Biochemical Engineering Journal 60 (2012) 156–160

Contents lists available at SciVerse ScienceDirect

Biochemical Engineering Journal

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

Short communication

Ionic liquid assisted enzymatic delignification of wood biomass: A new 'green' and efficient approach for isolating of cellulose fibers

Muhammad Moniruzzaman*, Tsutomu Ono**

Department of Material and Energy Science, Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-Naka, Kita-Ku, Okayama 700-8530, Japan

ARTICLE INFO

Article history:
Received 26 September 2011
Received in revised form 3 November 2011
Accepted 6 November 2011
Available online 15 November 2011

Keywords:
Enzymatic delignification
Ionic liquids
Wood biomass
Laccase
Green process
Cellulose rich materials

ABSTRACT

The objective of this study was to provide a new environmentally friendly and efficient approach for isolating cellulose fibers with minimum structural alteration from wood biomass. The method comprised enzymatic delignification of ionic liquid (IL) swollen wood biomass in ILs–aqueous systems with the aim of overcoming low delignification efficiency associated with the difficulties in enzyme accessibility to the solid substrate and the poor substrate and products solubility in aqueous system. It was found that the cellulose rich wood fibers obtained from biological pretreatment in IL–aqueous systems contained significantly lower amounts of lignin as compared to those found in conventional methods. The treated wood fibers were characterized using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and X-ray diffractometry (XRD) and compared those with untreated wood fibers.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The use of lignocellulosic biomass based materials in various sectors (*e.g.*, automotive and aerospace) over petro-materials has received increased attentions due to the growing global environmental awareness, concepts of sustainability and industrial ecology. Wood – the most abundant lignocellulosic resources on the world – consists of up to 50% cellulose that is rigid semi-crystalline embedded in amorphous hemicelluloses and lignin. To produce biocompatible and biodegradable materials, celluloses – Earth's most abundant biopolymer – have been used extensively as source of raw materials. Therefore, the extraction of cellulose fibers from wood biomass has gained a great deal of recent interest. To date, a number of pretreatment methods including physical [1], physico-chemical [2], chemical [3,4], and biological methods [5,6] have been investigated for separation of celluloses from wood biomass. Among these, the biological pretreatment of wood for degrading lignin has received much attention as an environmentally safe or "green" process [7]. For this purpose, generally enzymes isolated from naturally occurring fungi, or with enzymes produced by genetically engineered fungi have been used in aqueous systems. However, this process for lignin degradation has been found to be very slow (*i.e.*, several weeks needed for delignification) due to the difficulties in enzyme accessibility to the solid substrate and the poor solubility of lignin [5,8]. It is therefore desirable to develop a wood pretreatment process that is not only the environmentally friendly but also efficient and cost effective for biomass conversion to cellulose.

To address such issues, this study describes a new environmentally friendly approach for enzymatic delignification of wood biomass using room temperature ionic liquids (RTILs) as a (co)solvent as well as pretreated agent. Ionic liquids (ILs), a potentially attractive "green" recyclable alternative to environmentally harmful organic solvents, have been increasingly exploited as solvents and/or (co)solvents and/or reagents in a wide range of applications including pretreatment of lignocellulosic biomass [9,10]. The high solvating properties of ILs have been exploited in the dissolution of cellulose [11,12], lignin [13] and wood [14–18]. Enzymatic delignification of IL swollen wood biomass in IL–aqueous systems could be an efficient system over conventional route (Fig. 1). The system may have significant advantages due to (i) the improved solubility of substrates and products in ILs and (ii) easy enzyme accessibility to the IL swollen wood cell prior to the delignification. However, many ILs, particularly hydrophilic ones have negative effect on enzyme structure, resulting in deactivation [19,20]. Such effects could be balanced with the increase the solubility of substrates and products leading to better performances in terms of enhanced yield. The treated wood fibers were characterized by various methods including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM),

* Corresponding author. Tel.: +81 86 251 8938; fax: +81 86 251 8908.
** Corresponding author. Tel.: +81 86 251 8908; fax: +81 86 251 8908.
E-mail addresses: moniru-m@cc.okayama-u.ac.jp, mzaman49@yahoo.com (M. Moniruzzaman), tono@cc.okayama-u.ac.jp (T. Ono).

1369-703X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.bej.2011.11.001

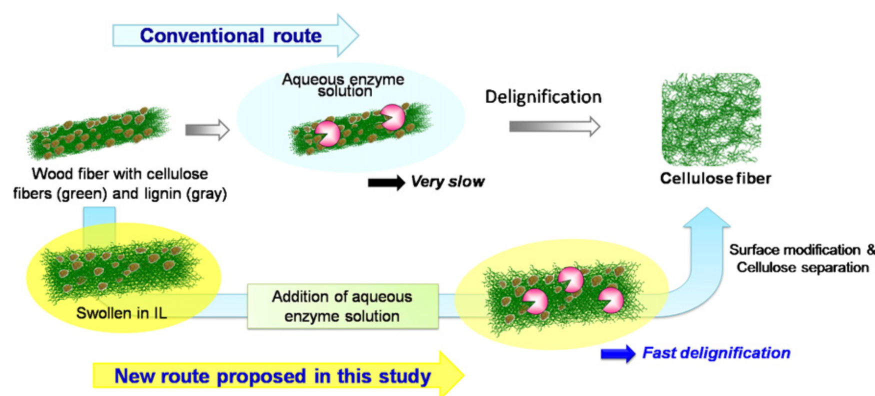

Fig. 1. Comparison of our proposed method to conventional enzymatic delignification in aqueous systems.

thermalgravimetric analysis (TGA) and X-ray diffractometry (XRD) and compared those with untreated wood fibers.

2. Materials and methods

2.1. Materials

Wood chips from hinoki cypress (*Chamaecyparis obtusa*) were received from Okayama Biomass Center, Japan. The IL $[C_2mim][OAc]$ (1-ethyl-3-methylimidazolium acetate) (≥95%) was obtained from Ionic Liquids Technologies GmbH (Heilbronn, Germany) and used as received. Commercial Laccase Y120 (EC. 1.10.3.2) (1000 U/g) from Trametes sp. was kindly supplied by Amano Enzyme Inc. (Nagoya, Japan).

2.2. Enzymatic delignification in IL–aqueous systems

A simplified overview of experimental method was shown in the Supporting Information. Firstly, wood chips were grounded into powders through a lab-scale roller mill and passed through sieves to separate fractions with 110–550 μm particle sizes which were dried overnight in an oven at 110 °C. In a typically experiment, 200 mg of wood were added to 2 g IL in a three neck flask and heated at 80 °C in an oil bath with magnetic stirring for 1 h. After cooling the wood–IL mixture to RT, acetate buffer (100 mM, pH 4.5) containing laccase were added to the flask, whereas 1-hydroxybenzotriazole (HBT) (1.5 wt% of wood chips) were added as a mediator. Reaction was carried out with the supply of O_2 bubbles with a small stirrer bar at 50 °C. After cooling the reaction mixture to RT, 0.1 M NaOH was used to wash ILs and lignin away from the cellulosic fibers. To remove traces of NaOH, the fibers were washed with distilled water until pH paper showing the final drops of washing liquid to be pH neutral. The lignin content in the filtrate NaOH solution was determined by measuring absorbance at 280 nm [15]. Alkali lignin from Aldrich Inc. was used to prepare the calibration curve (see Supporting Information). After drying the treated wood fibers in a convection oven at 65 °C for 48 h, sample was weighted and stored at vacuum desiccator. The recovery of IL for further use was carried out as described previously [16].

2.3. Characterizations

The fibers' morphology was characterized using a scanning electron microscope (SEM) (S-4700, Hitachi Ltd., Tokyo, Japan). Fibers were mounted on metal stubs by double-faced tap and images were taken. Prior to imaging samples were coated with gold–palladium in a sputter coater (E1030 Ion Sputter, Hitachi Ltd.). The crystallinity of the untreated and treated ground wood was examined using a XRD-6100 Diffraction System (Shimadzu, Japan). The diffraction patterns were measured from $2\theta = 8$–$40°$ with scan speed of $0.1° \text{ min}^{-1}$ using Cu Kα radiation at 40 kV and 30 mA. The FTIR spectra of the samples were recorded from a KBr disk containing 1% finely ground samples on an IRPrestise-21 FTIR spectrophotometer (Shimadzu, Japan) in the range of 4000–40 cm^{-1}. Spectral outputs were recorded in the transmittance mode as a function of wave number. Thermal stability of each sample was determined using a Pyris 1 Thermogravimetric analyzer by heating 10 mg sample in platinum pan at a rate of 10 °C/min in a nitrogen environment.

3. Results and discussion

Firstly, the lignin content of ground wood was determined using TAPPI methods [21,22] with a scaled down process. It was found that wood from hinoki contained about 28.5% Kraft lignin and 0.96% acid soluble lignin. Then, we have developed an experimental procedure for performing the IL assisted-enzymatic delignification of wood (see Supporting Information). In this study, IL $[C_2mim]$ $[OAc]$ was used due to its high ability in dissolution of wood [18] and its enzyme compatible nature [23]. This IL provides many desirable properties such as low toxicity, low corrosiveness, low melting point (<−20 °C) and low viscosity (10 mPa at 80 °C). To check thermal stability of the IL$[C_2mim]$ $[OAc]$, Rogers and co-workers [18] recorded ^{1}H and ^{13}C NMR spectra of original IL and of IL heated at 110 °C for 48 h and found no significant changes. Commercial laccase that are copper-containing oxidase enzymes obtained from white rot fungi was selected as biocatalyst because it can degrade the lignin of biomass with leaving the other components (*e.g.*, cellulose) virtually untouched [24]. Recently, it was reported that laccases can maintain their activity for the oxidation of 2,2′-azino-bis(3-ethyl-benzthiazoline-6-sulfonic acid) and catechol in ILs–aqueous systems containing over 80% of water [25,26]. This is consistent what was reported for the performances of others enzymes in IL–aqueous systems [20].

Table 1 shows the results obtained from various delignification methods. For comparison, enzymatic delignification in aqueous systems in the absence of IL (see entry 1) and delignification in IL–aqueous systems without enzyme (see entry 2) were also performed as control experiments. In case of entries 3–5, firstly, 200 mg wood chips were pretreated with 2 g IL under identical conditions. Then, as shown in explanatory note of Table 1, required amounts of buffer was added to fix the IL concentration 20 wt%, 10 wt% and 5 wt% in delignification reaction media for entries 3, 4 and 5, respectively. Note that the overall amount of enzyme and enzyme mediator kept constant for entries 3–5 to investigate the effect of IL contents on enzymatic delignification efficiency. In comparison to control experiments (entries 1 and 2), enzymatic

Download English Version:

https://daneshyari.com/en/article/3676

Download Persian Version:

https://daneshyari.com/article/3676

Daneshyari.com