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Enhanced hydrogen production from anaerobic fermentation of rice straw pretreated by hydrothermal technology

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HIGHLIGHTS

- Soluble carbohydrates had strongly positive correlation with subsequent H_2 yield.
- Rice straw pretreated at 210 °C with 0 min of holding achieved the highest H_2 yield.
- Holding time is crucial for HTT pretreatment when H_2 production being considered.

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ABSTRACT

This study tested the effect of hydrothermal treatment (HTT) at different peak temperatures (150 °C and 210 °C, i.e. HTT150 and HTT210, respectively) and holding time (0–30 min) on the solubilization of rice straw at total solids (TS) of 20% and then subsequent H_2 production from resultant substrates. No obvious degradation was detected in lignin content under all tested HTT conditions which did open up the surface structure and have efficient solubilization effect on rice straw. Soluble carbohydrates produced from straw particles during HTT210 was found to have strongly ($r = 0.9987$) positive correlation with the subsequent H_2 yield. The maximum soluble carbohydrates, 80 mg per gram of volatile solids (VS) was achieved under HTT210 and 0 min of holding condition, correspondingly yielding the highest hydrogen production (28 ml/g-VS), about 93-fold higher than the control. Results suggest that holding time is crucial for HTT pretreatment when taking subsequent H_2 production into consideration.

1. Introduction

Increased price of energy and rapid depletion of fossil fuels call for an urgent need for the development of renewable energy so as to reduce environmental pollution caused by fossil fuels. Renewable energy, especially biohydrogen, is a noncarbon based energy resource and regarded as an attractive candidate to replace fossil fuels.

Rice straw is an abundant agricultural waste with annual global quantity of 685 million tons (Lim et al., 2012). With the increased need of crop production and much dependence on fossil fuels, more and more crop straws are burned or discarded in the field due to lack of cost-effective treatment and recycling methods, triggering severe environmental problems. According to the report by UNEP (2009), open field burning carried out after harvesting season is perhaps the most common practice of handling rice straw in many Asian countries. Because of a large amount of cellulose and hemicellulose contained, rice straw can be used for biohydrogen production from fermentation, a prospective alternative for sustainable utilization of agricultural wastes (Guo et al., 2010).

The fermentation of rice straw, however, is very difficult in practice due to its lignocellulosic nature and high content of lignin, a major barrier for lignocellulosic biomass in the bioconversion process. Thus, in order to improve degradability of lignocellulose for anaerobic digestion, pretreatment of rice straw is prerequisite for a high yield of biogas (Zheng et al., 2014). Many methods including mechanical, chemical and biological pretreatment have been investigated for the hydrolysis of refractory lignocellulosic substances and then hydrogen production (Hendriks and Zeeman, 2009; Ren et al., 2009; Zheng et al., 2014). Some of the above-mentioned pretreatment methods do exhibit high efficiency in the hydrolysis of lignocellulosic biomass. Still, the following aspects hinder their practical application to some extent: (1) Solely mechanical pretreatment is not effective and thus always applied in combination with other methods like chemical or biological pretreatment; (2) Biological pretreatment process is complex and difficult to maintain its efficiency; (3) Chemicals addition in chemical

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pretreatment usually causes secondary pollution, demanding additional wastewater treatment facilities.

Hydrothermal treatment (HTT), an environmentally friendly process, possesses the following advantages: non-chemicals addition, handleability, opening up the plant cell wall structure, and thus efficient solubilization and degradation of lignocellulosic biomass (Merali et al., 2013; Rogalinski et al., 2008). HTT can be a prospective alternative for the pretreatment of rice straw, resulting in efficient hydrolysis of the organic matter contained. Previous studies have been carried out on the HTT treatment of biomass for gasification, bio-methane or ethanol production and compost stability (Chandra et al., 2012; Nakhshiniev et al., 2014; Petersen et al., 2009; Peterson et al., 2008). Among them, Chandra et al. (2012) tried HTT treatment on rice straw biomass at 200 °C for 10 min and achieved enhanced methane production. Nakhshiniev et al. (2014) tested HTT on rice straw at 180 °C for 30 min with improved compost stability. Up to now, however, little information could be found on the effect of HTT pretreatment on rice straw for bio-hydrogen production. In addition, no result about HTT effect on rice straw could be inferred from the literature for 0 min of holding at the designed HTT temperature. That is, the necessity of a longer holding time for HTT treatment should also be confirmed, which will greatly influence the reactor design and energy input.

In this study, HTT, carried out at the designated peak temperature (150 °C or 210 °C), was holding for 0 min, 10 min, 20 min, and 30 min, respectively. The effects of peak temperature and holding time on solubilization of rice straw and subsequent H_2 production were mainly explored. The relationship between H_2 yield and soluble products from rice straw during HTT pretreatment was also discussed.

2. Methods

2.1. Rice straw and seed sludge

Rice straw in this study was collected from a farm field in Tsukuba (Ibaraki, Japan), and then cut into short pieces manually and air-dried. The air-dried straw particles were milled to powders and then screened by a 30-mesh sieve (0.6 mm). The straw particles smaller than 0.6 mm were selected and kept in a plastic bag in dark at room temperature before further treatment (HTT and hydrogen fermentation).

The seed sludge was anaerobically digested sludge sampled from the Shimodate Sewage Treatment Center (Ibaraki, Japan), stored at 4 °C and used within 1 month. Table 1 lists the physico-chemical characteristics of rice straw and anaerobic sludge. No further treatment was conducted on the seed sludge used for the subsequent hydrogen production in this study.

Table 1
Physical and chemical characteristics of rice straw and anaerobic digested sludge used in the experiments.

Items	Unit	Rice straw	Sludge
pH	–	N.D.	7.2 ± 0.1
Total solid (TS)	%	90.1 ± 0.3	1.2 ± 0.0
Volatile solid (VS, of TS)	%	79.4 ± 1.1	76.6 ± 0.3
Chemical oxygen demand (COD)	mg/L	N.D.	7206.9 ± 374.1
Soluble chemical oxygen demand (SCOD)	mg/L	N.D.	3637.9 ± 126.4
Soluble carbohydrates	mg/L	N.D.	22.0 ± 1.0
Soluble proteins	mg/L	N.D.	705.3 ± 21.2
Lignin	g/100 g-DM	14.6 ± 1.9	19.7 ± 0.6
Cellulose	g/100 g-DM	28.2 ± 0.3	5.1 ± 1.7
Hemicellulose	g/100 g-DM	17.5 ± 3.1	26.1 ± 4.0

DM, dry matter; N.D., no determination.

2.2. HTT procedure

HTT pretreatment was conducted in an enclosed stainless steel reactor with working volume of 200 ml. The reactor was loaded with a mixture of 100 ml distilled water and the prepared straw with total solids (TS) content being adjusted to around 20% according to our preliminary experiments. Two different peak temperatures (150 °C and 210 °C, labeled as HTT150 and HTT210, respectively with pressure varied between 0.6 and 1.8 MPa) were applied in HTT experiments at different holding times, i.e. 0 min, 10 min, 20 min, and 30 min, respectively. Fig. 1 illustrates the temperature variation in the HTT reactor under each operation condition which was described in detail in Table 2. The temperature in the HTT reactor was averagely elevated at 15.4 °C/min and 11.0 °C/min during the heating process when HTT peak temperature was controlled at 150 °C and 210 °C, respectively. In addition, when conducting holding time of 0 min, the heater was powered off right after the temperature reached to the designated peak temperature.

2.3. Hydrogen fermentation

Batch hydrogen fermentation experiments were carried out in 250 ml glass bottles. After pretreated under above mentioned conditions (different peak temperature and holding time), the resultant substrate, a mixture of treated rice straw (solid fraction) and soluble substances (liquid fraction) produced during the HTT process, was firstly mixed homogeneously and sampled, and then inoculated with 150 ml of seed sludge with inoculation ratio ranged between 17% and 20% based on TS values of the inoculum and the initial fermentation substrate. 2 M sodium hydroxide or hydrochloric acid was used to adjust the initial pH of each reactor to be around 7.0. Their final volume was made up to 200 ml by using deionized water before fermentation. All the fermentation reactors were sealed with silica gel stoppers, and placed in a thermostat controlled at 35 ± 1 °C after their headspace being flushed with nitrogen gas for 5 min. Each stopper was connected with a 50 ml graduated plastic syringe for biogas collection and quantification.

All the trials were conducted in triplicate with their average values being taken for assessment.

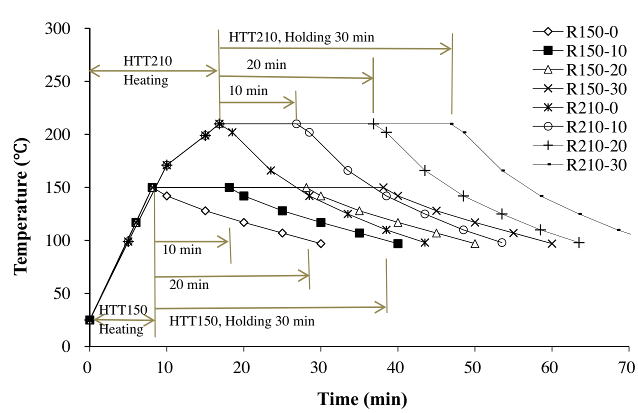

Fig. 1. Temperature changes in the HTT reactor when peak temperature is controlled at 150 °C and 210 °C, respectively. Holding for 0 min is realized by power off the heater right after the temperature reaches the designated peak temperature.