



Full Length Article

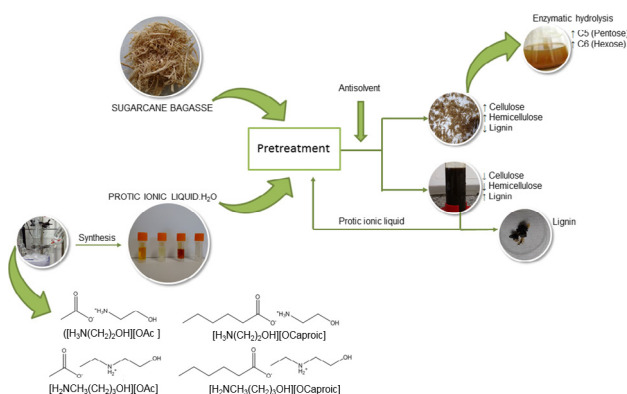
Evaluation of the use of protic ionic liquids on biomass fractionation

E.G.A. Rocha^a, T.C. Pin^{a,b}, S.C. Rabelo^b, A.C. Costa^{a,*}^a Faculdade de Engenharia Química, Universidade Estadual de Campinas – UNICAMP, Caixa Postal 6066, 13083-852 Campinas, São Paulo, Brazil^b Laboratório Nacional de Ciência e Tecnologia do Bioetanol – CTBE, Rua Giuseppe Máximo Scolfaro, 10.000, Polo II de Alta Tecnologia, Caixa Postal 6192, 13083-970 Campinas, São Paulo, Brazil

HIGHLIGHTS

- Four PILs were studied for the pretreatment of bagasse.
- $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$ showed the best performance, pure or mixed with water.
- Scale-up showed the variables studied did not affect the enzymatic conversions.
- $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$ has potential compared to H_2O_2 and hydrothermal pretreatments.
- Preliminary evaluation of $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$ recycle indicates need for optimization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 February 2017

Received in revised form 29 May 2017

Accepted 1 June 2017

Available online 8 June 2017

Keywords:

Sugarcane bagasse

Protic ionic liquid

2-Hydroxy ethylammonium acetate

Pretreatment

Enzymatic hydrolysis

ABSTRACT

This work evaluated the use of protic ionic liquids (PILs) in the pretreatment of sugarcane bagasse. Cations and anions with different chain lengths were used to synthesize four PILs, which had their performances evaluated by the solubilization of lignin in the pretreatment step and polysaccharides conversion in the enzymatic hydrolysis. The recovery and recycling of the best performing PIL (2-hydroxy ethylammonium acetate – $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$) was evaluated, as well as the addition of water in the PIL and the increase in solids concentration in the pretreatment and hydrolysis steps. Pretreatment of 10% (w/w) unground bagasse with $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$: water (5:1 w/w) followed by hydrolysis at 10% (w/v) solids yielded 0.355 g glucose/g raw bagasse and 0.150 g xylose/g raw bagasse.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The use of lignocellulosic biomass in biorefineries for the production of biofuels and other products depends upon the existence of an economically viable and efficient pretreatment that

makes its polysaccharides (mainly cellulose) available to subsequent hydrolysis.

In general, delignifying pretreatments are desirable, because they separate lignin from the carbohydrates that will be subsequently used in hydrolysis and fermentation. During hydrolysis, lignin forms a physical barrier that protects cellulose from enzymatic attack. It also adsorbs nonspecifically the enzymes, increasing the enzymatic loading necessary to obtain a given conversion [1]. Besides, the presence of lignin in the pretreated material

* Corresponding author.

E-mail address: accosta@feq.unicamp.br (A.C. Costa).

decreases the cellulose percentage in the solid [1]. Thus, for hydrolysis at a given load of solids and enzyme, sugars concentration and conversion are in general higher when the biomass was delignified in the pretreatment step [2–4].

Nevertheless, delignifying pretreatments, such as the pretreatments with alkaline hydrogen peroxide [2] or organosolv [3], are considered technologies economically unviable for 2G ethanol production. In general, low formation of inhibitors and efficient removal of lignin are achieved in these pretreatments. On the other hand, reagent costs are considered one of the main disadvantages for these technologies. In the case of the organosolv process, the removal of solvents from the system is necessary and they should be recycled to reduce operational costs and minimize the inhibitory effect on enzymatic hydrolysis or fermentative microorganisms [5]. On the other hand, pretreatments, such as steam explosion [4] or hydrothermal [5] are more attractive due to cost potential, since no catalyst is required and low cost reactor building material is demanded. They also present the major advantage that the hemicellulose and lignin degradation products are present in lower concentration, making them suitable to be developed at commercial scale [6]. However, the produced materials are poorly converted during enzymatic hydrolysis, presenting maximum conversions around 60% at high solids loadings [5].

It has been demonstrated that some ionic liquids (ILs) may be effective alternatives for the pretreatment of biomass, as their use can reduce by-product generation, solvent losses, energy use and carbon dioxide generation [7–9]. ILs are formed by a combination of organic cations with organic or inorganic anions, and the choice of ions is made to obtain the desired properties [10]. In general, they exhibit low vapor pressure, thermal stability, and several adjustable properties, such as polarity, hydrophobicity and solvent miscibility [11–14], besides many of them form two-phase systems that enable product separation and solvent recovery with low energy consumption [15,16]. Such properties make these solvents suitable and potentially capable of replacing most of the common (and toxic) organic solvents used by the chemical industry. However, toxicity is an important variable to be considered in the choice of the IL. In the case of amines, the toxicity is directly linked to the chain size and in the case of acids, its corrosion potential should be considered [18,19].

However, the cost of ionic liquids has been a challenge for their use in biomass pretreatment. An option to reduce the production costs is the use of protic ionic liquids (PILs), whose production is easier and less expensive than the production of aprotic ionic liquids (AILs) [9]. Nevertheless, the majority of studies in the literature evaluate AILs for lignocellulose pretreatment [17–19] and there are a few works considering pretreatment with PILs for further enzymatic hydrolysis [9,17,20,23,24]. Some works have shown that potentially low-cost PILs produced by acetic acid and amines can extract more than 70% of lignin from lignocellulosic biomass (corn stover) [22]. Lignin extraction in the pretreatment has been shown to increase enzymatic hydrolysis yields [2].

The objective of the present work was to evaluate the use of PILs in the pretreatment of sugarcane bagasse. Cations and anions with different chain lengths were used to synthesize the PILs, which were further characterized. The pretreatment performances of the PILs were compared by assessing their delignification capacity and the cellulose conversion obtained in enzymatic hydrolysis. The PIL presenting the best performance (2-hydroxy ethylammonium acetate, $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$) had its recovery and reuse in the pretreatment evaluated. Finally, conditions closer to an industrial process were evaluated. The solids loading in the pretreatment and hydrolysis steps were increased to 10% (w/w), water was added to decrease viscosity and unground bagasse, as it comes from the mill, was used. A patent application was filed for the

use of the PIL $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$ for biomass pretreatment (PCT/BR 2016/000067).

2. Materials and methods

2.1. Protic ionic liquids (PIL's)

PIL's were synthesized by proton transfer between a Brønsted–Lowry acid (acetic acid or hexanoic acid) to the Brønsted–Lowry base (2-Hydroxyethylamine or Bis(2-hydroxyethyl)amine). The general scheme of the reactions is shown in the [Electronic Supplementary Information \(ESI\)](#).

For the present study, the two anions were selected based on increasing alkyl chain length i.e. $[\text{CH}_3\text{COO}^-]$ and $[\text{CH}_3(\text{CH}_2)_4\text{COO}^-]$. The PILs (2-hydroxy ethylammonium acetate - $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OAc}]$ 2-hydroxy ethylammonium hexanoate - $[\text{H}_3\text{N}(\text{CH}_2)_2\text{OH}][\text{OCaproic}]$; 2-hydroxy diethylammonium acetate - $[\text{H}_2\text{NCH}_3(\text{CH}_2)_3\text{OH}][\text{OAc}]$ and 2-hydroxy diethylammonium hexanoate - $[\text{H}_2\text{NCH}_3(\text{CH}_2)_3\text{OH}][\text{OCaproic}]$) were prepared according to the procedures established by Iglesias and Álvarez [10,25]. All chemical agents (purchased from Sigma-Aldrich) were of analytical grade and used without further purification.

The PILs were produced in a jacketed glass reactor using an equimolar amount of acid and base. Since these reactions are exothermic, the dropwise addition of the acid to the ethanolamine was carried out by cooling the amine solution to 10 °C, using a thermostatic bath. The mixture was then stirred during the acid–base reaction and kept under stirring, at room temperature, for a further 24 h.

The process was monitored by refractive index analysis using an automatic refractometer (Mettler Toledo RE40D, Switzerland). The synthesis was considered complete when a constant refractive index was achieved and there was absence of solid precipitates or crystals in the mixture. The liquid was transferred to a 500 mL flask, properly closed and connected to a vacuum pump (70.0 Pa absolute pressure), with vigorous stirring and heating (60 °C), until the water content in the PIL was <1%. The remaining PIL moisture was determined by Karl Fischer titration (Mettler Toledo, DL31, Switzerland).

After synthesis and purification, physical and chemical properties of the PILs were determined. The production of the PILs was confirmed based on studies by Álvarez and Iglesias [10,25].

2.2. Lignocellulosic biomass

Sugarcane bagasse was supplied by São João Mill (Group USJ), located in Araras-SP, Brazil. The material was collected in the 2012/13 crop. It was mechanically harvested and resulted from the last milling before juice extraction. The material was dried at room temperature and the dry matter content was determined by an automatic infrared moisture analyzer (Gehaka, IV2500, Brazil). The bagasse was milled to pass through a 5 mm sieve (Fritsch, Pulverisette 16, Germany), according to the methodology describe by Machado [1]. The milled material was stored in plastic bags for further chemical composition analysis, pretreatment and enzymatic hydrolysis studies.

2.3. Pretreatment

PIL pretreatment was performed according to Holm and Vancov [26,27]: 16 g of bagasse (10% moisture content) were fed to a 1 L evaporating flask at 5% (w/w) solids loading. The reactions were carried out in a rotoevaporator (Ika, RV10 control VC, Germany), for 3.5 h, 150 rpm and 73.3 kPa. Four different temperatures were

Download English Version:

<https://daneshyari.com/en/article/4768559>

Download Persian Version:

<https://daneshyari.com/article/4768559>

[Daneshyari.com](https://daneshyari.com)