Bioresource Technology 186 (2015) 8–14

Contents lists available at ScienceDirect

Bioresource Technology

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

Subcritical water hydrolysis of rice straw for reducing sugar production with focus on degradation by-products and kinetic analysis

Richen Lin [a], Jun Cheng [a,*], Lingkan Ding [a], Wenlu Song [a,b], Feng Qi [a], Junhu Zhou [a], Kefa Cen [a]

[a] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China
[b] Department of Life Science and Engineering, Jining University, Jining 273155, China

HIGHLIGHTS

- Reducing sugar took competitive reactions in subcritical water hydrolysis of straw.
- Highest sugar production rate and lowest degradation rate were obtained at 280 °C.
- Hydrolysis conditions were optimised to give a reducing sugar yield of 0.346 g/g.
- Furans and acetic acid were main degradation byproducts of monosaccharides.
- A model was developed to elucidate competitive reaction kinetics of reducing sugar.

ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 7 March 2015
Accepted 9 March 2015
Available online 14 March 2015

Keywords:
Subcritical water hydrolysis
Rice straw
Reducing sugar
Kinetic model

ABSTRACT

The competitive reactions of reducing sugar production and degradation in the subcritical water hydrolysis of rice straw were investigated to optimise reducing sugar yield. The optimised conditions (280 °C, 20 MPa, rice straw concentration of 5 wt.% and agitation speed of 200 rpm) resulted in a reducing sugar yield of 0.346 g/g rice straw because of the enhanced reducing sugar production and decreased sugar degradation. The sugar yield increased when the temperature increased from 250 °C to 280 °C, but it decreased when the temperature further increased to 300 °C because of the degradation of monosaccharides (e.g. glucose and xylose) into by-products (e.g. 2-methyltetrahydrofuran and acetic acid). A first-order reaction model was developed to elucidate the competitive reaction kinetics of sugar production and degradation at various temperatures. The highest reducing sugar yield based on the model was achieved at 280 °C with the highest production and lowest degradation rates.

1. Introduction

The increasing energy demands and heavy consumption of non-renewable fossil fuels have emphasised the development and utilisation of lignocellulosic biomass as a sustainable source for renewable energy production (Hendriks and Zeeman, 2009; Magalhães da Silva et al., 2013; Monlau et al., 2013; Somerville et al., 2010). Research on the conversion of biomass to high-performance biofuels (e.g. bioethanol, biohydrogen and biogas) is being promoted (Ariunbaatar et al., 2014; Bauer et al., 2014; Xia et al., 2013). As an agricultural biomass waste, rice straw is abundant, inexpensive and readily available with annual global quantity of 685 million tons (Lim et al., 2012). Due to the lack of cost-effective treatment and recycling approaches, most straws are burned or discarded in the field. As a consequence, environmental pollution, especially high levels of particulate matter (i.e. PM2.5), has become a serious issue. Considering the high cellulose and hemicellulose contents of rice straw, it can be potentially used for biofuel production through fermentation, which is a prospective technology for the sustainable utilisation of agricultural wastes (Liu et al., 2013; Wall et al., 2013).

The fermentation of rice straw is difficult because of the recalcitrant lignocellulosic structure. Therefore, to improve biofuel production from lignocellulose, rice straw must be hydrolysed into reducing sugar (e.g. glucose and xylose) prior to fermentation. Numerous methods, including mechanical, chemical and biological pretreatments, have been investigated to remove or reduce the recalcitrance of lignocellulosic biomass before the hydrolysis (Zheng et al., 2014). However, the above-mentioned pretreatment methods have many disadvantages, including the following (He et al., 2014): (1) mechanical pretreatments alone are not effective and must therefore be combined with other methods, such as chemical or biological pretreatments; (2) biological pretreatment

* Corresponding author. Tel.: +86 571 87952889; fax: +86 571 87951616.
E-mail address: juncheng@zju.edu.cn (J. Cheng).

http://dx.doi.org/10.1016/j.biortech.2015.03.047
0960-8524/

process is complex and its efficiency is difficult to maintain; (3) chemicals addition in chemical pretreatments usually causes secondary pollution.

As an environmental friendly process, subcritical water hydrolysis (SWH) offers several advantages, including the avoidance of toxic chemicals, short reaction time, minimal corrosion, low residue generation and low by-products generation. Subcritical water is defined as liquid water in the temperature range of boiling point to critical point or near critical point (100–374 °C) (Prado et al., 2014b). The ionic product of water is relatively high in the subcritical range (10^{-12} compared with 10^{-14} at ambient conditions) (Toor et al., 2011). The high levels of H^+ and OH^- at subcritical conditions mean that many acid- or base-catalysed reactions (e.g. lignocellulose hydrolysis) can be effectively accelerated. Many reactions can be conducted in subcritical water without the addition of acids or bases. Furthermore, the relatively high density and high dissociation constant of subcritical water favour ionic reactions. SWH is considered to be a promising alternative technology for lignocellulosic biomass hydrolysis (Tangkhavanich et al., 2012; Toor et al., 2011; Wang et al., 2012; Watchararuji et al., 2008). Previous studies primarily focused on the production of fermentable sugars from different biomass residues (e.g. sugarcane bagasse, bean dregs and cornstalks) using SWH (Prado et al., 2014a; Zhao et al., 2009; Zhu et al., 2011). The operational conditions (e.g. reaction temperature, pressure, time and substrate loading rate) were investigated and optimised. Three biomass wastes (coconut husk, grape seed and palm fibre) were subjected to SWH with the aim of producing fermentable sugars (Prado et al., 2014b). Each raw material presented a different monosaccharide production profile, which indicates that SWH should be evaluated and optimised individually. The maximum reducing sugar yield from sugarcane bagasse was obtained at a temperature of 213 °C and a flow-rate of 33 mL/min using a semi-batch SWH reactor (Prado et al., 2014a). Glucose, xylose, and arabinose derived from lignocellulose hydrolysis were determined as the main components of monosaccharides.

However, the reducing sugar yield from lignocellulose was depended on the competitive reactions of both lignocellulose hydrolysis and monosaccharide degradation. To our knowledge, the competitive reactions of sugar production and degradation in the SWH of rice straw have rarely received recognition and should thus be addressed. In the present study, the hydrolysis of rice straw into reducing sugar and degradation by-products is studied at different operational conditions. The effects of reaction temperature, pressure, rice straw concentration and agitation speed are investigated and optimised to enhance reducing sugar production and decreased sugar degradation. The compositions of degradation products are analysed in detail to understand the decomposition of monosaccharides into by-products. A first-order homogeneous reaction model is proposed to reveal the competitive reactions of sugar production and degradation in the SWH of rice straw.

2. Methods

2.1. Materials

Rice straw was harvested and collected in Hangzhou, China, and it was chopped into pieces and then heated at 105 °C for 24 h. The pulverised rice straw with a size of ~200 μm was used in experiments. The organic components of the rice straw included the following: 34.3% cellulose, 21.7% hemicellulose, 17.6% lignin, 9.2% protein and 1.6% lipid (Cheng et al., 2011).

2.2. SWH

The SWH of rice straw was conducted in a batch reactor (Fig. 1). The SWH apparatus consisted of a gas inlet, a liquid inlet, a SWH

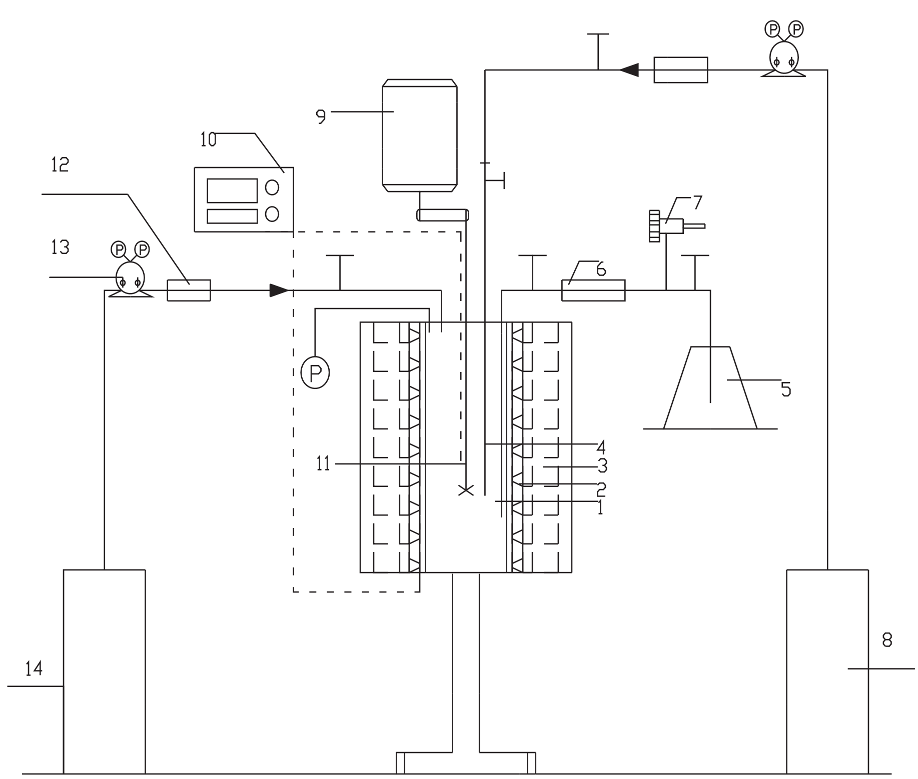

Fig. 1. Schematic of subcritical water hydrolysis apparatus for rice straw hydrolysis. (1) Subcritical water hydrolysis reactor, (2) electric heater coil, (3) insulation layer, (4) liquid inlet pipe, (5) sampling collector, (6) water cooling tube, (7) back pressure valve, (8) High-pressure liquid pump, (9) motor, (10) temperature controller and thermocouple, (11) agitator, (12) check valve, (13) pressure regulator, (14) high pressure cylinder.