Chemical Engineering Journal 260 (2015) 20–27

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Hydrolysis of wheat straw by dilute sulfuric acid in a continuous mode

Wenchao Ji, Zhemin Shen *, Yujuan Wen

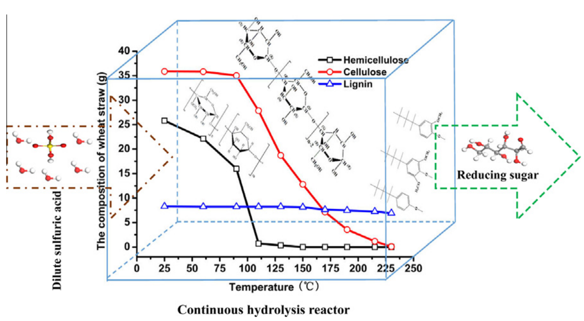
School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

HIGHLIGHTS

- Effective saccharification approach of wheat straw is established in a continuous dilute sulfuric acid medium.
- The maximum reducing sugar yield ratio is as high as 60.80%.
- The material balance and reaction mechanism are analyzed in the whole process.
- Hemicellulose and cellulose are converted to reducing sugar fully and the change of lignin is negligible.

GRAPHICAL ABSTRACT

Hydrolysis of wheat straw by dilute sulfuric acid in a continuous mode. The world is desperate need of renewable energy to solve vital strategic, economic and environment problems with the depletion of global fossil fuel. Wheat straw is an abundant agricultural residue worldwide which has great potential in bioethanol conversion. However, high production costs and low yield rate of fermentable sugar restrict its commercialization. We focus on developing more effective saccharification process with little inhibitors of wheat straw. Consequently, a continuous dilute sulfuric acid hydrolysis approach is established in which dilute acid is taken as flow phase. The hydrolysis of wheat straw was carried out in dilute sulfuric acid with temperature gradient elevating. Each sample of 250 mL was taken when temperature elevates from 60 to 230 °C (temperature interval 20–30 °C). The optimized saccharification conditions were achieved at the flow rate of 25 mL/min and sulfuric acid concentration of 1.00%. The maximum reducing sugar (RS) yield ratio is as high as 60.80% in the whole continuous hydrolysis reaction. Furfural is detected by GC–MS with a low content which is the only kind of by-product in the hydrolysate. The hydrolysis mechanism is clarified by analyzing the change of three main compositions in wheat straw under optimized conditions. Besides, SEM, FT-IR analysis techniques are used and the results show that the hemicellulose and cellulose in the wheat straw can be fully converted to RS, while the change in lignin is negligible. This approach is a novel and promising technique for utilizing real straw resource for high yield of RS.



ARTICLE INFO

Article history:
Received 12 November 2013
Received in revised form 22 August 2014
Accepted 25 August 2014
Available online 6 September 2014

Keywords:
Hydrothermal saccharification
Wheat straw

ABSTRACT

Wheat straw is an abundant agricultural residue with low commercial value worldwide which has great potential in bioethanol conversion. However, high production costs and low yield rate of fermentable sugar restrict its commercialization. A continuous dilute sulfuric acid hydrolysis process was established in which dilute acid (0–1.00%) was taken as flow phase. This process aims to reach high saccharification efficiency and low toxicity of reducing sugar (RS). The hydrolysis of wheat straw was carried out in dilute sulfuric acid with temperature gradient elevating. Each sample of 250 mL was taken when temperature elevates from 60 °C to 230 °C (temperature interval 20–30 °C). The optimized saccharification conditions were achieved at the flow rate of 25 mL/min and sulfuric acid concentration of 1.00%. The maximum RS

* Corresponding author. Tel./fax: +86 2154741065.
E-mail addresses: wenchaoji2012@gmail.com (W. Ji), zmshen@sjtu.edu.cn (Z. Shen).

http://dx.doi.org/10.1016/j.cej.2014.08.089

Dilute sulfuric acid
Reducing sugar
Furfural

yield ratio is as high as 60.80%. Furfural is detected by GC–MS with a low content which is the only kind of by-product in the hydrolysate. The hydrolysis mechanism is clarified by analyzing the change of three main compositions in wheat straw under optimized conditions. Besides, SEM, FT-IR analysis techniques are used and the results show that the hemicellulose and cellulose in the wheat straw can be fully converted to RS, while the change in lignin is negligible. This approach is a novel and promising technique for utilizing real straw resource for high yield of RS.

1. Introduction

The growing population combined with the increasing global demand for energy and the emergence of environmental problems in current society have simulated a lot of research effort to develop low environmental impact technologies on renewable raw materials to meet these targets [1–3]. Biomass is one of the largest renewable materials sources of energy in the world. Ethanol converted from biomass has been seen as an important alternative to fossil fuel. This process brings benefits to the environment and national energy security [4,5]. Increased biomass energy conversion efficiency means decreasing the impacts of both the carbon footprint and the water footprint on the environment. Wheat straw is one of the most abundant agricultural residues worldwide which presents great potential for ethanol production [6]. However, due to its complex structure, it is an obstacle to obtain high sugar release from this feedstock [7]. Thus, it affects the efficiency of producing ethanol in sugar fermentation stage. The saccharification of wheat straw is a key intermediate process to obtain ethanol.

Generally, enzyme, dilute acid and hydrothermal methods are widely used in hydrolysis of straw. Stable RS can be achieved by enzyme hydrolysis method with high efficiency. Nevertheless, long reaction time, thorough pretreatment, difficult separation and high cost make it hard to application [8–11]. As for dilute acid hydrolysis, compared to enzyme hydrolysis, it is a more economic process and the rate of hydrolysis is faster [12]. It usually employs sulfuric acid and hydrochloric acid at 1–10% using a moderate temperature range of 100–150 °C [13]. Sometimes, H_2SO_4 and H_3PO_4 are used to improve certain sugar yield [14]. This saccharification process is proved less effective as the decomposition of monosaccharide into less desirable compounds. The fermentation inhibitors increase when hydrolysis takes place at higher temperature and higher acid concentration [15]. Recent years, hydrothermal method [16] has been used in cellulose hydrolysis in which water plays an important role in saccharification process. It has been reported that combined supercritical and subcritical method have been studied for cellulose conversion to fermentable hexose production in a flow reaction system [17]. The operation of this system is too complex to control. From these methods, it can be concluded that a high sugar content with low fermentation inhibitors saccharification approach is the tendency in hydrolysis of straw.

Herein, it is imperative to develop a novel hydrolysis process which can obtain much sugar and little poisonous compounds. In this research, we report a hydrothermal saccharification approach of wheat straw using continuous dilute sulfuric acid. Compared to traditional methods, a smaller range of sulfuric acid concentration (0–1.00%) is adopted. The hydrolysis temperature ranges from 60 °C to 230 °C and the hydrolysate is collected at different temperature points. The aim of continuous dilute sulfuric acid mode is to realize the separation of sugar liquid in which the generation of inhibitors can be avoided to some extent. More importantly, the hydrolysis reaction mechanism of wheat straw is also studied. This study is very significant in utilizing farm residues and reducing the pollution problem brought by their burning.

2. Materials and methods

2.1. Material

Wheat straw was provided by a farm at Nanhui town, Shanghai, China. Its typical compositions are shown in Table 1. This material was ground to a particle size of 380–420 μm and passed through a 40 mesh sieve to separate particles to be added in our reactor. The original wheat straw particle surface morphology with a magnification of 1000 times is shown in Fig. S1 (Supplementary data).

2.2. Analytical methods

2.2.1. Composition analysis

The content of neutral dietary fibre (NDF), acid detergent fibre (ADF), lignin and cellulose were determined by the detergent method according to Van Soest [18,19]. Hemicellulose content was calculated from the difference between NDF and ADF.

2.2.2. RS analysis

RS was estimated by the DNS method [20]. Firstly, 1 mL filtered reaction solution was diluted into 10 mL. Then 1 mL diluted liquid was taken into a colorimetric tube (25 mL) followed by adding 1 mL DNS reagent. The mixture was boiled for 5 min in the water bath reactor, cooled to room temperature, and added distilled water into the mark. Absorbance values of samples were taken at 540 nm in UV-2450 spectrophotometer (SHIMADZU, JP, Ltd). The RS yield ratio is calculated by the equation below.

$$\text{RS yield ratio } (\%) = \text{Total mass of RS } (\text{g})/\text{Total mass of wheat straw } (\text{g}) \times 100$$

2.2.3. GC–MS analysis

To analyze the by-product in the thermal hydrolysate, GC–MS analyses were performed using a GCMS-QP2010 apparatus (SHIMADZU, JP, Ltd), equipped with DB-5 MS column (30 m × 0.32 mm, 0.25 μm film thickness).

The product in hydrolysate was extract with trichloromethane. 10 mL liquid hydrolysate sample and 10 mL trichloromethane were mixed and vibrated for 5 min. Repeat this operation for 3 times, condensed the extraction to approximately 1 mL for detecting. The chromatographic conditions were as follows: 2.41 cm^3/min as the carrier gas (He) flow rate; 40 °C as initial temperature for 5 min; 10 °C/min as temperature rising rate for 30 min; 250 °C as injector and transfer-line temperature. The split ratio is 1:10. MS detects at: voltage 1.01 kV, EI 70 eV, scan field 29–350 *m*/*z*, ion source temperature 200 °C.

Table 1
The chemical composition of wheat straw.

Composition	Proportion (%)
Cellulose	35.86
Hemicellulose	25.82
Lignin	8.31