



Deep eutectic solvents from hemicellulose-derived acids for the cellulosic ethanol refining of *Akebia*' herbal residues

Qiang Yu^a, Aiping Zhang^b, Wen Wang^a, Long Chen^{a,c}, Ruxue Bai^{a,c}, Xinshu Zhuang^a, Qiong Wang^{a,*}, Zhongming Wang^a, Zhenhong Yuan^a

^a Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China

^b College of Forestry and Landscape Architecture, South China Agricultural University, Guangzhou 510642, China

^c University of Chinese Academic of Sciences, Beijing 100039, China

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ABSTRACT

Here, the potential use of herbal residues of *Akebia* as feedstock for ethanol production is evaluated. Additionally, five deep eutectic solvents from hemicellulose-derived acids were prepared to overcome biomass recalcitrance. Reaction temperatures had more significant influences on solid loss and chemical composition than the molar ratios of choline chloride (ChCl) to derived acids. Glycolic acid resulted in the maximum levels of lignin, xylan and glucan removal, which were 60.0%, 100% and 71.5%, respectively, at 120 °C with a 1:6 M ratio of ChCl-glycolic acid. In contrast, ChCl-formic acid resulted in the greatest level of glucan retention, at 97.8%, with a lignin removal rate of 40.7% under the same pretreatment conditions. Moreover, ChCl loading could significantly enhance the selectivity of carboxylic acid for lignin dissolution. A 98.0% level of subsequent enzymatic saccharification and a 100% ethanol yield were achieved after ChCl-formic acid pretreatments of *Akebia*' herbal residues.

1. Introduction

Medicinal herbs, as an important part of traditional Chinese medicine, are widely used in China and are becoming increasingly available in Europe and North America. There are an estimated 1600 medicinal herb companies in China, and ~30 million metric tonnes of herb residues (solid waste of herbs after decoction) are generated annually. The waste management of these herb residues is an ongoing challenge for these companies and the government. For example, Guangzhou Jiaherb Pharmaceutical Company produces ~100,000 tons of herb residues per 20,000 tons of extract, and the cost to transport these solid wastes will reach 140,000 US dollars. The traditional disposal methods for disposing of herb residues, like burying and burning, will seriously pollute the environment. Because of their high nutrient contents, however, they can also be used for microbial composting (Wei-qu et al., 2009) and animal feeding (Li et al., 2017b; Su et al., 2016; Xiaoliang et al., 2006; Xiaoming et al., 2007). Recently, biochar (Chen et al., 2017; Shang et al., 2017; Yang and Qiu, 2011) or bioenergy production from herb residues has attracted global attention because of lignocellulose's characteristics, such as gasification (Dong et al., 2013; Guo et al., 2013; Zeng et al., 2016a,b) and pyrolysis (Guo et al., 2015;

Wang et al., 2010; Zhan et al., 2017).

Automobile ownership in Guangdong Province, which has the greatest number of medicinal herb companies and the highest total gross domestic product (GDP) on mainland China, is growing rapidly, with close to 26 million cars on the road in 2016. The implementation of new electric or ethanol-consuming vehicles in Guangdong would reduce its oil dependence and relieve urban air pollution. Here, the potential of herb residues as a source for cellulosic ethanol production is evaluated. The main processes in ethanol production from lignocellulose include pretreatment to reduce biomass recalcitrance, enzymatic hydrolysis to produce fermentable sugars, and microbial fermentation to generate ethanol (Bhatia et al., 2017). Biomass recalcitrance caused by the tight structure of hemicellulose–lignin–cellulose restricts sugar release, which opposes the cost-effective industrial conversion of lignocellulosic biomass to ethanol. The lignin content surrounding hemicelluloses and cellulose in the plant cell walls are negatively correlated not only to enzymatic digestibility but to the pretreatment process (Yu et al., 2016c), and the removal of lignin could be beneficial in reducing the downstream pressure. Compared with low pH-pretreatment methods, such as dilute acid and liquid hot water, alkaline pretreatments with a high pH value,

* Corresponding author.

E-mail address: wangqiong@ms.giec.ac.cn (Q. Wang).

such as sodium hydroxide and aqueous ammonia, perform well in terms of lignin removal (Wang et al., 2017; Yu et al., 2013). However, the formation of a black liquid is not environmentally friendly.

Deep eutectic solvents (DESs), sustainable alternatives to ionic liquids derived from natural and renewable components, are a promising solvent for delignification with high yields of 58–78% (Alvarez-Vasco et al., 2016). Compared with the traditional alkaline methods, DES pretreatments resulted in a greater enhancement in digestibility, lower energy consumption and simpler procedures for lignin purification and solvent recovery (Gunny et al., 2015). DESs based on choline chloride (ChCl) and a polyalcohol, such as ChCl-glycerol and ChCl-ethylene glycol enhanced the delignification and subsequent enzymatic hydrolysis efficiency of corncobs more than DESs from ChCl-carboxylic acids, like ChCl-lactic acid and ChCl-malic acid (Zhang et al., 2016). However, the effectiveness of ChCl-polyalcohol pretreatments was unstable, varying according to the physio-chemical properties of the biomass (Fang et al., 2017), and there was no significant enhancement in the enzymatic digestibility of corn stover after a ChCl-glycerol pretreatment (Xu et al., 2016). Moreover, most of the literature on DES' applications for biomass refinement neglect to evaluate the effects of DES pretreatments on the subsequent fermentation process. Thus, the applicability of the overall system is uncertain.

ChCl-carboxylic pretreatment is in its infant stage, and the research is not yet thorough or extensive. Here, five DES mixtures were prepared using ChCl as the hydrogen-bond acceptors (HBAs) with five hydrogen-bond donors (HBDs) from the hemicellulose derived acids, formic (Fa), acetic (Aa), glucuronic (Glca), glycolic (Glya) and levulinic (La). Then, the effects of the different DESs on the pretreatment of herb residues of *Akebia* (HRA) were investigated systematically. In addition, the comparative performances of DES and organic acid pretreatments in terms of enzymatic hydrolysis and ethanol fermentation were evaluated. The related results will provide insights into the industrial applications of DES technology and biofuel production from herb residues.

2. Materials and methods

2.1. Substrate

HRA, the solid residues left after the decoction of *Akebia*, was collected from the Guangdong Second Traditional Chinese Medicine Hospital in Guangzhou City, China. It was first dried at 105 °C to a constant weight, then milled and screened to 8–20 mesh. The chemical composition of the raw material (on a dry weight basis) was determined following the standard procedures of NREL (Sluiter et al., 2008), including 42.8% glucan, 24.5% xylan, 24.6% acid-insoluble lignin and 6.8% extractives. Commercial cellulase (151 FPU/g) was purchased from Imperial Jade Biotechnology Co., Ltd. (Ningxia, China). ChCl, Fa, Aa, Glca, Glya, La and other chemicals were analytical grade reagents obtained from Macklin (Shanghai, China).

2.2. DES preparation and pretreatment

The DES preparation was carried out by mixing ChCl and five different hemicellulose-derived acids in different molar ratios, followed by stirring at 200 rpm in an oil bath (60 °C) to form a homogeneous and transparent liquid. Then, the HRA was added to maintain a solid:liquid ratio of 1:10 (g:g) at 80, 100 and 120 °C for 8 h. The slurry was washed with absolute ethanol (~5 times more than the amount of DES) to remove DES and its soluble fraction using a glass crucible. The wet solid fraction was recovered and divided into two portions, one was used for the measurement of weight loss and chemical composition, and the other was evaluated the enzymatic digestibility. The formulas used were as follows:

$$\text{Solid loss \%} = \frac{\text{initial solid} - \text{residual solid}}{\text{initial solid}} \times 100,$$

$$\begin{aligned} & \text{Xylan/glucan/lignin removal \%} \\ &= \frac{\text{initial xylan/glucan/lignin} - \text{residual xylan/glucan/lignin in solid}}{\text{initial xylan/glucan/lignin}} \\ & \times 100 \end{aligned}$$

and

$$\text{Enzymatic digestibility \%} = \frac{\text{glucose in the liquid fraction}}{\text{potential glucose in the substrate}} \times 100.$$

2.3. Enzymatic digestibility and ethanol fermentation tests

Enzymatic hydrolysis tests were performed at 50 °C for 72 h in 100-mL Erlenmeyer flasks, each containing 40 mL of sodium citrate buffer (pH 4.8) and 5% (w/v) substrate (Yu et al., 2010). The cellulase-loading amounts were 10, 20 and 40 FPU per gram dry solid. The glucose content in the enzymatic hydrolysate was measured using a Waters HPLC. All experiments were performed in duplicate. Details of the ethanol fermentation process using *Saccharomyces cerevisiae* Y2034 (purchased from the National Center for Agricultural Utilization Research) were described in a previous work (Yu et al., 2016b). Samples were taken and analyzed for their ethanol concentrations and sugar consumption. The yield of ethanol was calculated according to the percentage of theoretical maximum ethanol yield (Chen et al., 2015).

2.4. Analytical methods

Sugars, acids, aldehydes and ethanol in the hydrolysate were determined using HPLC with a Shodex SH1011 column coupled with a refractive index-ultraviolet detector. The mobile phase was 0.005 M H₂SO₄ at a flow rate of 0.5 mL/min, with a column temperature of 50 °C. The recovery of xylose, glucose, furfural and 5-HMF in the pretreatment process were calculated based on the percentages of their theoretical maximum yields.

3. Results and discussion

3.1. Solid loss of HRA after DES pretreatment

Five DES mixtures were prepared using ChCl as the HBA with five independent HBDs from hemicellulose derived acids, Fa, Aa, Glca, Glya and La. Although a homogeneous and clear liquid was formed by ChCl and each of the five different HBDs at 60 °C, solid particles precipitated upon cooling ChCl-Aa at molar ratios of and ChCl-Glca at molar ratios of 2:1, 1:1, 1:2, 1:4 and 1:6. The proton affinities of the HBA and the HBDs for different DES mixtures may contribute to their phase behaviors (Vigier et al., 2015). Therefore, four DESs (ChCl-Fa, ChCl-Aa, ChCl-Glya and ChCl-La) at the molar ratios of 1:2, 1:4 and 1:6 were selected to further evaluate their abilities to solubilize different chemical compositions of HRA.

The loss of solids after ChCl-Fa pretreatment increased with the reaction temperature, especially for the low molar ratio of 1:2 (Fig. 1). The solid loss was only 7.5% at 80 °C but reached 42.5% at 120 °C. In contrast, the influence of molar ratio on the solid loss was insignificant. At 10 °C, for example, the losses were 36.6%, 42.8% and 45.1% for the molar ratios of 1:2, 1:4 and 1:6, respectively. Moreover, a similar relationship between reaction conditions and solid losses of HRA were observed for the ChCl-Aa pretreatment, which resulted in a maximum solid loss of 40.1% at 120 °C with a molar ratio of 1:2. Glya had properties of both carboxylic acids and alcohols, and a 17.9% solid loss was obtained after ChCl-Glya pretreatment even under of low acid-loading (molar ratio of 1:2) and low reaction-temperature (80 °C) conditions. Then, with an increase in temperature, it further increased to 35.3% at 100 °C and 55.1% at 120 °C. In contrast, at the high molar ratio of 1:6, the loss of solid was not significantly affected by the

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