Fuel 106 (2013) 484–489

Contents lists available at SciVerse ScienceDirect

Fuel

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

Improvement of biogas production from pine wood by alkali pretreatment

Peyman Salehian [a], Keikhosro Karimi [a,b], Hamid Zilouei [a], Azam Jeihanipour [c,*]

[a] Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Industrial Biotechnology Group, Institute of Biotechnology and Bioengineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[c] Department of Biotechnology, Faculty of Advanced Sciences and Technologies, University of Isfahan, Isfahan 81746-73441, Iran

HIGHLIGHTS

- Alkali pretreatment of pine wood can significantly improve the biogas yield.
- It resulted in reduction of cellulose crystallinity and lignin removal.
- Efficiency of the treatment highly depends on process time and temperature.
- Treatment at high temperature for a short retention time is more effective.

ARTICLE INFO

Article history:
Received 22 April 2012
Received in revised form 21 December 2012
Accepted 31 December 2012
Available online 27 January 2013

Keywords:
Biogas
Pine wood
Alkali pretreatment
FTIR
SEM

ABSTRACT

Alkaline pretreatment with NaOH was used to improve biogas production from softwood pine. The pretreatments were carried out with 8.0% w/w NaOH solution at two temperatures (0 and 100 °C) for different periods of time (10, 30 and 60 min). By anaerobic digestion of the treated and untreated materials to biogas, significant effects of the pretreatments on the yield of methane were clearly observed. The best improvement was achieved by the treatment at 100 °C for 10 min, which resulted in 181.2% improvement in the methane production yield. The treatment at 0 °C was also effective, in which 60 min treatment resulted in 118.6% improvement in the methane yield compared to the untreated wood. Fourier transform infrared (FTIR) was used to analyze the changes in chemical structure and physical characteristics of lignin, hemicellulose, and cellulose of the treated wood, which indicated a reduction of crystallinity of cellulose due to the pretreatment. Furthermore, scanning electron microscopic images revealed that disruption of the recalcitrant structure of the pine wood could be responsible for the improvement of methane yield.

1. Introduction

Lignocellulosic materials, e.g. wood and agricultural crops, are the most plentiful renewable resources in the world. Wood wastes are cost-competitive and environmentally friendly biomass resource. In general, less than 50% of a tree is converted to the end products and the rest remains as unused resources [1], which are usually sent to landfills or burned [2,3]. However, they can be converted to valuable products by different processes such as anaerobic digestion which produce biogas.

Pine wood residues are one of the widely produced lignocellulosic sources and can be considered as a potential source of biogas. However, the biodegradation of softwoods are difficult because of their highly recalcitrant structures.

The fiber structure and consequently wood properties are determined based on their constituting components, i.e. cellulose, hemicelluloses and lignin. The high crystalline cellulosic structure which is shielded with lignin and hemicelluloses make them difficult for efficient conversion to biogas by anaerobic bacteria. A suggested solution to this problem is to introduce a pretreatment prior to the biogas production, in order to increase the digestibility of the lignocellulosic materials. The final goal of the pretreatment is to decrease the crystallinity of cellulose and eliminate the resistance of lignin; hence, making them more accessible to the bacteria [4].

Several pretreatment methods have been suggested to improve the biogas production including physical, physicochemical, chemical, and biological pretreatments [4]. Among the physical pretreatments, milling was shown to improve enzymatic hydrolysis by increasing the surface area of lignocellulosic materials [5]. This is a typical process before most of any other pretreatment.

It has been frequently shown that smaller particles of lignocelluloses have better yield of biofuel [6–8]. Zhang and Zhang [9] studied the improvement of biogas production from rice straw and showed that the highest yield of biogas could be obtained by a combination of grinding and alkali treatment.

* Corresponding author. Tel.: +98 3117934342; fax: +98 3117932342.
E-mail address: a.jeihanipour@ast.ui.ac.ir (A. Jeihanipour).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.12.092

Alkali pretreatment with sodium hydroxide is one of the chemical pretreatments that have been applied for the lignocelluloses. In particular, the treatment at high concentration of NaOH (at 6–8%) can dissolve the lignin and/or cellulose (depending on temperature) of lignocelluloses [10] and efficiently improve the structure of these materials [11].

This method was investigated on different lignocellulosic materials like rice straw, cattle manure with corn stover, hardwoods, softwoods, and pulp and paper sludge [11–14] to improve the biogas production. However, it is shown that various process conditions, i.e. temperature, concentration, and the retention time, can lead to different results.

Only a few studies have investigated the effect of alkali pretreatment on improvement of biogas production from wood. Recently, Mirahmadi et al. [11] have examined the effect of NaOH pretreatment on the softwood spruce and hardwood birch to improve the yield of biogas and biethanol. They showed that the alkali pretreatment have different effects on the soft- and hardwood at different temperatures. Nieves et al. [15] also studied the NaOH pretreatment on the non-wooden lignocellulosic material, OPEFB (oil palm empty fruit bunch), at 100 °C for various periods of time and observed the same effects. To the best of our knowledge, there is no previous study on enhancing the biogas production from pine wood.

In the present work, the effects of NaOH pretreatment of pine wood, at high and low temperatures and different retention times, on the yield of methane production are studied. Furthermore, structural changes in the pine wood as a result of the treatments are investigated.

2. Materials and methods

2.1. Raw materials

A 10 years old pine wood was obtained from a forest around city of Isfahan (Isfahan University of Technology, Isfahan, Iran) (3234_0N, 5132_0E), and dried at 45 °C. They were debarked, cut, and grinded. The chips were screened to achieve a relatively homogeneous size of less than 1 mm (20 mesh). The dry weight content of the selected samples was measured by drying at 105 °C.

2.2. Pretreatment procedure

An amount of 5 g milled pine wood and 95 g NaOH solution (8% w/w) was mixed for 10 min at room temperature. The mixture was then incubated either at 0 or 100 °C for different periods of time (i.e. 10, 30, or 60 min) and mixed every 10 min during the incubation period. The mixtures were then centrifuged at 4500 rpm (5000 g) at room temperature for 10 min and the settled solid was washed with distilled water followed by vacuum filtration until pH 7 was achieved. The solids were kept in plastic bags at 4 °C until use.

2.3. Production of biogas

Anaerobic batch digestions of the treated and untreated pine woods were carried out at mesophilic conditions (37 °C) according to the method described by Hansen et al. [16]. The inoculum was obtained from a large scale biogas bioreactor (Isfahan municipal wastewater treatment, Isfahan, Iran), operating at mesophilic conditions (37 °C). The batch digesters were 118 mL serum glass bottles, closed with butyl rubber seals and aluminium caps. In each flask, 20 mL of inoculum was added to a certain amount of substrate to keep a VS (volatile solid) ratio of 2:1 (inoculum: substrate). Deionized water was then added to have a final volume of 25 mL. Moreover, inoculum and deionized water were applied as a blank, to be able to determine the gas production of the inoculum alone. Anaerobic conditions were provided by purging the flasks with a gas containing 80% N_2 and 20% CO_2 for about 2 min. The bioreactors were maintained at 37 °C in an oven and manually shacked every day. Gas samples were taken every 3 days during the first 15 days and then every 5 days until 45 days and analyzed for methane and carbon dioxide contents using gas chromatography. All the digesting experiments were carried out in triplicates.

2.4. Analytical methods

The composition of gas produced in anaerobic digestion was analyzed by a gas chromatograph (Sp-3420A, TCD detector, Beijing Beifen Ruili Analytical Instrument CO), which was equipped with a packed column (Porapack Q column, Chrompack). Helium was used as a carrier with 20 mL/min flow rate. Temperature of the column, injector, and detector were 5, 90 and 140 °C, respectively. The injections were carried out using a pressure-tight syringe (VICI, Precision Sampling Inc.) making it possible to take gas samples at the actual pressure of the bioreactors. The sample volume was 250 μL. Pure methane was used as a standard gas and all the results of methane volumes are presented at standard conditions.

The treated and untreated pine woods were analyzed for ash, total solids, volatile solids, carbohydrates, and lignin contents according to the standard method presented by Sluiter et al. [17].

High performance liquid chromatography (HPLC) was used to quantify sugars. It was equipped with a UV/vis and RI detectors (Jasco International Co., Tokyo, Japan) and an ion-exchange column (Aminex HPX-87P, Bio-Rad), using deionized water as an eluent with a flow rate of 0.6 mL/min at 85 °C.

Structural change of the treated and untreated wood was examined by scanning electron microscopy (SEM). The dry samples were mounted on double-sided tape placed on aluminium stubs. The samples were coated with gold (BAL-TEC SCD 005) and analyzed by a scanning electron microscope (PHILIPS, XL30) with an accelerating voltage of 15 kV. The crystallinity and structural features of the NaOH-treated and untreated wood species were examined using a Fourier transform infrared (FTIR) spectrometer (Bruker Tensor 27 FT-IR) equipped with a universal ATR (Attenuated Total Reflection) accessory and DTGS detector. Its spectra were obtained with an average of 64 scans and a resolution of 2 cm^{-1}, in the range of 600–4000 cm^{-1}.

3. Results

3.1. Effects of pretreatment on the pine composition and structure

The composition of the pine wood before and after pretreatment with NaOH was analyzed and their carbohydrates and lignin contents are shown in Table 1. The untreated sample included 34.4% lignin and 62.2% carbohydrates in which the major portion (38.8%) of the carbohydrates was glucan. Alkali treatment for 10 min at high temperature significantly affected the amount of lignin and carbohydrates contents by removal of the acid insoluble lignin (AIL) and increasing the glucan content. The results also showed that the shorter time of treatment at high temperature, the greater effect of the treatment. For example, by increasing the retention time from 10 min to 60 min at 100 °C, the glucan content was decreased from 46.8% to 40.5% and the AIL was increased from 23.6% to 30.5%. However, it was contrariwise in the treatment at 0 °C, where increasing the retention time from 10 to 60 min resulted in increasing the glucan content from 39.2% to 42.1% and decreasing the AIL from 27.9% to 24.4%. In other words, treatment at low temperature had a greater impact in longer retention times