



A green and efficient technology for the degradation of cellulosic materials: Structure changes and enhanced enzymatic hydrolysis of natural cellulose pretreated by synergistic interaction of mechanical activation and metal salt



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HIGHLIGHTS

- Mechanical activation and metal salt treatments were combined in a stirring ball mill.
- Al(NO₃)₃ showed better pretreatment effect for cellulose than NaNO₃ and Zn(NO₃)₂.
- Mechanical activation and Al(NO₃)₃ treatments showed a synergistic interaction.
- The presence of Al(NO₃)₃ remarkably enhanced the enzymatic hydrolysis of cellulose.
- A simple, efficient and green technology for the degradation of cellulosic materials.

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ABSTRACT

A new technology for the pretreatment of natural cellulose was developed, which combined mechanical activation (MA) and metal salt treatments in a stirring ball mill. Different valent metal nitrates were used to investigate the changes in degree of polymerization (DP) and crystallinity index (CrI) of cellulose after MA + metal salt (MAMS) pretreatment, and Al(NO₃)₃ showed better pretreatment effect than NaNO₃ and Zn(NO₃)₂. The destruction of morphological structure of cellulose was mainly resulted from intense ball milling, and the comparative studies on the changes of DP and crystal structure of MA and MA + Al(NO₃)₃ pretreated cellulose samples showed a synergistic interaction of MA and Al(NO₃)₃ treatments with more effective changes of structural characteristics of MA + Al(NO₃)₃ pretreated cellulose and substantial increase of reducing sugar yield in enzymatic hydrolysis of cellulose. In addition, the results indicated that the presence of Al(NO₃)₃ had significant enhancement for the enzymatic hydrolysis of cellulose.

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1. Introduction

At present, the pursue of alternative and renewable energy sources have attracted much more interest due to the growing demand for energy and the associated issues of fossil fuels such as global warming, greenhouse gas emissions and uncertain sources, and the production of bioethanol has received much attention (Brethauer and Studer, 2014). Although the current industrial production of bioethanol mainly relies on sucrose- and

starch-containing raw materials, the processes must increasingly rely on sustainable resources such as cellulosic biomass (Koppram et al., 2014). Natural cellulose, the most ubiquitous organic polymer in nature, is considered as an almost inexhaustible source of raw material for the increasing demand (Holt et al., 2010; Kim and Yun, 2006). The conversion of cellulose to monosaccharides or short oligosaccharides (especially glucose) is a critical process for large-scale production of renewable fuels, chemicals, and biomaterials, and the typical process of deconstructing cellulose to sugars is enzymatic hydrolysis (DeMartini et al., 2013). However, cellulose is very recalcitrant to its depolymerization in glucose units by enzymatic hydrolysis due to the high degree of

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crystallinity supported by strong inter- and intramolecular hydrogen bonds, low surface area for enzyme binding, and its general insolubility (Wahlström et al., 2012). Therefore, pretreatment is essential to disrupt the high crystallinity structure of cellulose and enhance its accessibility to enzyme, and pretreatment step is critical in the entire bioethanol production process as it involves high cost of operation (Baadhe et al., 2014). Effective pretreatment can dramatically improve enzymatic saccharification of cellulose and reduce enzyme loading and hydrolysis reaction time, contributing to significant reduction of production cost.

Currently, a number of pretreatment technologies of cellulose, such as microbial pretreatment, milling, steam explosion, hydrothermal pretreatment, dilute acid or alkali pretreatment, wet oxidation, microwave pretreatment, ionizing radiation, and varied combination pretreatments, have been extensively investigated (Alvira et al., 2010; Hendriks and Zeeman, 2009). Every method has its own advantages and disadvantages, and lots of efforts are underway to determine the type of pretreatment more efficient and environmentally friendly for cellulosic materials. Mechanical activation (MA), which refers to the use of mechanical actions to change the crystalline structures and physicochemical properties of the solids, has been successfully used for the pretreatment of lignocellulose (Huang et al., 2009; Liao et al., 2011). When subjected to intense mechanical milling, the stable hydrogen bonds and crystalline structure of cellulose were destroyed significantly, leading to the increase in accessibility of cellulose (Hu et al., 2014a). MA pretreatment is considered to be a relatively simple and environmentally friendly physical procedure attributed to the operations without the use of solvents, intermediate fusion, etc. (Baláz and Dutková, 2009). It is well known that the main disadvantage of MA is high energy requirement, and the energy cost of MA is proportional to the milling time (Zhu et al., 2010). Combining a chemical treatment with MA pretreatment can potentially overcome this drawback since the combination pretreatment process may initiate a synergistic effect thereby reduce the pretreatment time and energy consumption. Metal salts have been used for the pretreatment of cellulosic materials as they can disrupt the hydrogen bonds and induce the degradation of cellulose (Thulluri et al., 2013; Wang et al., 2013). Compared with common chemical pretreatments such as inorganic acids and organic solvents, melt salts are less corrosive to equipment and friendlier to environment, resulting in the feasibility of industrial applications for bioconversion of cellulosic biomass. Moreover, a suitable concentration of metal salt can improve the enzymatic hydrolysis of cellulose (Liu and Zhu, 2010). Commonly, metal salt pretreatment is carried out in molten state or aqueous solution but cannot be performed in solid phase condition because of the poor contact between melt salts and cellulose. During the process of MA, intense ball milling induces the destruction of stable hydrogen bonds and crystalline structure of cellulose and increases its specific surface area, which can make metal salts easily move and contact with cellulose in solid phase, leading to the direct and effective action on cellulose macromolecules. In addition, a part of mechanical energy quickly converts into heat and cause local high temperature. The good thermal conductivity of metal salts can effectively transfer the heat and result in the temperature uniformity during MA pretreatment. So, the combination of MA and metal salt treatments hopefully exhibits synergistic effect on the pretreatment of cellulose.

The present study is focused on investigating the synergism of the combined technology of MA and metal salt treatments on the structure changes and enzymatic hydrolysis of cellulose. MA combined with different metal salts (different metal cations with the same anion) were first applied to pretreat cellulose, and then an effective metal salt was chosen to systematically study the synergism of MA + metal salt (MAMS) pretreatment by comparing with MA pretreatment. The structure changes of cellulose before

and after pretreatments were analyzed by using degree of polymerization (DP) measurement, X-ray diffraction (XRD), and scanning electron microscopy (SEM), and enzymatic hydrolysis of different cellulose samples was also investigated and compared.

2. Methods

2.1. Materials

Defatted cotton fiber with a cellulose content of over 99 wt.% and a DP of 1010 was obtained from Hubei Xiangtai Cellulose Co., Ltd. (China), and it was used as natural cellulose material in this study. Commercial cellulase (90 filter paper units (FPU)/g) was purchased from Aladdin Industrial Corporation (Shanghai, China). Other chemical reagents were of analytical grade without further purification and obtained commercially, and deionized water was used throughout the work.

2.2. Pretreatments of cellulose

Cellulose was subjected to MAMS and MA pretreatments, respectively. MAMS pretreatment was performed in a customized stirring ball mill driven by a commercially available drill press equipped with a speed-tuned motor (Huang et al., 2008). For each experiment, fixed amount of milling balls (400 mL, 5 mm diameter) was first added into a jacketed stainless steel chamber (1200 mL), and then 15.0 g of cellulose, 1 wt.% of metal salt (weight percent compared to cellulose) were added into the chamber. The mixture was subjected to milling at the speed of 375 rpm under a constant temperature of 50 °C by circulating the thermostatic water in the jacket of chamber. When milled for different designated time, the balls were removed from the milled cellulose sample, which was then divided into two parts. One part was unwashed, and this unwashed sample was vacuum-dried at 50 °C and then sealed for the measurements of DP, XRD and SEM. The other part was first washed with water to remove metal salt and then with absolute alcohol to prevent cellulose hornification in the presence of water when vacuum-dried at 50 °C. Both the unwashed and washed samples were sealed for enzymatic hydrolysis experiments.

MA pretreatment of cellulose was operated the same way as in MAMS pretreatment, except for the non-addition of metal salts.

2.3. Determination of DP

The average DP of different cellulose samples was measured viscosimetrically in CuEn (copper ethylene diamine solution) using an Ubbelohde viscometer at 25 ± 0.1 °C, and the intrinsic viscosities obtained ($[\eta]$) were converted into the respective values of DP by the following equation (Cao and Tan, 2002):

$$DP^{0.905} = 0.75[\eta_{CuEn}(\text{cm}^3/\text{g})] \quad (1)$$

2.4. XRD analysis

XRD analysis was carried out by a D/MAX 2500 V diffractometer (Rigaku, Japan). XRD patterns were recorded from 5° to 40° with a speed of 0.02°. The determination was performed with Ni-filtered Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. Crystallinity index (CrI) of the sample was calculated by referring to diffraction intensities of crystalline region and amorphous region according to the following equation (Kim and Holtzapfle, 2006):

$$\text{CrI} = \frac{(I_{002} - I_{\text{am}})}{I_{002}} \times 100 \quad (2)$$

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