INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–12

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Production of bio-hydrogen and methane during semi-continuous digestion of maize silage in a two-stage system

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ARTICLE INFO

Article history:
Received 8 February 2016
Received in revised form
3 November 2016
Accepted 6 January 2017
Available online xxx

Keywords:
Dark fermentation
Two-stage process
Hydrogen
Methane
Co-production
Maize silage

ABSTRACT

The feasibility and performance of applying a two-stage configuration for co-production of hydrogen and methane from maize silage in continuously stirred reactors was investigated under mesophilic conditions. The high organic loading used in the first-stage hydrogen producing reactor (e.g. load shock treatment) was effective at ensuring hydrogen-producing conditions, with no methanogenic activity observed for more than 60 days. A hydrogen yield of up to 53.8 Nl_{H2}/kg volatile solid (VS) was measured in the first reactor, with a hydrogen content of 33.1%. The methane yield in the second stage reactor was 133.9 Nl_{CH4}/kgVS, with a methane content of 65%. Abnormally low concentration of acetic acid and high concentrations of caproic acid were measured in the first reactor in the pH range 5–5.5, which could be explained by the presence of strains such as *Clostridium kluyveri*. Of the estimated total energy yield in the two-stage system, only 4% was from hydrogen production. The mixture of hydrogen and methane produced in the system (after carbon dioxide removal) is in the range recommended for use as vehicle fuel.

Introduction

The European Union 'Framework Strategy for a Resilient Energy Union with a Forward-Looking Climate Change Policy' from February 2015 [1] calls for energy security and decarbonisation of the economy. Hydrogen (H_2) can play a key role to meet both these objectives. Indeed, the concept of H_2-based economy has been previously recognised as a cleaner and more sustainable alternative than the traditional fossil fuel based economies [2]. H_2 is a versatile energy carrier that can be used, for example, in internal combustion engines and in fuel cells for the production of electricity. Additionally, it has many industrial applications, such as the production of different chemicals, electronic devices or steel processing. Biologically produced H_2 (or bio-H_2), through dark fermentation, photo-fermentation, or biophotolysis, presents several advantages from a sustainability point of view. In particular, dark

Abbreviations: COD, Chemical oxygen demand; CSTR, Continuously stirred tank reactor; DMS, Dried maize silage; HAc, Acetic acid; HBu, Butyric acid; HCB, H_2-consuming bacteria; HPB, H_2 producing bacteria; HPr, Propionic acid; HPR, Hydrogen production rate; HRT, Hydraulic retention time; HVa, Valeric acid; LHV, Lower heating values; LST, Load shock treatment; MPR, Methane production rate; MSW, Municipal solid waste; n-HCa, n-caproic acid; OLR, Organic loading rate; SHP, Specific hydrogen production; SMP, Specific methane production; TIC, Total inorganic carbon; TS, Total solids; TVFA, Total volatile fatty acids; VFAs, Volatile fatty acids; VS, Volatile solids.

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http://dx.doi.org/10.1016/j.ijhydene.2017.01.020
0360-3199/

fermentation not only results in the production of H_2 (with higher rates than the other bio-H_2 producing technologies) but also can contribute to reduce wastes (e.g. municipal solid waste (MSW), slurries and manures, crops and landscape residues, etc.), requires considerably lower energy inputs, can be produced in decentralised installations, and can make use of local resources [3–7].

H_2 is a by-product of the acidogenic phase during the anaerobic digestion of organic substrates, usually detected in the biogas in small amounts (<0.2%) as it is consumed immediately by the H_2-consuming bacteria (HCB). H_2 production has been shown to be possible from a wide variety of feedstocks by using pure cultures and mixed cultures after inactivating HCB, such as homoacetogens and hydrogenotrophic methanogens. Indeed, a number of studies have investigated the production of H_2 from different soluble substrates, mainly simple sugars such as glucose and sucrose (e.g. Refs. [8–11]) and different types of wastewaters (for example from rice winery [12], palm oil mill effluent [13] or food processing [14]), and to a lesser extent, from different solid substrates, particularly food wastes (e.g. Refs. [15–18]). Reported production rates and yields for different substrates are tabulated in recent reviews [19,20]. In spite of its abundance and high content in carbohydrates, studies analysing the suitability of lignocellulosic material (i.e. plant biomass with high content of cellulose, hemicellulose and lignin) for H_2 production are still scarce. These addressed substrates such as corn straw [21], cornstalk [22], rice straw [23], and grass silage [24]. One of the main drawbacks of using lignocellulosic material is the need of treatment for delignification to speed up its degradation.

There is a number of studies analysing the factors influencing the production of H_2 during dark fermentation, including the pH, the hydraulic retention time (HRT), the temperature, the inoculum characteristics, the trace elements availability or the organic loading rate (OLR). The effects of these factors have been previously reviewed extensively [3,7,19,20,25,26]. As regards the inoculum, using mixed cultures in the digester has some advantages including easier operation and control as well as the possibility of digesting larger variety of feedstocks [17]. Different methods are possible to suppress the activity of HCB, including heat shock, acid and base treatment, aeration, freezing, and application of chloroform, sodium 2-bromoethanesulfonate or 2-bromoethanesulfonic acid, and gas sparging of the fermenter [26,27]. Some studies have investigated different methods [28–30], but there is still disagreement about the optimal method for enrichment from a H_2 production point of view, but also in terms of the energetic and economic feasibility. While the heat-shock treatment is the most widely applied method [26,31], it requires an energy input and it might inhibit the activity of some H_2-producing bacteria [28]. The so-called load shock treatment (LST), which consist on increasing the organic loading until generating acidic conditions in the reactor, has been previously suggested [24,30] as it results in a higher microbial diversity, useful for the digestion of complex substrates, and minimises the input of chemicals into the system. On the other hand, this method has been scarcely applied (only suited for semi-continuous and continuous feeding conditions) in comparison with other treatments, and thus lacks sufficient evidence of its effectiveness, particularly for long term operation [27].

Finally, two-stage anaerobic systems, with sequential dark fermentation and methanogenic reactors, can be particularly interesting from an energetic and substrate degradability point of view with the production of both H_2 and methane (CH_4). Indeed, the separation of the acidogenesis and methanogenesis phases can contribute to better meet the pH and environmental requirements of the bacterial groups involved [32,33], which enhances digestion performance. Such configuration has been tested and proven feasible for a variety of feedstocks, including sugar-rich substrates such as molasses [34], cassava stillage (and excess sludge) [35], olive pulp [36], and more extensively, food industry and municipal waste [18,37–41]. As explained earlier, and given its recalcitrance, lignocellulosic material poses some challenges and usually requires treatment. Up to now, only few studies have analysed the use of this type of material for two-stage systems, including for sweet sorghum [42], grass silage [43], maize [44–47], and cornstalk [48]). Maize is a complex lignocellulosic substrate largely used in biogas plants in central Europe. The few studies investigating long term system performance for the two stage process using this popular substrate for the co-production of H_2 and CH_4, apply most commonly percolation systems (leach-bed reactors) in the hydrogen-producing reactor [44,46,47]. Yet, most full-scale digesters of energy crops present stirred systems.

The current research aims at investigating the performance, stability dynamics, and energy yield of a two-stage system co-producing H_2 and CH_4 using maize silage (whole plant) under semi-continuous feeding conditions in continuously stirred tank reactor (CSTR). Additionally, the efficiency of the LST method is analysed.

Materials and methods

Inoculum

During the start-up of the hydrogenic reactor (R1), the LST method was applied to enrich the inoculum with H_2 producing bacteria (HPB) and inactivate HCB. Dried maize silage (DMS) was semi-continuously fed in a CSTR at an increasing loading rate, from 2 up to 10 g volatile solids (VS)/l/d, with addition of buffering capacity and trace elements solution for 125 days under mesophilic conditions. This period allowed analysing in detail the response of the system to increasing loadings in terms of performance and stability. The main results are described in detail elsewhere [49]. At the highest loading, the total volatile fatty acids (TVFA) concentration amounted to 5.9 g chemical oxygen demand (COD)/l (i.e. acidification). When the daily addition of buffering capacity was removed in day 125th, the pH rapidly dropped to a value close to 5. Given the methanogens requirements in terms of the pH (above a pH of 6.8), this change triggered a quick shift into the production of H_2 in the reactor, and the washout of the HCB. The inoculum used in the methanogenic reactor (second-stage reactor) was obtained from Beckerich agricultural biogas plant in Luxembourg, from the post-digesters storage tanks. This plant uses animal manure and a mix of grass and maize silages and

Please cite this article in press as: Benito Martin PC, et al., Production of bio-hydrogen and methane during semi-continuous digestion of maize silage in a two-stage system, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.01.020