Bioresource Technology 144 (2013) 429–434

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Synergistic benefits of ionic liquid and alkaline pretreatments of poplar wood. Part 1: Effect of integrated pretreatment on enzymatic hydrolysis

Tong-Qi Yuan [a], Wei Wang [b], Feng Xu [a,*], Run-Cang Sun [a,c,*]

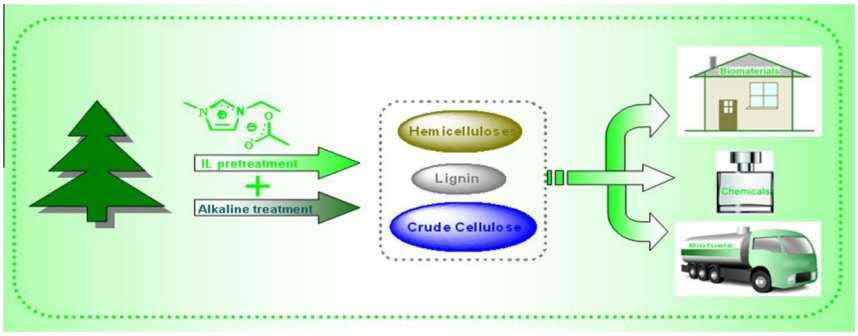
[a] Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, PR China
[b] Institute of Microbiology, Beijing Forestry University, Beijing 100083, PR China
[c] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

HIGHLIGHTS

- Ionic liquid and alkaline pretreatments were combined for biomass pretreatment.
- The yield of glucose for the integrated pretreated poplar wood was 99.2%.
- The reliable reasons for enhancing the enzymatic hydrolysis were investigated.
- The yield of hemicellulosic and lignin fractions was 59.3% and 74.4%, respectively.

GRAPHICAL ABSTRACT

Ionic liquid pretreatment coupled with mild alkaline extraction was developed as an environmentally friendly pretreatment process to fractionate hemicelluloses and lignin while integrating biofuels production into a biorefinery scheme.



ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form 3 December 2012
Accepted 5 December 2012
Available online 27 December 2012

Keywords:
Poplar wood
Ionic liquid
Biorefining
Integrated pretreatment
Enzymatic hydrolysis

ABSTRACT

An environmentally friendly pretreatment process was developed to fractionate hemicelluloses and lignin from poplar wood by ionic liquid (IL) pretreatment coupled with mild alkaline extraction. Hemicellulosic and lignin fractions were obtained in high yields, amounting to 59.3% and 74.4%, respectively, which can served as raw materials for production of value-added products. The yield of glucose for the integrated pretreated poplar wood was 99.2%, while it was just 19.2% for the untreated material. The synergistic benefits of the removal of lignin and hemicelluloses, the increase of the cellulose surface area, and the conversion of cellulose fibers from the cellulose I to the cellulose II crystal phase resulted in the high glucose yield for the integrated pretreated substrate. Therefore, the IL based biorefining strategy proposed can integrate biofuels production into a biorefinery scheme in which the major components of poplar wood can be converted into value-added products.

1. Introduction

Lignocellulosic biomass is composed of three major components: cellulose, a linear polymer of glucose with a very highly regular H-bonded network between its layers, especially in the case of crystalline cellulose; hemicelluloses, a complex branched polymer of xylose and other sugar derivatives; and lignin, a polyphenyl propanoid macromolecular assembly that is covalently cross-linked to hemicelluloses (Huber et al., 2006). This abundant renewable resource can serve as a source of carbon-neutral or carbon-negative feedstock for the production of biofuels, chemicals, and polymers, generally referred to as the biorefinery (Ragauskas

* Corresponding authors. Tel./fax: +86 010 6233 6903.
E-mail addresses: xfx315@bjfu.edu.cn (F. Xu), rcsun3@bjfu.edu.cn, ynsun@scut.edu.cn (R.-C. Sun).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.12.034

et al., 2006). It is becoming a logical alternative to petroleum in light of the longevity and stability of petroleum supply, as well as the environmental impacts of its production and use.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The concept of an integrated biorefinery combines the production of both fuels and chemicals, starting from the pretreatment of raw biomass, fractionation into its main fractions and the conversion to platform chemicals required for various consumer products (Stark, 2011). The pretreatment step has been recognized as a technological bottleneck for the cost-effective development of biorefinery, especially for the production of biofuels. The pretreatment technologies can be classified into biological, physical, chemical, and physico-chemical methods. The differences and advantages of each pretreatment method have been previously discussed and reviewed (Alvira et al., 2010; Hendriks and Zeeman, 2009).

The most promising strategy is to integrate biofuels production into a biorefinery scheme in which the major components of the lignocellulosic biomass are converted into value-added products to offset the costs of the whole process (Pan et al., 2005a). The more recent discoveries of dissolution of lignocellulosic biomass in ionic liquids (ILs), with at least partial separation of the major constituent biopolymers, promote IL pretreatment as a potential alternative to established pretreatment techniques (Muhammad et al., 2012; Ouellet et al., 2011; Stark, 2011; Sun et al., 2011; Tadesse and Luque, 2011). However, the current biorefinery cycle based on IL pretreatment focuses on cellulose (with a strong emphasis on the subsequent generation of ethanol as transportation fuel) as the main active participant, whereas less attention has been paid to hemicelluloses and lignin (Spronsen et al., 2011; Sun et al., 2009, 2011). It has been pointed out that recover high molecular weight fractions of the major biopolymers will find the most to gain by consideration of ILs (Sun et al., 2011).

Besides of advantages, each pretreatment method has its limitations. However, the limitations can be solved by considering the synergistic benefits of combined methods. For instance, cellulose crystallinity and lignin and hemicelluloses content could be declined during the IL pretreatment, which will benefit the rate and extent of hydrolysis (Labbé et al., 2012; Lee et al., 2009). But the residual lignin and hemicelluloses in the IL pretreated lignocellulosic biomass significantly affect the enzymatic hydrolysis. Lignin appears to limit cellulose hydrolysis by two distinct mechanisms: by forming a physical barrier that prevents enzyme access and by non-productive binding cellulolytic enzymes (Pan et al., 2005b). Xylooligomers, the hydrolysis products of hemicelluloses, are strong inhibitors of cellulose hydrolysis as their negative impact on cellulase adsorption (Qing et al., 2010; Qing and Wyman, 2011). Recently, a mild alkaline (sodium hydroxide) pretreatment method was proposed for improving the enzymatic hydrolysis efficiency of lignocellulosic biomass for ethanol production (McIntosh and Vancov, 2010; Vancov and McIntosh, 2011; Wu et al., 2011). The digestibility improvement was attributed to the removal of hemicelluloses and lignin, the reduction of acetyl content, and the disruption of the lignin–carbohydrate matrix.

A few previous studies have combined the IL dissolution/regeneration of biomass with alkaline extraction and desired results have been obtained (Geng and Henderson, 2012; Lan et al., 2011; Lee et al., 2009). However, there are only a very few published studies on integration this novel pretreatment into a biorefinery scheme, while neglecting the potential of hemicelluloses and/or lignin. In this study, a combination of IL pretreatment followed by mild alkaline extraction of biomass was proposed as a novel method to consider the synergistic benefits of them. The whole process was conducted under an integrated biorefinery scheme. Poplar wood, which has been identified as a short rotation woody crop with several desirable qualities for biofuels production including high cellulose content, pest and disease resistance and widespread geographic distribution (Sannigrahi et al., 2010), was selected as the lignocellulosic biomass in the present study. 1-Ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) was used as a representative IL because of its low viscosity, low melting temperature, low toxicity, and its capacity for dissolution of cellulose and whole biomass under relatively mild conditions (Samayam and Schall, 2010; Sun et al., 2009). The impacts of the integrated pretreatment steps on the enzymatic hydrolysis have been investigated. However, the chemical structures of the hemicellulosic and lignin fractions obtained will be published separately.

2. Methods

2.1. Materials

Triploid *Populus tomentosa* Carr., a fast-growing poplar tree, 3 years old, was harvested from Shandong province, China. The wood sample was ground to pass through a 0.8 mm size screen and was then extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 6 h. The material, which passed through a 80-mesh screen and was retained on a 100-mesh screen, was collected for subsequent experimentation. The ionic liquid [C_2mim][OAc] ($\geqslant$98.5%) was purchased from Lanzhou Institute of Chemical Physics, Lanzhou, China. Commercial cellulase preparation (Celluclast 1.5 L) and β-glucosidase, produced by *Tricoderma reesei* ATCC 26921 and almonds, respectively, were purchased from Sigma Aldrich. All other chemicals used were of analytical or reagent grade and directly used as purchased without further purification.

2.2. Pretreatment procedure

The procedure of combination of IL pretreatment followed by mild alkaline extraction of poplar wood is briefly described in Fig. 1. To ensure the complete dissolution of biomass, 5 g poplar wood (sample A) was added to 100 g of [C_2mim][OAc] in a 250 mL dried three-neck flask according to a previous literature (Sun et al., 2009). The mixture was then placed into an oil bath and heated on a hot plate (IKA RCT basic, Germany) with vigorous magnetic stirring (600 rpm) at 110 °C for 12 h under a N_2 atmosphere. After the complete dissolution, the regeneration of the dissolved wood was carried out by precipitation of the heated solution into 1000 mL deionized water under vigorous magnetic stirring. The regenerated wood (sample C) was obtained by filtering through a cellulose nitrate membrane filter (pore size 0.45 μm, Whatman®), thoroughly washing with deionized water, and freeze-drying. The filtrate, containing water, IL, and some degraded carbohydrates and lignin, was evaporated under reduced pressure. The resulting liquor was obtained as the recovered IL. The IL pretreated wood was successively treated with 1 M sodium hydroxide with a solid-to-liquid ratio of 1:15 (g/mL) at 75 °C for 3 h for isolation of lignin (RAL) and hemicellulosic (RAH) fractions. The purification procedure was performed according to the method of Sun et al. (1999). The residue obtained after alkaline extraction was labeled as sample D. The same alkaline extraction procedure was conducted for sample A and the residue obtained was named as sample B.

2.3. Compositional analysis

The chemical composition of the raw and pretreated poplar wood was determined in duplicate using concentrated acid hydrolysis followed by dilute acid hydrolysis according to the standard laboratory analytical procedures developed by the National