Chemical Engineering Journal 273 (2015) 37–45

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Mechanisms of sequential dissolution and hydrolysis for lignocellulosic waste using a multilevel hydrothermal process

Yan Zhao *, Siyuan Zhang, Jiajun Chen

School of Environment, Beijing Normal University, Beijing 100875, China

HIGHLIGHTS

- Multilevel hydrothermal process is used to dissolve and hydrolyze lignocellulose.
- Sequential dissolution mechanism in chemical structure of corn stalks was revealed.
- Variations in crystallinity, degree of polymerization and chemical bonds were studied.
- Lignin/hemicellulose dissolves at 190 °C, whereas cellulose dissolves at 240 °C.
- Rules on dissolution rates and activation energy were obtained by kinetic analysis.

ARTICLE INFO

Article history:
Received 30 December 2014
Received in revised form 27 February 2015
Accepted 10 March 2015
Available online 18 March 2015

Keywords:
Lignocellulosic waste
Cellulose
Multilevel hydrothermal treatment
Sequential dissolution
Kinetics
Mechanisms

ABSTRACT

Hydrothermal conversion normally results in fermentable sugar decomposition and inhibitor accumulation through dissolving and hydrolyzing lignocellulose synchronously. A multilevel hydrothermal process was applied to sequentially dissolve and hydrolyze lignocellulosic waste, and the dissolution mechanisms were investigated. The crystallinity of treated corn stalks increased from 43.1% to 72.5% with temperatures increasing from 190 to 220 °C and reaction times from 5 to 40 min. FT-IR analysis under these conditions showed gradual hemicellulose disappearance and cellulose retention. For cellulose dissolution, temperatures above 240 °C presented significant reductions in crystallinity and degrees of polymerization. Intermolecular and intramolecular H-bonds were broken with the increase in temperature, and glycosidic bonds remained until 260 °C. Thus, the amorphous structures of lignin and hemicellulose, as well as crystalline structure of cellulose, could be sequentially dissolved around 190 °C and 240 °C, respectively. Kinetic analysis revealed that the lignocellulosic dissolution reaction above 190 °C did not agree with the surface reaction rate equation because of the high dissolution rate and interaction in the lignocellulosic structure. By contrast, the reaction kinetics of cellulose dissolution did not exhibit a sudden change in the test hydrothermal conditions, and the activation energy was calculated as $189.8 \pm 8.6\ \mathrm{kJ\ mol^{-1}}$ according to the obtained reaction rate constants. These findings significantly enhance the understanding of the mechanism, and provide evidence for the sequential dissolution and hydrolysis of lignocellulosic waste using a multilevel hydrothermal process.

1. Introduction

In light of the global fuel issues, recovering biofuels, such as biodiesel and bioethanol, from lignocellulosic waste has gained considerable attention. Agricultural wastes including corn stalks and wheat straw, which are normally abundant, cheap, and easy to obtain, are typical lignocellulosic materials and potential sources of bioenergy. Given the special structure of lignocellulose, numerous pretreatment and hydrolysis technologies have been developed. These technologies are aimed toward removing the lignin wrapping around cellulose fibers, breaking down the crystalline and polymeric structures of cellulose and hemicellulose, and then hydrolyzing cellulose into fermentable sugars for further ethanol production [1,2]. The hydrothermal process, which has been proven to be efficient in breaking the lignocellulosic structure and hydrolyzing cellulose into fermentable sugars, is considered a promising technology for the pretreatment and hydrolysis of lignocellulosic waste [3].

Compared with conventional pretreatment and hydrolysis technologies such as acid treatment and enzymatic hydrolysis, hydrothermal technologies have the advantages of high efficiency,

---

* Corresponding author. Tel.: +86 10 5880 5768.
E-mail address: yanzhao@bnu.edu.cn (Y. Zhao).

http://dx.doi.org/10.1016/j.cej.2015.03.042
1385-8947/

no additional catalysts, and no intermediate inhibition [4]. However, most hydrothermal reactions, especially supercritical and subcritical water reactions, have been identified to present several major limitations in recent studies. In addition to the high energy cost derived from high temperatures and pressures, the relatively low yield of fermentable sugars, which are the target products of pretreatment and hydrolysis, is the key limiting factor of such processes [5]. Previous studies have found that, during cellulose dissolution and hydrolysis at relatively high temperatures, hexoses produced from cellulose rapidly decompose into unfermentable products, resulting in low yields of fermentable sugar and difficult system optimization of the hydrothermal process [6,7]. These limitations are mainly attributed to the fact that hydrothermal processes normally lead to synchronous dissolution and hydrolysis of cellulose, favoring the decomposition and loss of fermentable sugars at the same time [8]. Furthermore, synchronous reaction of lignin and hemicellulose results in the loss of fermentable pentoses derived from hemicellulose hydrolysis and affects cellulose hydrolysis by catalysis [9,10]. Various low-molecular-weight degradation products, such as phenolic and furfural compounds generated from hemicellulose and lignin in synchronous hydrothermal reaction, have been shown to be inhibitory for further ethanol fermentation [11].

Numerous findings have shown that lignin, hemicellulose, and cellulose exhibit distinct behavior under hydrothermal conditions [12]. Hemicelluloses hydrolyze and decompose at temperatures above approximately 180 °C, lignin degrades gradually in the range of 200–600 °C, and cellulose decomposes at around 300–400 °C [13,14]. Considering the differences in the hydrothermal treatment of these chemical components of lignocellulose, a multilevel hydrothermal process was previously proposed by Allen et al. to fractionate biomass, such as sugarcane bagasse and corn fiber, at around 200–230 °C [15,16]. The feasibility of this process was further proved, and a subsequent step of cellulose hydrolysis at higher temperatures (230–280 °C) was suggested [17]. The multilevel hydrothermal process was commercialized by a company for cellulosic sugar production. This process was also used in the hydrothermal carbonization of lignocellulosic biomass [13,18].

Moreover, the conditions for cellulose dissolution and hydrolysis are different. Only less than 10% of the soluble sugars were detected in the liquid products when most of the cellulose was recovered as fiber at 195–205 °C [19]. A study in structural chemistry has shown that the bond energy of intramolecular and intermolecular hydrogen bonds broken during cellulose dissolution ranges between 20 and 33 kJ mol^{-1}, but the bond energy of glycosidic bonds (C—O—C) broken during cellulose hydrolysis ranges from 335 to 377 kJ mol^{-1} [6]. Therefore, the multilevel hydrothermal technology has been applied to dissolve and hydrolyze lignocellulosic waste sequentially. In this technology, lignin and hemicellulose in lignocellulosic waste are dissolved at relatively lower hydrothermal conditions to remove the components wrapped around cellulose, followed by a secondary approach to further dissolve cellulose at relatively higher conditions. Finally, the dissolved cellulose is hydrolyzed into fermentable sugars at optimal hydrothermal conditions for the corresponding homogeneous reaction. This method is supposed to provide targeted multilevel treatment of lignocellulose, efficiently obtain a high yield of fermentable sugars, and also prevent their further decomposition into undesirable products.

Several related studies have investigated the sequential hydrothermal process and corresponding conditions. For example, experiments with Japanese beech showed that cellulose dissolution requires relatively higher conditions compared with hemicellulose and lignin [20]. A study on the conversion of switchgrass has also demonstrated that cellulose remains intact when most hemicellulose is hydrolyzed into xylan [21]. However, the differences in dissolution and hydrolysis conditions of lignocellulose are derived from its molecular structures and chemical bonds, and only a few studies have focused on the reaction mechanisms on the chemical structure of lignocellulosic waste during multilevel hydrothermal treatment. Therefore, the aim of this study is to investigate the sequential dissolution mechanisms of lignocellulose and cellulose by performing hydrothermal experiments with lignocellulosic waste and cellulose under varying conditions. This study especially focuses on the changes of the major components in solid phase after hydrothermal dissolution to reveal the dissolution mechanisms on the chemical structure through the changes in crystallinity, degrees of polymerization (DPs), and chemical bonds. The results will be beneficial in enhancing knowledge on lignocellulosic dissolution, and provide important evidence for the application of the multilevel hydrothermal process on lignocellulose resources.

2. Materials and methods

2.1. Raw materials

Corn stalks, which were collected from farms in the suburbs of Beijing, China, were used as lignocellulosic substrate. The corn stalks were mechanically crushed into powder and sieved using a 0.63 mm sieve prior to experiments. To avoid interference of hydrothermal products from corn stalks, microcrystalline cellulose (in powders smaller than 0.63 mm, purity >99.9%, Beijing Fengli Jingqiu Commerce and Trade Co., Ltd.) was used for investigating the process of cellulose dissolution instead of cellulose reserved after treatment of corn stalks.

2.2. Experimental apparatus and designs

A batch hydrothermal reaction system was used to investigate the dissolution of lignocellulosic materials under different hydrothermal parameters. The reaction system consists of reactors, a temperature controller, a salt bath, and a water cooler. The salt bath was preheated to a selected temperature before experiments. For experimental parallelity and repeatability, two parallel reactors loaded with the same amounts of raw materials and deionized water were equipped abreast in an operating arm, immersed horizontally into the salt bath, and then shaken to enhance mixing and heat transfer. When the selected reaction time was reached, the reactors were immediately removed from the salt bath and placed into the water cooler to terminate the reaction. The detailed experimental apparatus and operation were similar to those in our previous research [5]. However, different from the previous reactors, the current reactors had a 14 mm inner diameter, 4 mm wall thickness, and 132 mm length, providing an effective volume of 20 mL.

In the dissolution experiments of corn stalks, 200 mg of substrate and 10 mL of deionized water were mixed and then sealed in the reactor. Six groups of experiments were operated under reaction temperatures of 170 °C, 180 °C, 190 °C, 200 °C, 210 °C, and 220 °C, respectively. In each group, four batches with reaction times of 5, 10, 20, and 40 min were performed. In the cellulose dissolution experiments, the substrate mass was 250 mg, the assigned temperatures were 220 °C, 230 °C, 240 °C, 250 °C, and 260 °C, and the assigned reaction times were similar, except for those at 260 °C (3, 5, 10, and 20 min).

2.3. Analysis methods

The corn stalk composition was analyzed using the following methods: water and ash content, weighting after drying and