Bioresource Technology 135 (2013) 697–703

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

High glucose selectivity in pressurized water hydrolysis of cellulose using ultra-fast reactors

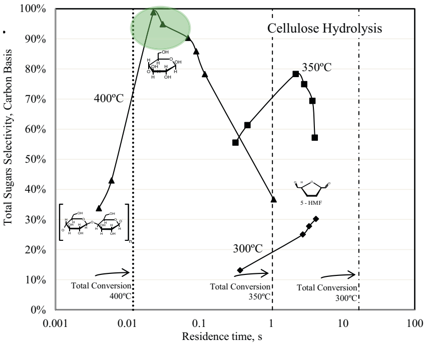
Danilo A. Cantero [a,b,1], M. Dolores Bermejo [a], M. José Cocero [a,*]

[a] *Department of Chemical Engineering and Environmental Technology, University of Valladolid, Prado de la Magdalena s/n, 47011 Valladolid, Spain*
[b] *Department of Applied and Industrial Chemistry, School of Exacts, Physical and Naturals Sciences, National University of Córdoba, Av. Vélez Sarsfield 1611, 5000 Córdoba, Argentina*

HIGHLIGHTS

- ▶ Total cellulose hydrolysis to glucose and oligomer can be achieved with residence times 0.02–0.03 s.
- ▶ Very low concentration of derived-products by the control of the residence time.
- ▶ The ultra fast reactor allows the control of extremely low the residence time.
- ▶ The supercritical water medium avoids the ionic degradation reactions.
- ▶ The residence time could control the glucose radical degradation reactions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 29 September 2012

Keywords:
Biorefinery
Hydrothermal medium
Cellulose
Glucose

ABSTRACT

A new reactor was developed for the selective hydrolysis of cellulose. In this study, the glucose selectivity obtained from cellulose was improved by using ultra-fast reactions in which a selective medium was combined with an effective residence time control. A selective production of glucose, fructose and cellobiose (50%) or total mono-oligo saccharides (>96%) was obtained from the cellulose in a reaction time of 0.03 s. Total cellulose conversion was achieved with a 5-hydroxymethylfural concentration lower than 5 ppm in a novel micro-reactor. Reducing the residence time from minutes to milliseconds opens the possibility of moving from the conventional m^3 to cm^3 reactor volumes.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Vegetal biomass grows globally in different climates and types of soils providing an alternative renewable source for the sustainable production of chemicals and fuels. The average production of biomass energy crops in the world (Klemm et al., 2005; Ragauskas et al., 2006) is ~10 dry tons ha^{-1} $year^{-1}$. Biomass is composed of 34–50% cellulose, 16–34% hemi-cellulose and 11–29% of lignin (Bobleter, 1994). The challenging step in the processing of cellulose is the production of glucose. Glucose is a target product because it can be used as a raw material in the production of chemicals, materials and bio-fuels.

Although traditional methods for the hydrolysis of cellulose have been remarkably improved in recent years, they still present limitations in carrying out the hydrolysis to provide high yield and selectivity through energetically efficient and environmentally friendly processes. Acid hydrolysis can be done with sulfuric acid (0.5–10% w/w) at temperatures between 150 °C and 220 °C, obtaining 52% in mass basis (w/w) of glucose in 10 h of treatment (Shuai and Pan, 2012). This acid catalysis can be improved using solid catalysts (Dora et al., 2012; Guo et al., 2012). This hydrolysis procedure using chloromethyl polystyrene resin as catalyst support, with sulfonic acid groups as catalyst yields 93% w/w of

---

[*] Corresponding author. Tel.: +34 983423174; fax: +34 983423013.
E-mail addresses: da.cantero@iq.uva.es (D.A. Cantero), mjcocero@iq.uva.es (M. José Cocero).
[1] Tel.: +54 3514333078; fax: +54 3514334139.

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.09.035

glucose in 10 h of hydrolysis time at 120 °C (Shuai and Pan, 2012). The typical yield for enzymatic hydrolysis is 60% w/w of glucose in 1–60 min of pre-treatment time and 24–72 h of hydrolysis time (Wyman et al., 2005). Enzymatic hydrolysis was also studied in combination with additives (Tween 20/80), reporting glucose selectivity of 45% w/w at 50 °C with an experimental time of 22 h (Yang et al., 2011). The enzymatic hydrolysis of cellulose has been enhanced by a cellulose pre-treatment, of the cellulose achieving a glucose selectivity of 92% w/w in 48 h (Abushammala and Hashaikeh, 2011) or 92% w/w in 6 h (Khodaverdi et al., 2012), without considering the pre-treatment time. It is also possible to hydrolyze cellulose through dissolution and hydrolysis in ionic liquids, with or without acid catalyst. It takes about 3 h, achieving 25–27% w/w of oligosaccharides (Amarasekara and Wiredu, 2011; Hsu et al., 2011). A high concentration of derived products such as 5-hydroxymethylfurfural (5-HMF) has been reported in the experiments with ionic liquids without acid catalyst (Hsu et al., 2011). Cellulose hydrolysis in ionic liquids was improved by adding small quantities of water along the course of the reaction, obtaining a glucose and cellobiose selectivity of 99% w/w in 3 h of treatment, at temperatures between 105–135 °C (Morales-delaRosa et al., 2012).

The use of pressurized fluids has been proposed as a clean technology to integrate the depolymerization-reaction-separation processes. Particularly, high temperature pressurized water has proved to be a good solvent for clean, safe and environmentally benign organic reactions(Akiya and Savage, 2002; Arai et al., 2009; Ehara and Saka, 2002, 2005; Peterson et al., 2008; Ragauskas et al., 2006; Sasaki et al., 2000; Zhao et al., 2009b). The main reasons that make the hydrothermal media a promising alternative for biomass processing are as follows (Peterson et al., 2008): (1) it is not necessary to reduce the water content in the raw material, thus avoiding energy losses; (2) the reaction media permits the transformation of the different biomass fractions; (3) the mass transfer limitations are reduced or avoided, thus allowing faster reaction rates. Furthermore, the adjustable properties of the reaction media work as a control factor for the reaction selectivity, avoiding the generation of by-products. The density (ρ), dielectric constant (ε) and ionic product of water (K_w) from 0 °C to 600 °C at a pressure of 25 MPa are plotted in Fig. 1. The properties were calculated according to the equations developed in literature (Marshall and Franck, 1981; Uematsu and Franck, 1980). The change in the dielectric constant is proportional to the density and inversely proportional to the temperature. Hydrogen bonds present a behavior analogous to that of the dielectric constant (Akiya and Savage, 2002). Another important property of the organic reaction media is the ionic product of water. Around 300 °C the value of the ionic product of water reaches its maximum (1.10^{-11}), which creates a medium with high H^+ and OH^- concentrations, thus favoring in this way acid/basis catalyzed reactions. Above the critical temperature of water (374 °C), the K_w decreases drastically (1.10^{-25}) (Akiya and Savage, 2002). At higher pressures ($P > 60$ MPa) the K_w again presents values similar to those of ambient water.

Sugar selectivity (glucose, fructose and oligomers of glucose up to 6 units) of between 20 and 77% was achieved in residence times (t_r) from 0.01 s to 30 s when cellulose was hydrolyzed in a supercritical water medium. The reactions of cellulose hydrolysis under supercritical conditions are fast, but, if the reactions are not controlled, a high quantity of derived products are yielded (Sasaki et al., 2000,1998). The hydrolysis of cellulose is completed at subcritical temperatures, obtaining a high concentration of glucose and oligosaccharides, but the reaction has a low selectivity and needs bigger reactors and higher residence times (Rogalinski et al., 2008). Using subcritical water hydrolysis in the presence of a catalyst, the process can take place at a low temperature (150 °C), but the residence time is increased up to 24 or 48 h (Fang et al., 2011).

In this work, a novel reactor capable of operating under supercritical conditions with an effective control of the residence time was developed. In the facility described here, high selectivity of glucose and oligosaccharides of up to six units of glucose (98% carbon basis -c.b.-) can be achieved.

2. Methods

2.1. Materials

The cellulose used in the experiments was micro-crystalline cellulose with a particle size of between 20 and 137 μM, purchased from VWR. Distilled water was used in the experiments. The reagents used in HPLC analysis were: cellobiose (+98%), glucose (+99%), fructose (+99%), glyceraldehyde (95%), pyruvaldehyde (40%), erythrose (+75%) and 5-hydroxymethylfurfural (99%), purchased from Sigma. The reagents used in the enzymatic analysis were: β-glucosidase (glucose oxidase plus peroxidase

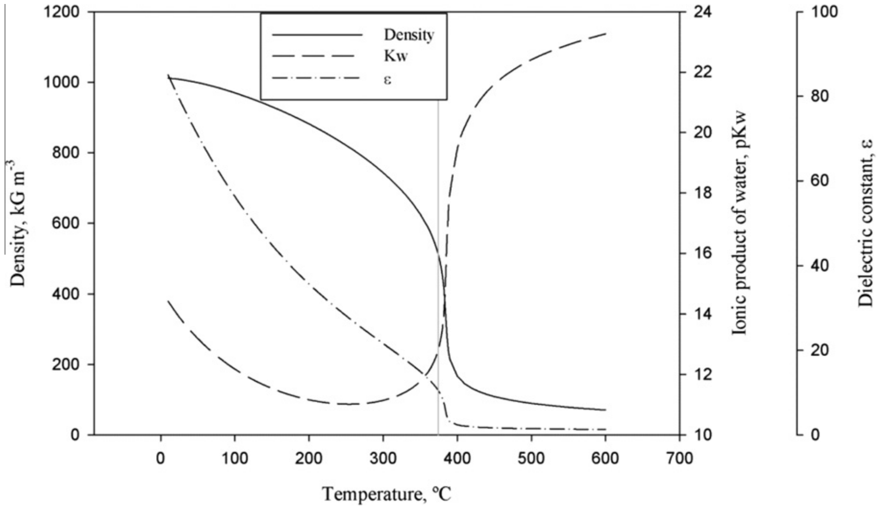


Fig. 1. Properties of pressurized water below and above critical point. Continuous line density (kg/m^3); dashed line represents ionic product of water (pKw) and dashed-dotted line represents the dielectric constant. (Marshall and Franck, 1981; Uematsu and Franck, 1980).

Download English Version:

https://daneshyari.com/en/article/7083923

Download Persian Version:

https://daneshyari.com/article/7083923

Daneshyari.com