Applied Energy 154 (2015) 190–196

Contents lists available at ScienceDirect

Applied Energy

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

# Pretreatment of rice straw for ethanol production by a two-step process using dilute sulfuric acid and sulfomethylation reagent

Shengdong Zhu *, Wenjing Huang, Wangxiang Huang, Ke Wang, Qiming Chen, Yuanxin Wu

*Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, People's Republic of China*

## HIGHLIGHTS

- Novel two-step pretreatment of rice straw to improve its ethanol production economy.
- High purity xylose recovered from the acid treatment liquor with 83.2% yield.
- Sulfomethylation treatment liquor recovered as a cement water reducer.
- SSF of the two-step treated rice straw to ethanol with 86.4% yield.

## ARTICLE INFO

*Article history:*
Received 6 December 2014
Received in revised form 1 May 2015
Accepted 2 May 2015

*Keywords:*
Rice straw
Acid treatment
Sulfomethylation treatment
Simultaneous saccharification and fermentation
Ethanol
Bio-refinery

## ABSTRACT

Ethanol is now one of the most widely used transport bio-fuels and production of ethanol from rice straw (RS) is an effective RS utilization way. This work investigated a novel two-step RS pretreatment process with the goal of decreasing the ethanol production cost through complete utilization of its components. In the process, RS was first treated with dilute sulfuric acid to remove the hemicellulose and recover the xylose from its hydrolyzate as a feedstock for xylitol production, and then the residue was treated with the standard sulfomethylation reagent to remove the lignin and recover its hydrolyzate containing the lignosulfonate as a cement water reducer. Among tested conditions, the best acid treatment (AT) conditions were 100 °C, 1.0 wt% sulfuric acid, 10% (w/v) RS and 2 h, and the hydrolyzate recycled 5 times. After AT, the xylose was recovered from its hydrolyzate with 83.2% yield. The best sulfomethylation treatment (ST) conditions were 160 °C, 15% (w/v) acid treated RS, and 5 h using the standard sulfomethylation reagent. After ST, its hydrolyzate containing 5.0% lignosulfonate was directly recovered as a cement water reducer. Under the above best two-step treatment conditions, 94% hemicellulose and 92% lignin in the origin RS were removed, but cellulose had almost no loss. After the simultaneous saccharification and fermentation of the two-step treated RS (100 g $L^{-1}$) for 72 h, the ethanol concentration and its yield reached 40.6 g $L^{-1}$ and 86.4% respectively. It suggests the two-step pretreatment process was an efficient RS pretreatment method for its ethanol production. This process can be an example of RS bio-refinery for bio-fuel production.



## 1. Introduction

As the world population has grown and more countries have industrialized, energy consumption has increased steadily [1]. Petroleum is currently being used as a major energy source, but it poses great concerns in terms of its future utilization because of its resources limitation, increasing costs, and the associated environmental issues [1–3]. Therefore, there is great interest in exploring alternative energy sources to maintain the sustainable growth of society [4–6]. Ethanol, as a clean and renewable energy source, which can be produced from sugars through fermentation has drawn much attention in recent years. Ethanol is now one of the most widely used transport bio-fuels in the world and its consumption as transport fuel has kept increasing steadily [3,4]. Apart from an alternative to traditional energy source, ethanol can also be a versatile chemical and organic solvent. However, the production of ethanol through fermentation has been limited using the current sugar cane or maize starch-based technology because of raw materials shortage and high cost [4–6]. A potential method for solving this problem is to utilize lignocellulosic materials such as agricultural wastes [4–8]. Production of ethanol from rice straw (RS), one of the most abundant agricultural wastes, has been

* Corresponding author. Tel./fax: +86 27 87447996.
*E-mail address:* whictzhusd@sina.com (S. Zhu).

http://dx.doi.org/10.1016/j.apenergy.2015.05.008
0306-2619/

extensively studied, but its high production cost still prevents its commercialization based on current technology [9–11]. Therefore, it is of great importance in improving the present technology and decreasing its cost. The RS bio-refinery is an effective way to achieve this goal by fully utilizing its components and co-producing high value-added chemicals [5,12–14].

Production of ethanol from RS generally includes three sub-processes: pretreatment, saccharification and ethanol fermentation. The RS is mainly composed of cellulose, hemicellulose and lignin. The complex structure of lignin and hemicellulose and cellulose in RS limits its effective saccharification. Hence, some pretreatment procedures need to be performed before its saccharification. Traditionally, the purpose of its pretreatment is to remove lignin and hemicellulose, to reduce cellulose crystallinity, and to increase the porosity, thus improving its saccharification efficiency [15–17]. Various methods have been used for its pretreatment to achieve this goal [18–22]. However, most of these pretreatment methods focus only on improving its saccharification efficiency based on its cellulose utilization, and little attention has been paid on the recovery and utilization of its hemicellulose and lignin. Currently, the most studied ethanol production process from RS is utilizing its cellulose and hemicellulose for ethanol production and burning its lignin residues for electricity [11]. This leads to high ethanol production cost and also causes some environmental problems. In order to decrease the ethanol production cost from RS, it is necessary to fully utilize its components and co-produce high value-added products by combining its pretreatment, fraction of its components and recovery of useful chemicals together, which is often called RS bio-refinery. The objective of this work is to establish such a RS bio-refinery for decreasing its ethanol production cost. In this work, RS was first treated with dilute sulfuric acid to remove its hemicellulose and recover xylose as a feedstock for xylitol production, and then the residue was treated with the standard sulfomethylation reagent to remove its lignin and recover its hydrolyzate containing lignosulfonate as a cement water reducer, finally the simultaneous saccharification and fermentation (SSF) of the two-step treated RS to produce ethanol. The acid treatment (AT) and sulfomethylation treatment (ST) conditions were optimized based on their pretreatment effectiveness and useful chemicals recovery. The SSF of the two-step treated RS for ethanol production was examined and a brief comparison between our process and the currently most studied ethanol production process was also made.

## 2. Materials and methods

All experiments were carried out three times, and the data reported were expressed as the mean values ± standard deviation. The RS composition or its hydrolyzed residues were expressed on a wet basis throughout this work.

### 2.1. Materials and chemicals

Raw RS was obtained from local farmers in Yichang, Hubei province, China. Before any pretreatment, it was cut to nominally 1–2 cm lengths and washed thoroughly with tap water until the washings were clean and colorless and then air dried for further treatment. Its main composition was as follows: moisture 11.3 ± 0.2%, cellulose 38.4 ± 0.5%, lignin 16.2 ± 0.4%, and hemicellulose 21.8 ± 0.5%.

The Cellulase (Onozuka R-10) and β-glucosidase (Novozyme 188) used in this study were purchased from Sigma-Aldrich (St. Louis, MO). The cellulase activity of Onazuka R-10 was 10 FPU $mg^{-1}$, and β-glucosidase activity of Novozyme 188 was 500 CBU $mL^{-1}$. All other chemicals employed in this study were of reagent grade and purchased from Wuhan Chemicals & Reagent Corp., China.

### 2.2. Two-step pretreatment of rice straw

AT was used as the first step pretreatment. During the first step pretreatment, 20 g of RS after cutting and washing and 180 mL given concentration sulfuric acid were added to a three-necked flask with reflux and kept it boiling for a given time. The AT residues (acid treated RS) were collected and washed extensively with tap water until neutral pH, dried at 65 °C and weighted. Then they were cut to 10–20 mesh for their composition analysis and subsequent ST. The AT hydrolyzate was reused for AT of RS after adjusting its volume to 180 mL with fresh given concentration sulfuric acid. After the AT hydrolyzate was recycled to certain times, it was used to recover xylose. The xylose recovery from the AT hydrolyzate and its purification were carried out as described by Curreli et al. [23]. The xylose yield was calculated as follows:

$$\text{Xylose yield}\ (\%) = \text{The recovered xylose} \times 0.88/\text{The total dissolved hemicellulose} \times 100$$

ST was used as the second step pretreatment. During the second step pretreatment, 35 g of acid treated RS and 200 mL standard sulfomethylation reagent [1% (w/v) sodium hydroxide, 3% (w/v) formaldehyde and 2% (w/v) sodium bisulfite] were added to a 500 mL high pressure reactor and kept it react at a given temperature for a certain time. After the reaction, it was cooled to room temperature. The ST residues (the two-step treated RS) were collected and washed extensively with tap water until neutral pH, dried at 65 °C and weighted. Then they were used for their composition analysis and subsequent ethanol fermentation. The ST hydrolyzate containing the lignosulfonate was directly recovered as a cement water reducer.

### 2.3. Simultaneous saccharification and ethanol fermentation

The yeast *Saccharomyces cerevisiae* YC-097 was used throughout this study. The stock cultures were maintained on YPD agar plates at 4 °C and transferred to fresh plates every 4 weeks to avoid the micro-organism degradation. The inoculum preparation was by means of micro-organism transfer from stock cultures to a fresh plate and grew for 48 h at 30 °C. Following this period, single colonies were transferred to a 250 mL flask with 100 mL YPD medium. The flask was placed on a orbital shaker with a shaking diameter 5 cm and a shaking frequency 200 rpm and incubated at 30 °C for 24 h. This was used as the inoculum for ethanol fermentation, its yeast concentration is about $1.5 \times 10^8$ cells $mL^{-1}$. The ethanol fermentation was carried out in a 250 mL flask with 95 mL ethanol fermentation medium and 5 mL inoculum at 40 °C and 200 rpm for 72 h. During the fermentation, small samples were taken at regular intervals for later analytic usage. The compositions of culture medium were as follows (g $L^{-1}$):

The YPD agar medium: D-glucose 20, peptone 20, yeast extract 10, agar 15.
The YPD medium: D-glucose 20, peptone 20, yeast extract 10.
The ethanol fermentation medium: two-step treated RS 100, peptone 20, yeast extract 10.
The YPD agar medium and the YPD medium were autoclaved at 121 °C for 20 min after pH was adjusted to 7 by addition of 1 M NaOH or 1 M HCl. The ethanol fermentation medium was autoclaved at 121 °C for 30 min after pH was adjusted to 5.5 by addition of 1 M NaOH or 1 M HCl. Then 150 mg Onazuka R-10 and 5 mL Novozyme 188 were added to 1 L sterilized ethanol fermentation medium.