Chemical Engineering Science 151 (2016) 16–24

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Hydrolysis kinetics of inulin by imidazole-based acidic ionic liquid in aqueous media and bioethanol fermentation

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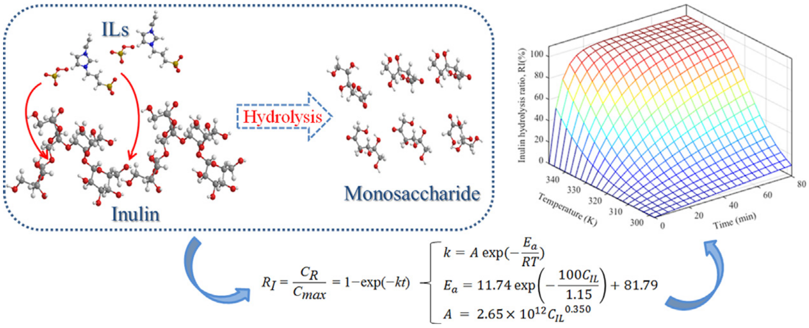
HIGHLIGHTS

- A potentially environment-friendly technology was developed to produce ethanol.
- Hydrolysis rate by ILs in water media was higher than by dilute sulfuric acid.
- A concise kinetic model of inulin hydrolysis by ILs was firstly proposed.
- The kinetic model predicted well the inulin hydrolysis by ILs.
- Conversion efficiency of inulin-type sugars to ethanol reached 94.21%.

GRAPHICAL ABSTRACT



$$R_I = \frac{C_R}{C_{max}} = 1 - \exp(-kt) \quad \begin{cases} k = A\exp(-\frac{E_a}{RT}) \\ E_a = 11.74\exp\left(-\frac{100C_{IL}}{1.15}\right) + 81.79 \\ A = 2.65\times 10^{12} {C_{IL}}^{0.350} \end{cases}$$

ARTICLE INFO

Article history:
Received 26 December 2015
Received in revised form
12 April 2016
Accepted 7 May 2016
Available online 9 May 2016

Keywords:
Inulin-containing biomass
Acidic ionic liquid
Hydrolysis kinetics
Fermentation
Bioethanol

ABSTRACT

This article focused on the inulin-containing energy biomass, Jerusalem artichoke, to explore environment-friendly processes for bioethanol production. An imidazole-based acidic ionic liquid (VImalLs) was prepared as the catalyst of inulin hydrolysis in aqueous media. The hydrolysis kinetics was studied under different conditions. The kinetic parameters of hydrolysis by VImalLs and dilute sulfuric acid were estimated and compared. This work demonstrated that the hydrolysis rate of inulin into reducing sugars by VImalLs was obviously faster than that by the latter. The proposed kinetic model successfully predicted the inulin hydrolysis in wider ranges of experimental conditions. The hydrolysate was fermented into ethanol by *Saccharomyces cerevisiae* which activity was not inhibited by the VImalLs. The conversion efficiency of inulin-type sugars to ethanol was greater than 92.5% of the theoretical yield. And the ethanol production capacity reached 123.76 g/(L). This system integrated the chemical and biological processes to prepare ethanol in an environment-friendly way.

1. Introduction

With the development of industry and agriculture, a great deal of energy has been consumed. One of the major problems facing on the world today is that the shortage of fossil energy source is becoming more and more serious. Sustainability of biofuels is increasingly taken into account (Klein-Marcuschamer and Blanch, 2015; Menegaki and Tsagarakis, 2015). Raw plant biomass is an abundant bioresource for energy sustainability. At present, the main raw materials for bioethanol production include cassava starch, corn starch, sugarcane, wheat starch, sweet potato starch and sweep sorghum starch, most of which are starchy grains and food (Balat et al., 2008; Jensen et al., 2008; Lai et al., 2011; Mojovic et al., 2006). However, the starchy grains should be gelatinized before hydrolysis, and this process consumed much energy (Alex Marvin et al., 2012). On the other hand, it has been recognized globally that our population is increasing faster than the supply of

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http://dx.doi.org/10.1016/j.ces.2016.05.017

food, moreover, local natural disasters are frequent and the supply of grain falls short of demand (Chi et al., 2011). Under this background, the production of ethanol as fuel from grain, particularly corm, has been politically knocked down in most countries (Bai et al., 2008; Kunz, 2008). Simultaneously, the non-grain biomass resources have attracted increasing attention. Although lignocellulose is the most abundant renewable non-grain biopolymers on earth, the hydrolysis processes with a complex pretreatment are progressing slowly. And the economics of the complete life-cycle for lignocellulosic derived biofuels production remains unclear (Langan et al., 2011).

Among the different raw materials, Jerusalem artichoke is an ideal non-food energy crop, due to it is a salt-tolerance species that is easily grown in saline and alkaline soils. The growing traits of Jerusalem artichoke such as cold and drought tolerance, wind and sand resistance, strong fecundity and high pest and disease resistance make it be widely cultivated (Long et al., 2014; Zhao et al., 2010). Tubers yield of Jerusalem artichoke is between 10 and 15 t of dry weight per hectare (Denoroy, 1996). Long et al. (2013) also reported Jerusalem artichoke commonly yields around 7 and potentially up to 14 t of carbohydrate per hectare. For the reason of the preferential advantages of the Jerusalem artichoke, it has recently received increasing attention as a renewable and abundant raw material for fructose syrup production and ethanol fermentation. In this way, sustainable production technologies are needed (Matías et al., 2011). Thus, we focus on this particular raw material in this article. Jerusalem artichoke contains 10–20 (w/w)% carbohydrates of which approximate 78% is inulin (Pan et al., 2009). Inulin is a mixture of polysaccharides, the number of fructose units can range from a few units to more than 60, depending on the source. Inulin consists of linear chains of D-fructose units in the β (2–1) position, the chain is terminated by a glucose residue through a sucrose-type linkage at the reducing end (Zhang et al., 2010).

The main steps of inulin bioethanol production include inulin hydrolysis, hydrolyzates fermentation and ethanol separation. And the hydrolysis of inulin may be considered as a key step in the processing for bioethanol production. This reaction can be carried out by employing acidic catalysts or biocatalysts (Blecker et al., 2002; Hu et al., 2015; Ricca et al., 2009). To obtain bioethanol, traditional processes which employ several acids such as dilute sulfuric acid, maleic acid, and fumaric acid to hydrolysis cellulosic materials can be applied. Especially dilute sulfuric acid which is used to cellulosic hydrolyzation is the most popular catalyst (Lenihan et al., 2010; Rafiqul and Mimi Sakinah, 2012). However, it has drawbacks such as equipment corrosion and issues in the recovery and recycle of the acids and it does not fit in with the green chemical concept. Enzymatic process is specific and it provides an efficient raw material usage (Cateto et al., 2011). Sometimes, this conventional process tends to be expensive for the high cost and a long time cultivation of microorganism (Hu et al., 2015). Therefore, more efficient and economical processes of hydrolyzing inulin should be applied.

There has been much interest in the application of ionic liquids (ILs) in biomass processing recently. As ILs have some properties favorable to chemical reactions, they are currently used as "green" solvents and catalysts, and especially the acidic functionalized ILs (Amanda et al., 2002; Ding and Armstrong, 2005; Wilkes, 2004). Compared with traditional organic solvents, ILs are non-volatile, and possess good dissolving capacity (Hsu et al., 2011). As novel catalysts, they show many advantages of both homogenous and heterogeneous catalysts. When the biomass is treated by acidic functionalized ILs, anions which form strong hydrogen bonds are capable to interfere with the inter and intramolecular hydrogen bond network of cellulose, leading in effect to dissolution (Amarasekara and Owereh, 2009; Gupta and Jiang, 2015). Furthermore, The ILs which has acidic centers on both the cation and anion, for example, SO_3H-functionalized acidic ionic liquids, shows strong acid strength and good hydrolysis performance of cellulose (Liu et al., 2013). Besides, the ILs possess the characteristics of easy separation and recyclability. Several separation methods to recover the ILs had been proposed (Alvarez et al., 2014). So the inulin hydrolyzation by the acidic functionalized ILs could be regarded as a green catalytic process.

This study focused on exploring a novel and efficient catalytic hydrolysis system of inulin, using an imidazole-based acidic ILs, 1-(3-sulfonic group)propyl-3-vinylimidazolium hydrosulfate ($[(CH_2)_3SO_3HVIm]HSO_4$, VImaILs) that contain terminal olefinic bond, as the catalyst. The hydrolysis kinetics was systematically studied. Meanwhile, the kinetic parameters of inulin hydrolysis processes by VImaILs and dilute sulfuric acid were estimated and compared, respectively. The other purpose was to establish the hydrolysis kinetic model for predicting the conversion of inulin into reducing sugars by the VImaILs. The general objective was to obtain ethanol from inulin via environment-friendly chemical and biological technologies.

2. Materials and methods

2.1. Materials

Inulin (polysaccharide content 90.86%, free sugars content 3.90%, water and ash content 5.24%), main storage carbohydrate of Jerusalem artichoke, was purchased from Likang Company (Gansu, China). *Saccharomyces cerevisiae* was purchased from Angel Company (Wuhan, China). 1-vinylimidazole (≥ 98%) and 1, 3-propane sultone (≥ 99%) were purchased from Baishun Chemical Technology Company (Beijing, China). Other chemicals (analytical grade) were commercially available and used without further purification.

2.2. Preparation of VImaILs

The 1-vinylimidazole (9.4 g, 0.1 mol) was dissolved in acetone (40 mL) in a flask, and 1,3-propane sultone (12.2 g, 0.1 mol) was added dropwise. Then the reaction mixture was stirred at 0 °C for 3 h before filtrated. The retentate was purified by washing with ether and dried under vacuum to obtain $(CH_2)_3SO_3HVIm$ (18.1 g, 83.8% yield) as a white solid.

The $(CH_2)_3SO_3HVIm$ (18.1 g, 0.838 mol) was dissolved in 50 mL of distilled water, where an anion exchange reaction occurred after adding equal molar sulfuric acid and the mixture was stirred at 50 °C for 12 h. The solvent was removed by vacuum distillation, the residual crude ionic liquid was purified by ether and dried under vacuum to get acidic ionic liquid VImaILs (25.6 g, 81.5% yield) as a yellowish liquid. The VImaILs was analyzed by ^{13}C nuclear magnetic resonance spectroscopy (NMR, Varian mercury-plus-400) and Fourier transform infrared spectroscopy (FTIR, Nicolet IS10). The reaction route is shown as supplemental Fig. 1.

2.3. Hydrolysis of inulin

In order to investigate the effect of hydrolysis conditions on reducing sugars yield, a series of experiments were carried out. The inulin aqueous solutions with needed concentration (w/w%, the weight ratio of the inulin to water, the same as the following) were prepared and heated to the required temperature in a 50 mL glass flask which was equipped with a magnetic agitator. Then the VImaILs was added according to the needed concentration (w/w%, the weight ratio of VImaILs to water and VImaILs). During the hydrolysis experiments, the solution was sampled at regular