Available online at www.sciencedirect.com

SciVerse ScienceDirect

http://www.elsevier.com/locate/biombioe

Enhanced biogas production from rice straw, triticale straw and softwood spruce by NMMO pretreatment

Anna Teghammar [a,b,*], *Keikhosro Karimi* [a,c], *Ilona Sárvári Horváth* [a], *Mohammad J. Taherzadeh* [a]

[a] *School of Engineering, University of Borås, 501 90 Borås, Sweden*
[b] *Department of Chemical and Biological Engineering, Chalmers University of Technology, Göteborg, Sweden*
[c] *Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran*

ARTICLE INFO

Article history:
Received 26 February 2010
Received in revised form
10 October 2011
Accepted 19 October 2011
Available online 16 November 2011

Keywords:
Spruce
Rice straw
Triticale straw
Biogas
N-methylmorpholine-N-oxide
Pretreatment

ABSTRACT

Softwood spruce (chips and milled), rice straw and triticale (a hybrid of rye and wheat) straw, were pretreated with N-methylmorpholine-N-oxide (NMMO or NMO) prior to anaerobic digestion to produce biogas. The pretreatments were performed at 130 °C for 1–15 h, and the digestions continued for six weeks. The digestions of untreated chips (10 mm) and milled (<1 mm) spruce, rice straw and triticale straw resulted in 11, 66, 22 and 30 Nml CH_4/g raw material. However, the pretreatments have improved these methane yields by 400–1200%. The best digestion results of the pretreated chips and milled spruce, rice straw and triticale straw were 125, 245, 157 and 203 Nml CH_4/g raw material (or 202, 395, 328 and 362 Nml CH_4/g carbohydrates) respectively, which correspond to 49, 95, 79 and 87% of the theoretical yield of 415 Nml CH_4/g carbohydrates. Although the experiments were carried out for six weeks, one and a half weeks was enough to digest the materials.

1. Introduction

Biogas with methane as the major component is nowadays considered as a source of energy for heating and electricity production and as a car fuel in many countries in the world. It is produced from a wide variety of waste materials and energy crops, which can be degraded by microorganisms. The theoretical or stoichiometric production of methane in anaerobic digestion can be calculated according to [1]:

$$C_\alpha H_\beta O_\delta N_\gamma S_\varepsilon + y\,H_2O \rightarrow x\,CH_4 + \gamma\,NH_3 + \varepsilon\,H_2S + (\alpha - x)CO_2$$

in which $x = (4\alpha + \beta - 2\delta - 3\gamma - 2\varepsilon)/8$ and
$y = (4\alpha - \beta - 2\delta + 3\gamma + 2\varepsilon)/4$.

The theoretical methane production from starch, cellulose, fat and proteins can be calculated as 415, 415, 636 and 397 l/kg, respectively. However, the biodegradability of the substrate is a key factor in what percentage of the theoretical yield can be achieved. While starch is almost fully biodegradable, the lignocellulosic materials are more resistant to anaerobic digestion [2–4]. The lignin in these materials cannot be degraded by anaerobic bacteria, while most of the cellulose and hemicellulose is often left untreated after a typical 1- to 2-month digestion process [2–4]. This can be a major concern, since lignocellulose-rich materials such as wood residuals, paper waste and crop residuals are available in large amounts around the world. They are often used in less energy-efficient ways, being burned or land filled or even left on farmland.

* *Corresponding author*. School of Engineering, University of Borås, 501 90 Borås, Sweden. Tel.: +46 33 435 44 01; fax: +46 33 435 40 08.
E-mail address: anna.teghammar@hb.se (A. Teghammar).
0961-9534/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biombioe.2011.10.019

A potential solution to this problem is to introduce a pretreatment prior to the biogas production, in order to increase the biodegradability. The goal of a pretreatment is to open up the structure of the substrate, making it less crystalline and therefore more accessible for enzymatic attack. These structural changes will facilitate the adsorption of bacterial enzymes on the cellulose and the hemicellulose, which will further lead to higher production of biogas [5]. Different pretreatment methods have been developed to increase the degradability of lignocellulose-rich materials [2,5,6]. These methods can be divided into mechanical, thermal and chemical (i.e. alkali, acidic, oxidative) as well as biological pretreatments. However, many of these methods require high-energy input, such as mechanical and thermal pretreatments, or are economically non-profitable such as enzymatic treatments. Furthermore, the formation of toxic compounds and the consumption of chemicals in many chemical pretreatments make these methods less environmentally friendly [5,6].

Pretreatment with an organic solvent, N-methylmorpholine-N-oxide (NMMO or NMO), has recently been investigated for ethanol production from sugarcane bagasse [7], cotton [8,9] and softwood and hardwood [10]. NMMO can dissolve cellulose and efficiently decrease its crystallinity [11]. Moreover, NMMO is an environmentally friendly solvent which can be recovered by more than 98%, with no chemical derivatization and no production of toxic waste pollutants [12,13]. NMMO is today commercially used as an industrial solvent in the fiber-making industry known as the Lyocell process [12,14]. Furthermore, NMMO has shown a positive impact in biogas production from cotton [15]. No data were found in the literature on NMMO treatment of lignocellulosic materials to enhance the biogas production.

The purpose of this study was to investigate the effects of pretreatment with NMMO on lignocellulosic waste materials for biogas production. Three different materials were selected: spruce chips from the Swedish forests, rice straw from Indonesian fields, and triticale straw from Swedish farmland. The two straw samples were milled before the treatment whereas the spruce was studied in different particle sizes, both with and without milling.

2. Materials and methods

2.1. Raw materials

The spruce (*Picea abies*) was obtained from the forest around the city of Borås in Sweden. The wood was debarked and cut to 10 mm chips, or it was milled to achieve a particle size less than 1 mm. The straw from the triticale (*Triticale x Triticosecale*), a hybrid of rye and wheat, was obtained from farmland near Borås, whereas the rice straw (*Oryza sativa*) was obtained from rice fields in Yogyakarta (Indonesia). The straw samples were cut to sizes less than 10 mm long.

2.2. NMMO treatment

A commercial grade, 50% w/w NMMO solution obtained from BASF (Ludwigshafen, Germany) was used in all experiments. This solution was first concentrated to 85% by boiling under vacuum to evaporate the water, followed by supplementing 0.25 g/l propyl galate in order to avoid oxidation and degradation of the NMMO during the pretreatments [16]. The pretreatments were performed in 500 ml Erlenmeyer flasks containing 100 g of either 7.5% straw or 6% spruce in the NMMO solution and heated in an oil bath at 130 °C and atmospheric pressure for 1, 3 and 15 h, while mixing every 15 min. For the long pretreatment of 15 h, the materials were left overnight without mixing. After the pretreatments, 100 ml boiling water was added to each flask in order to stop the reaction. The pretreated materials were then filtered by vacuum filtering using Whatman filter paper (Grade 42) and washed with boiling water until no NMMO remained. The pretreated materials were then freeze-dried and stored in 4 °C until use.

2.3. Biogas production

Batch anaerobic digestion experiments were carried out at thermophilic conditions (55 °C) according to previous publications [17,18]. The inoculum was obtained from a 3000 m^3 municipal solid waste digester (Borås Energi och Miljö AB, Sweden). The reactors used in all setups were sealed serum glass bottles of 118 ml and all experimental setups were run in triplicate. Each flask contained 40 ml inoculum and 0.2–0.25 g substrate. The VS ratio was determined for each setup as two parts VS from the inoculum and one part from the substrate. The blank samples used contained the same amount of inoculum but water instead of the lignocellulosic substrate.

2.4. Analytical methods

Total solids, volatile solids and ash contents of the investigated materials were determined by drying to constant weight at 105 °C and 575 °C [19]. Cellulose, hemicellulose and lignin contents of the pretreated or untreated wood or straw species were determined according to NREL procedures [20]. In these methods, a two-step acid hydrolysis with concentrated and diluted sulfuric acid was performed to liberate the sugars from the cellulose and the hemicellulose. The formed sugars were then quantified by HPLC. The acid-soluble and acid-insoluble lignin contents were determined using UV spectroscopy at 205 nm and after drying the samples at 575 °C, respectively. All lignin and carbohydrate analyses were performed in duplicate.

The sugars were analyzed on HPLC (Waters 2695, Millipore, Milford, USA) equipped with a refractive index (RI) detector (Waters 2414) and an ion-exchange column (Aminex HPX-87P, Bio-Rad, USA) at 85 °C using ultra-pure water as eluent with a flow rate of 0.6 ml/min.

Methane and carbon dioxide content produced in the anaerobic digestion were analyzed as described earlier [18]. There were samplings two to three times a week during the first two weeks of the incubation periods, followed by once a week in the following weeks. For the gas analysis a gas chromatograph (Auto System Perkin Elmer, USA) equipped with a packed column (Perkin Elmer, 6' × 1,8"OD, 80/100, Mesh, USA) and a thermal conductivity detector (Perkin Elmer, USA) with the inject temperature of 150 °C was used. The