Bioresource Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

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

Effects of water states on steam explosion of lignocellulosic biomass

Wenjie Sui [a,b], Hongzhang Chen [a,*]

[a] State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100039, China

HIGHLIGHTS

- The complexity and roles of water states in steam explosion were revealed.
- Two water states existed in corn stalk and took effects in steam explosion.
- Bound water being a good plasticizer that softened fiber texture was conducive.
- Free water taking buffering effects and consuming much energy was not conducive.
- Water states were thus optimized at fiber saturated point of corn stalk.

ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 31 August 2015
Accepted 1 September 2015
Available online xxxx

Keywords:
Lignocellulosic biomass
Water states
Steam explosion
Enzymatic hydrolysis

ABSTRACT

The work aimed to identify the complexity and roles of water states in steam explosion process of corn stalk to enhance the treatment efficiency. Results showed that two main water states with different mobility existed in corn stalk and influenced steam explosion treatment. By correlating dynamic water states data to feedstock mechanical properties and treatment process characteristics, the bound water being the excellent plasticizer that reduced the mechanical strength of fibers by over 30%, was conducive to treatment; while, the free water presenting buffering effects in treatment by hindering heat transfer which was reflected by the increase of temperature rising time by 1.29 folds and steam consumption by 2.18 folds, was not conducive. The distinguished point of these two waters was fiber saturated point. By considering treatment efficacy and energy consumption, the significance of fiber saturated point was highlighted as the optimal water states for steam explosion of corn stalk.

1. Introduction

Climate changes and shortage of fossil fuels have sparked a growing demand for liquid biofuels which in turn increased the amount of research into production of lignocellulose-derived bioethanol (Cheng et al., 2015; Pu et al., 2013). However, being the insoluble and heterogeneous substrate, lignocellulosic biomass poses several challenges in conversion to fermentable sugars (DeMartini et al., 2013). In recent years, studies in bioconversion have continuously sought processing strategies to overcome close physical association between lignocellulosic matrices (Alvira et al., 2010; Chundawat et al., 2011; Ko et al., 2015; Li et al., 2014). To a lesser extent, studies have sought to understand biophysical factors responsible for pretreatment efficiency of lignocelluloses (Ferreira et al., 2014; DeMartini et al., 2013; Pu et al., 2013).

Today, the most cost effective processes in the biomass to fuels industry utilize biological conversion process and indispensable pretreatment where water most certainly takes great effects (Selig et al., 2012). The vital roles water commonly plays in common pretreatments are summarized as: (1) reactant, constructing mild acidic conditions due to a decrease of p*Kw* at elevated temperature (Alvira et al., 2010; Felby et al., 2008); (2) solvent or mass transfer medium of catalytic substances, intermediates and end-products (Kristensen et al., 2009); (3) heat transfer medium, determining the heat pattern and efficiency throughout the cellular structure (Brownell et al., 1986; Sui and Chen, 2014); (4) plasticizer, maintaining a moist and soft texture of fibers by the influence on cell size and fiber strength (Berry and Roderick, 2005); (5) explosion medium for analogous explosion pretreatments, tearing materials into small pieces and disrupting micro-structures at sudden decompression (Zhang and Chen, 2012). These indicate that water is directly related to the interaction between substrate and pretreatment and meanwhile highlight the necessity of rehydration operation before pretreatment since most pretreatment objects are dry feedstocks with water content (WC) $\leqslant$15%.

In recent years, research efforts have seen a gained interest in the underlying work of water responsible for complicating

* Corresponding author. Tel.: +86 01082627071.
E-mail address: hzchen@ipe.ac.cn (H. Chen).

http://dx.doi.org/10.1016/j.biortech.2015.09.001
0960-8524/

pretreatment efficiency (Brownell et al., 1986; Cullis et al., 2004; Ewanick and Bura, 2011; Ferreira et al., 2014). Most focus has strategized toward elucidating the water hydrolysis mechanism in pretreatment process and optimizing the initial WC of feedstock. While, their strides made from apparent and quantitative research on water are not enough for revealing water's acting essence in pretreatment without the consideration of complex interactions between water and biomass. When water is sorbed to lignocellulosic matrix, it is subjected to interactions caused by chemical composition and physical structure of lignocellulosic matrix which in turn produces different states and locations of water (Felby et al., 2008). Within the matrix, these associating water molecules have properties highly different from properties of bulk water. They become localized, more structured, and comparatively limited in available degrees of freedom, kinetic motion and ability to exchange with other water molecules compared to water in bulk (Selig et al., 2014). Various water states influencing feedstock properties have multiple effects in pretreatment process as summarized above, which could be the key issue that closely related to the extent of pretreatment efficiency. Thus, to unveil the fundamental mechanism of water function in pretreatment, it is required to develop an adequate consideration of water states in the architecture of biomass.

With this study we aim to highlight the criticality of water states in pretreatments of lignocellulosic biomass. Through investigating the lignocellulose-water interactions and their effects on pretreatment process and efficacy, we explored the degree with which water states can impact the pretreatment efficacy and how they function during the pretreatment process, finally determined the optimal water states and the corresponding rehydration strategy to achieve the desirable pretreatment efficacy. Low field nuclear magnetic resonance (LF-NMR) measurement was used to address this fundamental issue on corn stalk (CS) samples subjected to steam explosion (SE) pretreatment. The spin–spin relaxation information (T_2) measured by LF-NMR was used to discriminate among various states in which water existed in the complex environment and trace their dynamic migration in rehydration preparation (Selig et al., 2012, 2014). CS was chose as study object due to its potential as an abundant, low cost and typical lignocellulosic feedstock. SE pretreatment applied in the conditions has been proved to be very efficient to disrupt the lignin-carbohydrate structure and improve the enzymatic digestibility (Liu and Chen, 2015; Sui and Chen, 2015). It applies only water and heat during process to produce auto-hydrolysis effects at steam cooking stage and mechanical forces at instantaneous explosion, thus saving the cost of processing, avoiding the corrosion of equipment and reducing the pollution to environment under neither acidic nor alkaline conditions (Alvira et al., 2010; Chen and Liu, 2014; Langan et al., 2014). Through correlating the water states data to feedstock properties and process parameters, the underlying water function in SE was explored and afterward the optimal water states and corresponding rehydration strategy were obtained. Thus, the work highlights the complexity and roles of water states in biomass pretreatment and gives important insights for designing industrial process to achieve the desired water states of lignocelluloses for the development of pretreatments.

2. Methods

2.1. Feedstock and rehydration preparation

CS was obtained from the suburb of Beijing, China. Initial WC of green CS was 776%. CS was air-dried to around 10% of WC after one year storage and manually processed using scissors to 3–5 cm long. The composition of dry CS after one year storage was glucan 31.66 ± 1.25%, xylan 12.02 ± 0.82%, arabinan 2.73 ± 0.21%, acid-insoluble lignin (AIL) 11.87 ± 0.20%, acid soluble lignin (ASL) 0.94 ± 0.08%, water extractives 32.15 ± 1.38%, ethanol extractives 2.04 ± 0.33%, ash 0.85 ± 0.06% and others 5.74 ± 0.57%. Before pretreatment, CS was rehydrated by uniformly spraying with deionized water to WC of 20%, 30%, 40%, 60%, 80%, 100%, 200% and 411% (totally immersible) for 10 h. WC was measured by an oven method and expressed on the dry weight basis of biomass (%, dwb).

2.2. Steam explosion pretreatment (SE)

SE was performed in a lab-made automatic batch reactor with the volume of 20 L including a reactor chamber, a reception chamber and a steam generator. 400 g CS of predetermined water levels was loaded into the reactor and then high-pressure steam was charged to the reactor. The reactor temperature was raised and then maintained at 198 °C for 5 min as reported before (Sui and Chen, 2015). Afterward, CS was suddenly exploded into the reception chamber by opening the ball valve. The pretreated CS was washed by water with a ratio of water to biomass 10:1 (w/v). The SE hydrolysate was separated from the solid fraction by filtration through 4-layer gauze.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis was performed using a commercial cellulase (Cellic CTEC 2, Novozymes) obtained from Novozymes (China) Biotechnology Co., Ltd. The filter-paper and β-glucosidase activities were determined as 81.4 and 93.4 IU mL^{-1}, respectively. Enzymatic hydrolysis was conducted with 5 g dry substrates in 100 mL 50 mM citric acid buffer (pH 4.8) with addition of 1 mL cellulase solution at 323 K for 48 h. Hydrolysate sample was heat-treated at 100 °C for 20 min to denature the enzyme. The experiments were performed in triplicate.

2.4. Chemical analysis

Compositional analysis was performed according to Laboratory analysis protocol of National Renewable Energy Laboratory (NREL) Colorado, USA ("Determination of Structural Carbohydrates and Lignin in Biomass"). The total sugars (monosaccharides and oligosaccharides), carbohydrate degradation products (HMF and furfural) and acetic acids were determined according to the NREL standard protocol ("Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples"). Oligomeric sugars in SE hydrolysate and enzymatic hydrolysate were converted into the monomeric form using acid hydrolysis and quantified by HPLC.

Soluble sugars (glucose and xylose) and acetic acids were analyzed using Agilent 1200 HPLC system equipped with a RI detector. The analysis was carried out using an Aminex HPX-87H column (Bio-Rad, Sunnyvale, CA, USA) operating with 5 mM H_2SO_4 as the mobile phase at 0.6 mL min^{-1} at a column temperature of 65 °C. Furfural and HMF were determined by HPLC equipped with a DAD detector at 280 nm. The analysis was carried out using a COSMOSIL Packed Column 5C18-MS-II column (Nacalai Tesque, Inc., Japan) operating with methanol–water-acetic acid (40: 59.4: 0.6, v/v) as the mobile phase at 0.5 mL min^{-1} at a column temperature of 35 °C.

2.5. Low field nuclear magnetic resonance (LF-NMR) and magnetic resonance imaging (MRI)

Water distribution and migration in CS during rehydration process were detected by LF-NMR on a 22.4 MHz NMR Analyzer PQ001 (Niumag Co., Ltd., Shanghai, China). Approximately 3 cm

Please cite this article in press as: Sui, W., Chen, H. Effects of water states on steam explosion of lignocellulosic biomass. Bioresour. Technol. (2015), http://dx.doi.org/10.1016/j.biortech.2015.09.001