



Enhanced lignin extraction process from steam exploded corn stalk



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ABSTRACT

In this work, the alkaline extraction processes of lignin from untreated and steam-exploded corn stalk were compared and the enhanced extraction process was investigated by neutral solvent extraction and structural analysis of lignin. It was found that a first order model could readily simulate the lignin extraction from untreated stalk while it was helpless to describe the enhanced process after steam explosion due to the intense dissolution of lignin at the beginning stage of extraction. The lignin extracted by neutral solvent from ball-milled corn stalk and its structural characterization demonstrated that the poor description of extraction process by a first order model was mainly attributed to the considerable depolymerization during steam explosion. Due to the depolymerization of lignin, the alkaline extraction after steam explosion became the direct dissolution of depolymerized lignin and was successfully simulated by a second-order model. Finally, the activation energy of lignin alkali-extraction decreased 37.78% after steam explosion treatment with 1.8 MPa and 5 min, which indicated that milder extraction conditions were available to extract lignin from steam-exploded corn stalk. This study also provides a basic guidance for delignification approaches of lignocelluloses after steam explosion.

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1. Introduction

The slow decline of fossil resources and the deterioration of human environment prompt people to rethink the adverse impacts brought by thoughtless use of non-renewable resources and look attentively for sustainable resources and energy. Lignocellulosic biomass is an apt resource to displace fossil resources for energy and useful chemicals production owing to its renewable character and abundance in nature [1]. However, actual lignocellulosic biomass shows a highly tight architecture that contains cellulose fibrils and complex “matrixing” polymers mainly including hemicelluloses and lignin. Thus, pretreatments of biomass to destroy the compact network structure and enhance the accessibility of saccharification are normally necessary [1]. Among the alternative pretreatments, steam explosion is considered to be an efficient pretreatment due to fewer environmental impacts, investment costs and energy demand compared with other treatments which require the addition of other chemicals [2]. During a steam explosion process, biomass is subjected to high-pressure steam followed by rapid decompression, in which partial hemicelluloses are degraded and the fibrous materials are shattered by the instantaneous expansion force. The degraded hemicelluloses are

eliminated by the subsequent water washing and the lignin-rich loose fibrous materials are proposed for enzymatic hydrolysis and ethanol fermentation. However, the remaining lignin is still a main limitation for the effective enzymatic saccharification of cellulose due to the spatial obstacle [3,4]. In addition, lignin also decreases the activity of cellulase by non productive binding [5]. Therefore, lignin removal is important for steam-exploded lignocelluloses to produce ethanol and other bioenergy.

Unlike the other two major components in lignocelluloses which are released as monomeric carbohydrates, lignin is composed of three different phenylpropane monomers and polymerized randomly by ether linkages or C–C bonds. It contributes as much as 30% of the weight and 40% of the energy content of lignocellulosic biomass [6]. Lignin's native structure allows its versatility of applications as phenol substitution for synthetic resins, dispersant for dyes and pesticides, binder for feeds and fertilizers. Currently, other value-added applications such as lignin-based polymers, carbon fibers, antioxidant and depolymerized chemicals, [7] are also being developed. Since the bioconversion of fractionated cellulose to biofuels is not economically competitive due to the little use of other biomass components, the effective utilization of lignin offers a significant opportunity for the commercial operation of a lignocellulosic biorefinery [8].

Extraction is the first step in isolation and utilization of lignin from steam-exploded lignocelluloses. Alkaline extraction is a relatively facile and efficient process to obtain lignin from

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lignocellulosic biomass compared with other solvent extraction due to the high solubility of the polymer in alkali. Generally, lignin is supposed to be depolymerized by aryl ether breakage in a heated alkaline medium and dissolved in the liquid [9,10]. During this cooking process, depolymerization of lignin into fragments destroys the impact triaxial structure and increases the solubility of lignin by reducing the molecular weight and enhancing the content of hydrophilic groups, such as phenolic hydroxyl groups. Therefore, the depolymerization of lignin is essential for alkaline extraction. When steam explosion is used to assist the extraction of bioactive compounds from plant tissues, it is suggested to enhance the extraction efficiency by increasing the specific surface area due to the formation of large fissures and micropores [11–13]. However, the high temperature and weak acid during steam explosion also induce severe changes of original lignin in the cell wall due to the high sensitivity of protolignin structure [14,15]. The reactions of lignin can change its solubility in an alkaline medium, which also enhances the kinetics of lignin extraction after steam explosion. However, whether the increase of specific surface area or the changes of lignin structure contribute more to the lignin alkaline extraction kinetics after steam explosion is still ambiguous.

In this work, the alkaline extraction processes of lignin from untreated and steam-exploded corn stalk were firstly investigated and compared. In order to eliminate the effects of alkali-induced lignin depolymerization, a neutral solvent of dioxane/water (96:4, v/v) was used to extract lignin from ball-milled corn stalk before and after steam explosion treatment. Moreover, gel permeation chromatography (GPC), heteronuclear single quantum coherence (HSQC) and quantitative ^{13}C NMR spectra were applied to characterize the variation of lignin structure and explore the enhancement mechanism of lignin extraction process after steam explosion treatment. Finally, a second-order extraction model was employed to simulate the lignin extraction process according to its extraction behavior from steam-exploded corn stalk and the extraction activation energy (E_a) was calculated.

2. Materials and methods

2.1. Experimental materials

Corn stalk harvested in September 2012 was kindly provided by the Chinese Academy of Agricultural Sciences, Beijing. The corn stalk compositions were determined according to the modified National Renewable Energy Laboratory (NREL) analytic methods [16,17]. Specifically, 0.3 g corn stalk was treated with 3 mL 72% H_2SO_4 at 30 °C for 2 h, then diluted to 4% and autoclaved at 121 °C for 45 min. The hydrolysis solution was filtered and analyzed for sugar content. The sugar content was determined by HPLC (1200 series, Agilent Technologies) equipped with a refractive index detector (RID) and an organic acid analysis column (Aminex[®] HPX-87H Ion Exclusion Column). The column was operated at 65 °C and eluted with 5 mM H_2SO_4 solution at a flow rate of 0.5 mL/min. The solid residue was dried at 105 °C for 12 h and further placed in the muffle furnace at 550 °C for 2 h. The weight of ash was recorded and the content of Klason lignin was calculated by deducting the ash content from the solid residue. Each sample was analyzed in triplicate. The average chemical compositions of dried corn stalk were cellulose $46.54 \pm 1.87\%$ (w/w), hemicellulose $28.41 \pm 0.87\%$ (w/w), Klason lignin $20.42 \pm 1.56\%$ (w/w) and ash $4.62 \pm 0.30\%$ (w/w). All laboratory reagents were chemically pure.

2.2. Steam explosion pretreatment

Steam explosion pretreatment was performed in a 5 L batch vessel (Weihai Automatic Control Reactor Ltd., China) with

previously established optimum conditions of 1.8 MPa pressure and 5 min treatment time [16]. After pretreatment the corn stalk was cleaned with distilled water to dissolve the water soluble hemicelluloses and squeezed to obtain solid residue. The solid residue, named steam-exploded corn stalk, was dried in a forced-air oven at 55 °C for 48 h and stored in a dry place at room temperature until usage. According to the analysis method in Section 2.1, the average chemical compositions of steam exploded corn stalk were cellulose $55.34 \pm 1.03\%$ (w/w), hemicellulose $11.49 \pm 0.25\%$ (w/w), Klason lignin $30.31 \pm 1.47\%$ (w/w) and ash $2.90 \pm 0.34\%$ (w/w).

2.3. Lignin extraction and evaluation

2.3.1. Lignin alkaline extraction

The untreated and steam-exploded corn stalks were smashed and screened through a 40 mesh sieve (Zhejiang Yingchao Instrument Co., Ltd., China). About 0.08 g (measured precisely) of dried corn stalk was extracted with 1 ml of 1% NaOH in a sealed pressure-tolerant glass tube placed in a digester (Shanghai Yidian Co., Ltd., China) which was heated to the desired temperature. These experiments were performed at 40, 60, 80, 100, 120 and 140 °C in two repetitions. After extraction, the sealed tube was opened carefully (especially when extraction temperature was over 100 °C) and quickly placed in an ice bath. After that, the extract was diluted to 40 ml with distilled water and centrifuged at 4 °C for 5 min. The supernatant was separated from solid residue, diluted by 10-fold distilled water and detected by ultraviolet (UV) absorption at 280 nm (UVmini-1240, SHIMADZU).

2.3.2. Milled corn stalk lignin (MSL) extraction by neutral solvent

Before ball-milling the sample without steam explosion was firstly extracted with ethanol/benzene (1:2, v/v) using Soxhlet extractor to eliminate the extractives which might influence the content of neutral solvent extraction. Ball-milling of untreated and steam-exploded corn stalk was carried out in an agate ball mill (Tianjin Shengyuan Electrical Equipment Co., Ltd., China) for 8 h. In order to avoid increase of temperature, the agate jar with samples was placed in a cold water bath (15 °C) for 10 min after every 30 min ball milling. 5.00 g of ball milled samples were extracted with 125 ml of dioxane/water (96:4, v/v) solvent in sealed flasks placed in a shaker at 120 rpm at 25 °C. When the desired extraction time was attained, 2 ml extract was collected and centrifuged at 4 °C for 5 min immediately. The supernatant was diluted by dioxane/water solvent and detected by UV absorption at 280 nm. The extraction yields of MSL before and after steam explosion were presented by the proportion of extracted lignin to the Klason lignin in the corn stalk.

2.3.3. Establishment of lignin content measurement by UV absorption

The dried solid lignin sample from alkali extract was obtained by acid precipitation of alkali extracting solution to pH 2.0 followed by the sufficient water washing to eliminate the ash [18], while the solid MSL sample from neutral solvent extraction was purified according to the method outlined by Björkman [19]. 1.00 g L⁻¹ standard lignin solutions were prepared by dissolving 0.10 g alkali-extracted lignin and MSL into 100 ml alkaline water (pH = 11.5) and dioxane/water solvent respectively. The standard lignin solutions were then diluted to obtain different concentrations for the establishment of standard curve with concentration versus UV absorption. The relationship between UV absorption and lignin concentration in extracted liquor was established by linear regression firstly (Fig. 1). It was found that UV absorption precisely predicted the concentration of both alkali-extracted lignin and MSL obtained from untreated and steam-exploded corn stalk. The slightly different absorption of lignin samples before and after

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