Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

Ozone pretreatment of wheat straw for enhanced biohydrogen production

Jiangning Wu, Simant Upreti, Farhad Ein-Mozaffari*

Department of Chemical Engineering, Ryerson University, 350 Victoria St., Toronto, Ontario M5B 2K3, Canada

ARTICLE INFO

Article history:
Received 1 March 2013
Received in revised form
28 May 2013
Accepted 16 June 2013
Available online 15 July 2013

Keywords:
Biohydrogen
Ozonation
Pretreatment
Wheat straw
Lignin degradation
Dark fermentation

ABSTRACT

Ozonation was tested as a pretreatment method for enhanced biohydrogen production from wheat straw. Ozone pretreatment effectively degraded wheat straw lignin, and the delignification increased with increase in the applied ozone dose. Results of reducing sugar measurement showed that under our experimental conditions ozone pretreatment significantly increased reducing sugar yields. A simultaneous enzyme hydrolysis and dark fermentation experiment was then conducted using a mixed anaerobic consortium, and the results demonstrated that ozone pretreatment significantly increased biohydrogen production. Compared to the untreated one, hydrogen production in the samples ozonated for 15, 30, 45 and 90 min increased 107%, 134%, 158% and 138%, respectively. Slight inhibitory effect on the dark fermentation was observed with the sample ozonated for 90 min, and the inhibitory effect was due to prolonged ozonation. These results proved that enhancement of biohydrogen production from lignocellulosic biomass using ozone as a pretreatment method is technically feasible.

1. Introduction

Hydrogen is a viable alternative fuel and is also considered to be a promising energy carrier to replace fossil fuels [1]. It is a clean fuel with no CO_2 emissions and can overcome the air pollution and global warming problems caused by fossil fuels [2]. Hydrogen can easily be used in fuel cells for generation of electricity [3], and can also be used as a fuel directly in an internal combustion engine not much different from the engines used with gasoline [4]. Hydrogen is also energy dense, it has a high energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [3,5]. The use of hydrogen as a fuel for transportation and stationary applications is now receiving much favorable attention as a technical and policy issue [6], and many believe that hydrogen will replace fossil fuels as the next generation of energy supply [7].

In recent years hydrogen production through biological methods has attracted worldwide attention, due to its potential as an inexhaustible, low-cost and renewable energy source [8]. Among biological H_2 production methods the dark fermentation processes carried out by anaerobic bacteria is generally regarded as the more favorable method because of its high production rates, process simplicity and the utilization of low-value waste as feed material [9–11].

Diverse biomass is available for dark fermentation, and lignocellulosic biomass is considered to be one of the most attractive feedstocks [9,12,13]. Lignocellulosic biomass contains approximately 70–80% carbohydrates. If properly hydrolyzed, these carbohydrates are ideal for fermentative hydrogen production [14]. Lignocellulosic biomass is cheap and widely available, the worldwide annual yields of lignocellulosic residues were estimated to exceed 220 billion tons,

* *Corresponding author*. Tel.: +1 416 979 5000x6549; fax: +1 416 979 5083.
E-mail address: j3wu@ryerson.ca (J. Wu).

0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.06.063

equivalent to 60-80 billion tons of crude oil [8]. Progress in hydrogen production from lignocellulosic biomass will not only decouple the food and biofuel production but also ensure a secured renewable energy supply [15].

Successful biological conversion of lignocellulosic biomass to hydrogen is strongly dependent on processing the raw materials to produce fermentable substrates for the microorganisms [14]. Lignocellulosic biomass mainly consists of cellulose, hemicellulose and lignin, and biohydrogen is basically converted from the cellulose and hemicellulose portion [16,17]. To produce biohydrogen, the cellulose and hemicellulose have to be degraded into sugar so that the fermentative microorganisms can use the sugar as substrate to produce hydrogen. However, in lignocellulosic materials cellulose and hemicellulose are covered rigidly with lignin Refs. [16], and this coverage hinders their digestibility [14]. As a result, direct conversion of biohydrogen from lignocellulosic biomass without pretreatment is usually insufficient.

To achieve an efficient biohydrogen production from lignocellulosic biomass an integrated process is generally conducted that involves three basic steps: pretreatment, hydrolysis and fermentation [8,13,16,18,19]. The main goal of the pretreatment is to alter or remove structural and compositional impediments to hydrolysis and subsequent degradation processes in order to enhance digestibility, improve the rate of enzyme hydrolysis and increase the fermentation yields [20–22].

Pretreatment by physical, chemical or biological means is a well-investigated process for ethanol production from lignocellulosic materials [20,23–25], however, many of these methods may not be suitable for biohydrogen production because they target ethanol, not hydrogen, as the final product. Monlau et al. [26] pointed out that bioethanol production uses only cellulose and the objective of pretreatment is to separate lignin and hemicelluloses from cellulose in order to enhance enzymatic cellulose hydrolysis, whereas biohydrogen production may use both cellulose and hemicelluloses. The application of pretreatments to improve the dark fermentation of lignocellulosic biomass has been less well investigated than their use in bioethanol production [26].

Ozone is a powerful oxidizing agent, it degrades lignin, non-selectively releasing both cellulose and hemicellulose to the enzymes, therefore, it has advantage at this point over some pretreatment methods when applied to biohydrogen production. In addition, ozone does not produce toxic residues for the downstream processes; and the reactions are carried out at room temperature and pressure [20,23,27]. It has been reported that by using ozone pretreatment, the enzymatic hydrolysis yields from wheat and rye straw were increased to 88.6% and 57%, respectively, far higher than those of 29% and 16% without ozone pretreatment [28].

Despite the fact that pretreatment is an import step in producing biohydrogen from lignocellulosic biomass and ozonation is effective for pretreating such biomass, to the author's best knowledge, to date no ozone pretreatment of lignocellulosic materials for biohydrogen production has been reported. Therefore, this study was conducted to fill this gap. This study is novel in that it is the first of its kind in applying ozone technology to lignocellulosic biohydrogen production. The objective of this study was to examine the effect of pretreatment of wheat straw, a representative lignocellulosic biomass, using ozone for biohydrogen production.

2. Materials and methods

2.1. Wheat straw

Wheat straw used in this study was obtained from a farm at Shanty Bay, Ontario, Canada. The wheat straw was received dry. Cellulose, hemicellulose and acid insoluble lignin contents of this straw were 35.1, 24.8 and 20.4 (g/100 g dry straw), respectively. The straw was ground by a Retsch cutting mill, model SM 100 (Retsch Inc., Newtown, PA, USA), and then passed through a 2 mm sieve. Milled wheat straw was stored in sealed plastic bags at room temperature until being used for the experiments.

2.2. Ozone pretreatment

Ozonation of the wheat straw was conducted in a semi-batch reactor, which was a 350-mL gas-washing bottle (Fisher Scientific Canada, Ottawa, Ontario, Canada). The gas diffuser diameter of the washing bottle was 60 mm and the diffuser pore size was 40–60 μm.

Ozone was produced from pure oxygen in a Model-GL-1 ozone generator (PCI-WEDECO Environmental Technologies, Charlotte, NC, USA). The ozone concentration in the output gas of the ozone generator was measured by an ozone monitor (Model HC-400) from the same company. The applied ozone dose could be easily adjusted by varying ozone weight percentage and/or gas flow rate. Excess ozone leaving the reactor was destroyed by a catalytic ozone-destruct column filled with Carulite catalyst (Carus Chemical Company, Peru, IL, USA). More details of the experimental setup were described elsewhere [29].

For each experimental run, three swashing bottle reactors were operated in parallel simultaneously. Ozonation began when the ozone–oxygen mixture was fed to the reactor from the bottom. In each experimental run the reactor contained 5 g (dry weight) milled wheat straw, mixed with water to reach 40% water content. The feed gas was running continuously under a constant pressure of 75.84 kPa (11 psi) and at a constant flow rate of 0.63 SLPM (standard liter per minute). Ozonation was ended by sparging into the reactor pure oxygen instead of the ozone–oxygen mixture.

After ozone pretreatment each sample (5 g) was divided into 3 parts: 1 g for analysis of lignin contents, 2 g for dark fermentation experiment, and the rest for enzyme hydrolysis experiment to measure the reducing sugar contents.

2.3. Enzyme hydrolysis

Three enzymes were used in these experiments: NS22086, NS22083 and NS22118, all were provided by Novozymes (Franklinton, NC, USA). NS22086 is a cellulase complex used for the hydrolysis of lignocellulosic material, it catalyzes the breakdown of cellulosic material into glucose, cellobiose, and higher glucose polymers; NS22083 is an endoxylanase used to supplement NS22086 for hydrolysis of the intact