Bioresource Technology 191 (2015) 229–233

Contents lists available at ScienceDirect

Bioresource Technology

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

Hydrolysis behavior of regenerated celluloses with different degree of polymerization under microwave radiation

Jinping Ni, Na Teng, Haizhen Chen, Jinggang Wang, Jin Zhu, Haining Na *

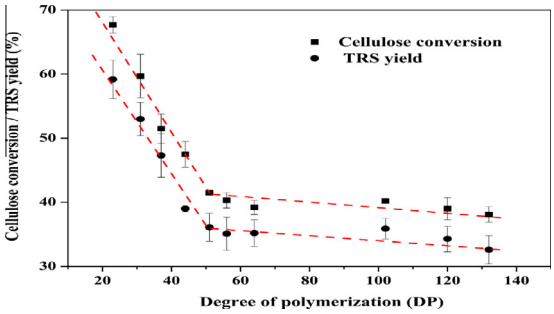
Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China

HIGHLIGHTS

- Degree of polymerization (DP) plays a crucial role on hydrolysis of cellulose.
- Low DP can alleviate the recrystallization of cellulose then promote hydrolysis.
- The hydrolytic efficiency is significantly improved when the DP is lower than 51.

GRAPHICAL ABSTRACT

The reactivity of regenerated cellulose is significantly enhanced when the degree of polymerization of cellulose is lower than 51.



ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form 11 May 2015
Accepted 12 May 2015
Available online 16 May 2015

Keywords:
Cellulose
Hydrolysis
Degree of polymerization

ABSTRACT

This work studied the hydrolysis behavior of regenerated celluloses (RCs) with different degree of polymerization (DP) by using the catalyst of dilute acid under microwave radiation. Results showed that the DP had a considerable influence on hydrolysis of cellulose. The reactivity of RCs was significantly improved when DP was lower than 51. The highest sugar yield of 59.2% was achieved from RC with lowest DP of 23 at 160 °C for 15 min. But the lowest yield of 32.6% was obtained when RC with highest DP of 132 was used. Recrystallization of cellulose was found to hinder the further hydrolysis particularly with the high DP. The effect of recrystallization can be reduced by the decrease of DP of RCs. This research demonstrates that the DP of RCs plays a crucial role on hydrolysis and it provides a preliminary guide based on DP to find a suitable pretreatment method for cellulose hydrolysis.

1. Introduction

Concerns about the gradual depletion of fossil fuel and global warming make it extremely urgent to introduce biomass as green and sustainable resources in the chemical industry (Gupta and Verma, 2015; Saha and Abu-Omar, 2014; Wang et al., 2015). Glucose, which is derived from biomass, is considered as a versatile platform chemical for the production of value added chemicals and liquid fuels (Huo et al., 2014; Yabushita et al., 2014; Zhou et al., 2011). Until today, starch and cellulose are polysaccharides made of glucose and starch is the major resource of glucose (Farrell et al., 2006). However, after checking the annual production of cellulose about 1×10^{11} t (Klemm et al., 2005), the production of nonfood-competing glucose from cellulose is no doubt much more important for large-scale use of glucose.

Cellulose is a polymer of glucose moieties linked together in particular β-1,4 fashion. Extensive hydrogen bonding networks

* Corresponding author. Tel.: +86 574 87619806; fax: +86 574 86685186.
E-mail address: nahaining@nimte.ac.cn (H. Na).

http://dx.doi.org/10.1016/j.biortech.2015.05.036
0960-8524/

are formed between its molecular chains, which results in water-insoluble and highly crystalline structure. In comparison with starch, the crystalline structure of cellulose is rather robust so that it cannot be destroyed in boiling water (Deguchi et al., 2006). Hence, hydrolysis of cellulose in water is a heterogenous reaction. Crystalline structure of the cellulose is considered as major factor to affect the hydrolysis reaction (Zhao et al., 2006). Accordingly, effective means of disrupting recalcitrant structure of cellulose before hydrolysis reaction is important and indispensable, such as regeneration (Ha et al., 2011; Kim et al., 2010), ball milling (Moeller et al., 2013; Peng et al., 2013) and physicochemical pre-hydrolysis (Ma et al., 2014), etc. In our previous work, regenerated celluloses (RCs) were prepared for producing glucose and the reactivity of cellulose was significantly improved under mild conditions (Ni et al., 2014, 2013). However, with the depletion of amorphous cellulose, recrystallization of RCs was observed during cellulose hydrolysis process, which imposed restrictions on cellulose hydrolysis. So that the sugar yield obtained was not satisfactory even when RCs with low crystallinity was used. Crystallinity and DP are two major parameters to affect the properties of cellulose. The DP was found to be the key factor governing dissolution of cellulose in NaOH aqueous (Isogai and Atalla, 1998). So the DP of cellulose is expected to play an important role on cellulose hydrolysis while few works have investigated the influence of DP on cellulose hydrolysis (Boissou et al., 2014). Hence, there is a strong demand for us to carry out the systematically research to elucidate the influence of DP of cellulose on hydrolysis reactivity.

In this study, as considering the DP of RCs plays a crucial role during the hydrolysis of RCs, the hydrolysis behavior of RCs with different DP was investigated. The conversion of cellulose and sugar yield obtained from RCs were compared and discussed in details.

2. Methods

2.1. Materials

Microcrystalline cellulose (MCC) powder (containing over 97% cellulose) was purchased from Jiangsu Longhao new materials company (Jiangsu, China). It was vacuum dried at 100 °C for 6 h before used. D-(+)-Glucose (GR grade, >99.5%) was supplied by Aladdin Reagent and was dried under vacuum at 100 °C over 6 h for further use. All the other chemicals were in chemical grade and used without purification.

2.2. Preparation of RCs with different DP

Cellulose samples with different degree of polymerization (DP) were prepared by treating MCC in 85% H_3PO_4 at different temperature and duration time followed by regeneration with water, filtration, washing and drying. Typical process was as follows: 15 g cellulose was mixed with 200 mL 85% H_3PO_4 at 50 °C and stirred for 1 h. After reaction, the mixture was poured slowly into 4 L water with slow stir and precipitate was formed immediately. The precipitate was filtered and washed with plenty of water to remove the residual acid. After that, the precipitate was suspended in ethanol and filtered to remove the residual water. After vacuum dried at 80 °C for 10 h, the precipitate was grounded into powders (<0.35 mm). In accordance with the DP, this material is denominated as RC-56 (56 represents the DP of cellulose measured by viscosity-average molecular weight).

2.3. Hydrolysis of RCs under microwave radiation

The hydrolysis of cellulose was performed using a microwave synthesis system (Mwave-5000, Shanghai Sineo Microwave Chemistry Technology Co., Ltd.) with frequency of 2.45 GHz. The reactor is equipped with a stirrer and a thermocouple. The maximum output power is 1000 W and the power can be adjusted automatically by the inner temperature. 0.5 g RCs powder and 50 mL sulfuric acid (0.04 mol/L) was charged in 300 mL Teflon vessels and closed. Then the vessel was heated to 160 °C with 5 min of microwave power supply and the temperature of mixture was kept at 160 °C for desired time. After that, the microwave radiation was shut down to stop the reaction and the temperature was cooled down to 60 °C.

After hydrolysis, the reactive mixture was filtered. The residual cellulose solid was washed with water and weighted after drying. The aqueous solution after filtration was used to analyze the content of total reducing sugar (TRS) applying the (3,5-dinitrosalicylic acid) DNS method (Miller, 1959). The concentration of TRS was calculated based on a standard curve obtained with glucose. The absorbance was measured at 540 nm. All determinations were conducted in triplicate. Cellulose conversion and yield of TRS were calculated as follows,

$$\text{Conversion of cellulose } (\%) = \text{mass of residual cellulose solid}/\text{mass of initial loaded cellulose} \times 100\%,$$

$$\text{Yield of TRS } (\%) = \text{mass of TRS}/\text{mass of initial loaded cellulose} \times 0.9 \times 100\%.$$

2.4. Characterization of cellulose

Fourier transfer infrared (FT-IR) spectra of MCC and RCs samples prepared with KBr were recorded by one spectrophotometer (Nicolet FTIR 6700 infrared spectrophotometer) over wave numbers range of 4000–400 cm^{-1}.

The degree of polymerization (DP) of cellulose was determined by intrinsic viscosity measurements. DP was determined from the limiting viscosity number $[\eta]$ mL/g in cadoxen (cadmium oxide–ethylenediamine–NaOH–H_2O = 5:28:1.4:165.6, *w*/*w*/*w*/*w*) at 25 °C using the following equation: $[\eta] = 3.85 \times 10^{-2} M_v^{0.76}$, DP = M_v/162 (Kamide et al., 1992).

Crystal structure and crystallinity of cellulose was measured with a Siemens D5000 X-ray Diffractometer. The diffracted intensity of Cu K_α radiation generated at 40 kV and 40 mA was measured in a 2θ range between 5° and 45°. The degree of crystallinity (*Cr*) was calculated as follows: $Cr = F_c/(F_c + F_a) \times 100\%$, where, F_c and F_a are the areas of crystal and amorphous regions, respectively (Zhang et al., 2010).

3. Results and discussion

3.1. DP and chemical structure of RCs

Concentrated phosphoric acid has been used as a decrystallization and depolymerization agent to prepare cellulose with different DP (Liebert et al., 2008; Wei et al., 1996; Zhang et al., 2006). Applying homogeneous degradation of microcrystalline cellulose in concentrated phosphoric acid at various conditions, RCs with DP from 132 to 23 were obtained. As shown in Table 1, the DP of cellulose was decreased after pretreatment with H_3PO_4. RC with DP of 132 was isolated after hydrolysis at 5 °C for 1 h. Variation of the time and temperature of pretreatment can produce RC with lower DP. In the experiment, RC with the lowest DP of 23 was achieved after pretreatment of cellulose at 50 °C for 9 h.

The FTIR spectra of MCC and RCs are shown in Supplement materials. It can be seen that significant characteristic peaks of