAD or XAD-ED) removed fermentation inhibitors more efficiently. Compared with XAD-ED, ED-XAD produced higher ethanol yields of 0.48 g/g and 0.49 g/g in mixed hardwood and yellow poplar hydrolysates, respectively. Ferulic acid concentration was high in the XAD-ED treated hydrolysate compare to that of ED-XAD treated hydrolysate. For this reason, ethanol fermentability was higher with ED-XAD-treated hydrolysates compared with XAD-ED-treated hydrolysates. Simultaneous saccharification and fermentation was performed with pretreated biomass. Ethanol production was 23.20 g/L with yellow poplar and 19.14 g/L with mixed hardwood after 120 h of fermentation.

1. Introduction

Owing to growing concerns about the carbon emissions produced by fossil fuel, lignocellulosic biomass is drawing increasing attention as an alternative energy resource. Efficient bio-refinery processes using lignocellulosic biomass may also provide chemicals and bio-products [1]. Lignocellulosic biomass such as woody materials and agricultural residues is an abundant, environmentally feasible, easily available, and renewable feedstock [2].

Cellulose, hemicelluloses, and lignin are the main components of lignocellulosic biomass. Cellulose has a high crystalline structure with complex connections to hemicellulose and lignin [3]. Due to the complex and recalcitrant structure of lignocellulosic biomass, various pretreatment processes are required for carbohydrate hydrolysis depending on the biomass. Pretreatment increases biomass digestibility for efficient fermentable sugar production, which reduces the cost of bioethanol production [1]. Various pretreatment methods have been suggested depending on the pur-

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pose of removing hemicellulose or lignin from biomass [4,5]. Dilute acid pretreatment is a promising pretreatment capable of high solubilization of hemicellulose [6]. This process degrades most of the hydrogen bonds in hemicelluloses, and partially degrades of cellulose and lignin [7].

Oxalic acid catalyst is superior to inorganic acids such as sulfuric or hydrochloric acid, as a catalyst for fermentable sugar production and ethanol fermentation [5]. Compared with inorganic acid catalysts, oxalic acid selectively degrades hemicelluloses, has higher hydrolytic efficiency, and produces more monosaccharide than oligosaccharide fractions from hemicelluloses during pretreatment [5]. Monosaccharide production during pretreatment should be considered for downstream processes such as ethanol fermentation [8].

In general, fermentation inhibitors such as furan derivatives (furfural and 5-hydroxymethylfurfural) aliphatic acids (acetic, formic, and levulinic acid), and lignin degradation products are produced during dilute acid pretreatment [9]. Among these products, acetic acid is one of the main by-products of hemicellulose. The hemicellulose of hardwood consists primarily of glucuronoxylan, the major constituent unit of which is O-acetyl-4-O-methylglucurono-β-D xylan [10]. Most xylose residues contain approximately 7 acetyl groups per 10 xylose units [11,12]. Therefore, a high concentration of acetic acid is generated by dilute acid pretreatment. Furan derivatives are generated by conversion from pentose and hexose under severe pretreatment conditions.

These components have negative effects on microorganism growth and ethanol production. Therefore, detoxification processes have been developed to remove fermentation inhibitors from hydrolysate [13]. The hydrolysate obtained from acid pretreatment contains different inhibitors in various concentrations depending on the biomass. Therefore, a single detoxification process is unlikely to remove all inhibitors. Researchers have tried to remove fermentation inhibitors from hydrolysate via evaporation, activated charcoal adsorption, overliming, neutralization, ion exchange, enzyme treatment, electrodialysis and combination processes [4,13–15]. However, some researchers have reported that high ethanol was obtained from hardwood without detoxification [16,17].

Electrodialysis (ED), an electrochemical membrane separation process, employs cation and anion exchange membranes for the separation and purification containing ionic species in the solution. ED has been widely applied in the separation of organic acids, such as lactic acid, citric acid, acetic acid and their salts as well as in the area of desalination of saline solution, production of table salt, and wastewater treatment [18,19]. In this study, ED was applied to ionic species of inhibitors such as acetic acid. Meanwhile, the hydrophobic polymeric adsorbents, Amberlite XAD-4 is one of the best commercially available polymeric adsorbents of the second-generation styrene–divinylbenzene copolymers. The application of XAD-4 was considered to be one of the excellent adsorbents for adsorption of small organic molecules dispersed in aqueous media such as furfural, 5-HMF and TPC [18].

In a previous study, we investigated the effect of a two-step detoxification process, electrodialysis (ED) and XAD-4 resin to remove fermentation inhibitors from mixed hardwood hydrolysate [18]. In this study, we evaluated the effect of detoxification process order (ED-XAD, XAD-ED) on inhibitor removal from hydrolysate. The influence of detoxification on ethanol fermentation performance was compared between the detoxified and the original hydrolysate. Furthermore, ethanol production via simultaneous saccharification and fermentation (SSF) of solid fraction was evaluated.

2. Materials and methods

2.1. Raw materials and pretreatment

Mixed hardwood (*Quercus mongolica*, *Robinia pseudoacacia* L., and *Castanea crenata*) and yellow poplar (*Liriodendron tulipifera* L.) chips were used as sources of woody biomass. The chips were milled and screened to a size of 20–80 mesh and stored under conditions of less than 10% moisture until further use. The chemical composition of these raw materials were determined with National Renewable Energy Laboratory protocols (Determination of carbohydrates and lignin content in biomass, NREL, Golden, CO, USA) [20] and is shown in Table 1.

Pretreatment was performed in three stainless steel vessels that were placed in turn into a larger tumbling digester (DM-848; Daeil Machinery, Daejeon, Korea). Each vessel was loaded with 50 g biomass (dry weight) and 100 mM of oxalic acid solution to give a solid/liquid ratio of 1:4 (w/w). Pretreatment conditions were fixed at 170 °C for 50 min. After pretreatment, the liquid fractions (hydrolysates) were separated via vacuum filtration, and the solid fractions (pretreated biomass) were stored in plastic bags at 4 °C to preserve their integrity.

2.2. XAD-4 resins adsorption to remove fermentation inhibitors from hydrolysate

To remove furan derivatives and lignin degradation products from the hydrolysate, Amberlite XAD-4 resin (Sigma–Aldrich, St. Louis, MO, USA) was packed in a glass column (ID 0.9 cm, height 15 cm). Water was first pumped through the column and then the original hydrolysate or ED treated hydrolysate were fed to the column. The column effluent was collected periodically. Ethanol (200 mL) was supplied through the column to separate furan derivatives and lignin degradation products from the adsorbents. Then, water was used as fed to the column to clean ethanol from the column.

Table 1
Chemical compositions of the raw materials and pretreated biomass.

Composition (%)	Raw materials		Pretreated sample	
	Mixed hardwood	Yellow poplar	Mixed hardwood	Yellow poplar
Glucan	41.63 (0.16)[a]	42.85 (0.24)	54.58 (0.27)	57.33 (0.16)
Xylan	16.58 (0.03)	15.77 (0.08)	0.81 (0.02)	0.73 (0.03)
Lignin	28.92 (0.31)	26.34 (0.22)	38.73 (0.12)	35.30 (0.15)
Arabinan	2.42 (0.04)	2.82 (0.04)	ND[b]	ND
Ash	0.50 (0.02)	0.64 (0.03)	0.35 (0.06)	0.41 (0.02)
Organic solvent extract	1.07 (0.06)	1.60 (0.12)		
Acetyl group (%)	3.16 (0.03)	3.53 (0.06)	ND	ND

[a] The parentheses contains the standard deviation with the analysis repeated three times.
[b] ND means not detectable.