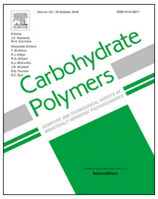
Carbohydrate Polymers 197 (2018) 414–421

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Revealing the importance of non-thermal effect to strengthen hydrolysis of cellulose by synchronous cooling assisted microwave driving

Chengkai Zhai[a,b], Na Teng[a], Baohai Pan[a,c], Jing Chen[a], Fei Liu[a,*], Jin Zhu[a], Haining Na[a,*]

[a] *Key Laboratory of Bio-based Polymeric Materials of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, PR China*
[b] *Nano Science and Technology Institute, University of Science and Technology of China, Hefei, Anhui 230026, PR China*
[c] *Department of Polymer Materials, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, PR China*

ARTICLE INFO

Keywords:
Non-thermal effect
Microwave driving
Hydrolysis of cellulose

ABSTRACT

Non-thermal effect of microwave is precisely revealed as an important factor to strengthen the hydrolysis of cellulose to sugar by a new method of synchronous cooling assisted microwave driving. Using this particular method, the thermal effect is mandatorily removed from the hydrolysis of cellulose. After systematic analysis of the hydrolysis of low crystalline regenerated cellulose (RC), the non-thermal effect of microwave is proved to strengthen hydrolysis. The enhancement of non-thermal effect effectively weaken the interaction between the hydroxyl groups of -O(2)H and -O(6)H, as well as strengthen interaction between the hydroxyl groups of -O(3)H and -O(5)H within one single molecular chain. It leads to the reduction of regularity of molecular chain and thus inhibits the recrystallization of RC. As a result, the efficiency of hydrolysis is greatly improved. This research provides an important theoretical support and technical guidance to construct new microwave driven hydrolysis with high efficiency in the future.

1. Introduction

In recent years, introduction of microwave driving into the hydrolysis of cellulose to maximize efficiency has gradually become one of the key research ideas in the area of biomass conversion and application (De Bruyn et al., 2017; Huang & Fu, 2013; Wu et al., 2010). Accordingly, it has achieved an obvious improvement of the hydrolytic capability of cellulose to sugar and thus greatly contributes to highly effective conversion and utilization of renewable cellulosic biomass. Microwave-driven hydrolysis of cellulose demonstrates very important strategic significance to save petrochemical resources, to fabricate bio-based chemical platforms, and to maintain sustainable development of polymer industry in the future (Isikgor & Becer, 2015; Jerome, Chatel, & Vigier, 2016; Kawaguchi, Hasunuma, Ogino, & Kondo, 2016; Khoo, Ee, & Isoni, 2016; Li, Zhang, & Zhao, 2009).

Some studies have narrated in detail the actual effect of microwave-driven hydrolysis of cellulose to sugar (Li et al., 2012; Orozco, Ahmad, Rooney, & Walker, 2007; Zhang & Zhao, 2009). From these studies, the conversion of cellulose and the yield of total reducing sugar products were significantly improved under microwave radiation, compared with traditional heating. However, despite of its high hydrolytic efficiency, few studies have roughly mentioned the mechanism of the microwave radiation to accelerate hydrolysis of cellulose. The importance to accelerate hydrolysis of cellulose by microwave radiation was simply attributed to the strong thermal effect, due to the fast heating of microwave radiation observed in daily life (Chen, Rosana, Dudley, & Stiegman, 2014; Kappe, 2002). However, this statement is somewhat inaccurate. Generally, thermal effect is directly related to the change of internal energy of molecules, together with strong heat conduction and high temperature, which is very common in traditional heating. Although the thermal effect is usually strong, the indispensable long reaction time even under an equivalent high temperature is still required in the hydrolysis of cellulose driven by traditional heating (Guo, Lian, Yan, Qi, & Smith, 2013; Ni et al., 2013; Xiong, Zhang, Wang, Liu, & Lin, 2014). This observation is totally different from the fact that fast hydrolysis can be easily achieved by microwave driving. Therefore, simply attributing positive reinforcement to hydrolyze of cellulose to the ordinary thermal effect of microwave radiation is inadequate and inaccurate. In fact, until today, to the best of our knowledge, no deep and systematic research has been reported to carefully reveal the effect of microwave to strengthen the hydrolysis of cellulose to sugar.

As we know, the fundamental difference between microwave radiation and traditional heating is the way to transmit energy.

---

* Corresponding authors.
E-mail addresses: liufei@nimte.ac.cn (F. Liu), nahaining@nimte.ac.cn (H. Na).

https://doi.org/10.1016/j.carbpol.2018.06.031
Received 17 March 2018; Received in revised form 4 June 2018; Accepted 5 June 2018

Microwaves are the electromagnetic waves between infrared and radio frequency waves with frequencies ranging from 300 MHz to 300 GHz. The energy transmission is mainly through the activation of dielectric loss of polar units in molecules, which obviously differs from regular heat conduction (de la Hoz, Diaz-Ortiz, & Moreno, 2005). In fact, the action exhibited in the polar units of molecules firstly tends to produce non-thermal effect, which only affects the interaction between polar units. Until the action produces adequate absorption of energy to cause thermal motion of molecules, thermal effect begins to fully display. At this stage, it usually accompanies with the strong heat conduction and rapid rise in temperature. As to the molecule of cellulose, owing to its relatively large volume, thermal motion and thermal effect excited by microwave radiation is no doubt slow and weak (Soykeabkaew, Thanomsilp, & Suwantong, 2015). Considering the rather rapid hydrolysis driven by microwave radiation, although heating is necessary to initiate the dissociation of glycosidic bonds, thermal effect should not be sole key factor to accelerate hydrolysis of cellulose. The real key factor (very probably concerning with non-thermal effect) to accelerate hydrolysis is hidden in the short-term but high temperature process driven by microwave radiation.

Based on our previous research in the hydrolysis of cellulose to sugar (Ni et al., 2013; Ni et al., 2014; Ni et al., 2015; Teng et al., 2016), we develop a new method called synchronous cooling assisted microwave-driven hydrolysis of cellulose in current research. This new method enable us to utilize the microwave radiation to drive the hydrolysis of cellulose and mandatorily to remove the thermal effect of ambient medium by synchronous cooling at the same time. Therefore, the non-thermal effect of microwave radiation on the improvement of hydrolysis efficiency of cellulose will be clearly exhibited. As a result, the real key factor of microwave driving to strengthen hydrolysis of cellulose is expected to be revealed.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC, amount of cellulose, > 97%) from Longhao New Material Company (Jiangsu) was vacuum dried at 100 °C for 24 h and kept in a desiccator for further use. D-(+)-glucose (GR grade, > 99.5%) was provided by Aladdin Reagent and dried under vacuum at 100 °C for 6 h before test. All the other reactants were in chemical grade and used without further purification.

2.2. Preparation of regenerated cellulose

The regenerated cellulose (RC) was prepared from MCC according to literature (Ni et al., 2013). MCC was dissolved in 85% H_3PO_4 at 50 °C for 3 h, and then precipitated by water. The precipitation was then filtered and washed with water until neutral. Subsequently, it was vacuum dried at 80 °C, and then grinded and sifted to give RC. The obtained RC has controlled homogeneous microscopic and molecular structure with uniform molecular weight and low crystallinity. Therefore, it was used as a standardized model of cellulose for the study of hydrolysis in our current work.

2.3. Synchronous cooling assisted microwave-driven hydrolysis of cellulose

Hydrolysis of RC was carried out in a high energy density laboratory (35 mL) CEM Discover SP Microwave autoclave vessel (300Psi) with a frequency of 2.450 ± 0.050 GHz and output power ranging from 60 to 150 W. All experiments were run in dynamic mode with synchronous cooling provided by a functional component named PowerMAX (from CEM Company). Accordingly, cooling gas can be quantitatively injected into the system to maintain a constant temperature under different microwave power. The whole system was equipped with an infrared (IR) temperature sensor placed at the bottom of the reaction vessel and a fiber optic probe was used to measure the temperature. Diluted sulfuric acid (0.1 M) as a catalyst was mixed with RC in a sealed glass vessel to initiate the hydrolysis. Continuous magnetic stirring was also used in all experiments to guarantee uniform hydrolysis. The hydrolysis was carried out in two steps. In the first step, the vessel was heated to a temperature of 160 °C from room temperature under 300 W microwave power. In the second step, the temperature of the vessel was kept constant under different microwave powers for various time period ranging from 5 to 20 min. As soon as the reaction time was reached in the second step, the vessel was cooled rapidly from 160 °C to 50 °C by compressed air.

2.4. Characterization

The total reducing sugar (TRS) was detected by 3,5-dinitrosalicylic acid (DNS) method (Miller, 1959). The percentage of residual RC retrieved after hydrolysis (rRC), conversion of cellulose, and yield of TRS were calculated according to Eqs. (1), (2), and (3), respectively,

$$\mathrm{Rrc}(\%) = \mathrm{m_{rRC}}/\mathrm{m_{RC}} \tag{1}$$

$$\text{Conversion of cellulose}(\%) = (\mathrm{m_{RC}}\text{-}\mathrm{m_{rRC)}}/\mathrm{m_{RC}}{*}100\% \tag{2}$$

$$\text{Yield of TRS}(\%) = \mathrm{m_{TRS}}/\mathrm{m_{RC}}{*}0.9{*}100\% \tag{3}$$

where m_{rRC} is the mass of rRC, m_{RC} is the mass of initial loaded RC, and m_{TRS} is the mass of TRS. Three parallel hydrolysis experiments were carried out for each reaction condition to get an average value. The yield of TRS in one hydrolysis experiment was calculated based on three measurements.

FT-IR analysis was carried out in a Nicolet 6700 infrared spectrometer using KBr pellet method (cellulose/KBr = 1:100). The spectrum from 4000cm^{-1} to 400cm^{-1} was recorded with a resolution of 0.9cm^{-1} and 32 scans. The rRC was washed by deionized water and then dried under vacuum at 80 °C before test. The ratio of various hydrogen bond was calculated according to Eq. (4), (Hinterstoisser & Salmen, 1999; Fan, Dai, & Huang, 2012)

$$\text{Ratio of H-bond}(\%) = A_i/A_{total}{*}100\% \tag{4}$$

where A_i and A_{total} refer to the areas of a single type of H-bond and total amount of all the H-bold regions, respectively.

Crystalline structure of the rRC was characterized with a Siemens D5000 X-ray Diffract meter. The diffracted intensity, tested with monochromatic Cu K_α radiation ($\lambda = 0.154$ nm) generated at 40 kV and 40 mA, was recorded in a 2θ range between 5° and 45°. The degree of crystallinity (C_r) was calculated according to the Eq. (5) (Puri, 1984),

$$C_r\ (\%) = F_c\ /(F_c + F_a){*}100\% \tag{5}$$

where F_c and F_a are the areas of crystal and amorphous regions, respectively. The calculation was carried out with Jade 5 software.

The surface morphology of rRC was assessed by scanning electron microscope (SEM, S4800, Hitachi). All the samples were sputter-coated with ~10 nm gold using an anion sputter coater (E-1045, Hitachi) for 120 s before test, in order to improve the conductivity of the samples and the quality of the SEM images.

3. Results and discussion

3.1. Non-thermal effect on accelerated hydrolysis of cellulose

MCC was pretreated to get RC according to the method reported in our previous work (Ni et al., 2015). Majority crystallization of MCC can be removed after the dissolving-precipitating pretreatment. The obtained RC contains only small amount of type II crystalline cellulose (cellulose II) with crystallinity of 27–28%. Moreover, it has degree of polymerization (DP) of about 40 and particle diameter lower than 0.35 mm. Therefore, the obtained RC with low crystallinity was used as