Bioresource Technology 128 (2013) 330–336

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

# Influence of acidic and alkaline aqueous regeneration on enzymatic digestibility of the cellulose fraction recovered from [amim]Cl-treated rice husk

Anika Salanti, Luca Zoia, Paola Frigerio, Marco Orlandi *

*Department of Environmental and Earth Sciences, University of Milano-Bicocca, Piazza della Scienza 1, Milan I-20126, Italy*

## HIGHLIGHTS

- ▶ The enzymatic digestibility of regenerated rice husk depends on the regeneration technique.
- ▶ Ionic liquid pretreatment is marginal in increasing the saccharification yield of rice husk.
- ▶ Hemicellulose is the lignocellulose constituent mainly influencing the enzymatic activity.

## ARTICLE INFO

*Article history:*
Received 11 June 2012
Received in revised form 3 October 2012
Accepted 12 October 2012
Available online 23 October 2012

*Keywords:*
Rice husk
Enzymatic hydrolysis
Ionic liquid
Nuclear magnetic resonance
Gel permeation chromatography

## ABSTRACT

The recalcitrance of lignocelluloses toward enzymatic hydrolysis necessitates pretreatments. Ionic liquid pretreatment with 1-allyl-3-methylimidazolium chloride ([amin]Cl) was applied to risk husk and cellulose-containing fractions were recovered from the ionic liquid solutions by acidic, alkaline, and alkaline–acidic regeneration respectively. Enzymatic hydrolysis of the recovered materials was carried out and results demonstrated that: (i) acidic regeneration was not substantial to ensure enhanced enzymatic digestibility; (ii) alkaline regeneration increased the enzymatic hydrolysis; (iii) alkaline–acidic regeneration led to an almost complete hydrolysis of the carbohydrate fraction. The obtained results were rationalized by means of chromatographic analyses of soluble fractions collected after the different regeneration processes: the removal of hemicellulose, which increased going from the acidic to the alkaline–acidic regeneration, seemed to play a crucial role in enhancing the rice husk saccharification.

## 1. Introduction

Overcoming the recalcitrant structure of lignocellulose to release sugars is one of the priorities for the emerging cellulosic ethanol and bio-based chemical industries (Sun and Cheng, 2002). A number of lignocellulose pretreatment technologies have been investigated, but all of them suffer from relatively low sugar yields, severe reaction conditions, and high processing costs (Yanez et al., 2006; Saha and Cotta, 2008; Banarjee et al., 2011; Magawati et al., 2011). Moreover, the current leading lignocellulose pretreatments cannot efficiently disrupt the highly organized hydrogen bond network among polysaccharides chains in crystalline cellulose, often resulting in slow hydrolysis rates and low cellulose digestibility (Wyman et al., 2005a,b). Mechanical pretreatments are necessary to enhance biomass digestibility by reducing particle size and partially disaggregating the highly organized and cemented structure of lignocellulose (Vidal et al., 2011); however, these treatments cannot overcome the negative influence of cellulose crystallinity and morphology, and lignin and hemicellulose contents on enzymatic saccharifcation (Yoshida et al., 2008; Mussatto et al., 2008; Kim et al., 2011).

Ionic liquids (ILs) such as 1-allyl-3-methylimidazolium chloride ([amim]Cl) and 1-butyl-3-methylimidazolium chloride ([bmim]Cl) have been recognized as ideal non-derivatizing solvents for lignocellulosic substrates (Kilpelainen et al., 2007; Fort et al., 2007). The aromatic electron-rich cationic moiety creates strong interactions for polymers which undergo $\pi$ stacking as is the case of the lignin polymer, while the chloride counter-anion is the most efficient in disrupting the extensive inter- and intramolecular hydrogen bonding interactions present in cellulose. As a result, the ionic liquid diffuses into the interior of the material and progressively destroys its cell wall structure. The cellulose fraction can then be recovered by the addition of an anti-solvent, such as water or ethanol (Swatloski et al., 2002). The regenerated cellulose mostly retains its original degree of polymerization and polydispersity, but its morphology is significantly changed and its microfibrils are fused into a relatively homogeneous structure (Li et al., 2009). The regeneration process impacts the microstructure of cellulose, modifying its degree of crystallinity, porosity, and surface area (Zhu et al.,

---

* Corresponding author. Tel.: +39 02 64482812; fax: +39 02 64482835.
*E-mail address:* marco.orlandi@unimib.it (M. Orlandi).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.10.057