Energy Conversion and Management 108 (2016) 202–209

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Pretreatment of macroalgal biomass for biogas production

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ARTICLE INFO

Article history:
Received 13 August 2015
Accepted 4 November 2015

Keywords:
Macroalgae
Laminaria spp.
Pretreatment
Methane

ABSTRACT

The objective of this study was to evaluate the effect of beating (BT), ball milling (BM) and microwave pretreatment (MW) on the conversion of the macroalgae *Laminaria* spp. into biogas by anaerobic digestion (AD). The AD was carried out in batch at 38 ± 1 °C, over an incubation time of 25 days. After 3 days of digestion the BT pretreated samples yielded the best result by achieving a methane increase of up to 37% with respect to the raw seaweed. At 25 days, both BM and MW pretreatment lowered the methane yield with respect to the raw seaweed. Since BT produced higher methane yields with respect to the untreated sample, it was considered for energy balance analysis. After 3 days of digestion, the BT resulted in an energy gain of 28%, while at the end of digestion the break-even point was reached.

1. Introduction

Under the EU Directive 2009/28/EC, Ireland has been set a legally binding target of 16% renewable energy of its total energy consumption by 2020 [1]. In the National Renewable Energy Action Plan, Ireland has set out to achieve the 16% overall target through 10% renewable energy supply in transport (RES-T) by 2020, 12% in the heat sector, and 40% in the electricity sector. Biomethane as transport fuel has been addressed as a possible solution in order to achieve and even surpass the 10% RES-T target [2–4]. This gas can be obtained through the upgrading of biogas produced by AD [5]. Other gases such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) are removed and as a result the methane (CH_4) content can be raised to ca 97%. Biomethane can then be introduced into the gas grid or used as a transport fuel [6]. In other European countries such as Germany, Sweden, and Switzerland, it has been proven that a more efficient use of biogas can be achieved through upgrading biogas to biomethane [6,7]. Biogas is commonly used to power Combined Heat and Power (CHP) systems to generate heat and electricity [8]. Electricity from biogas can also be produced by using solide oxide fuel cell (SOFC). Unlike traditional fuel cells, these systems are able to use biogas directly, without prior reformation of the gas for hydrogen production [9,10]. Macroalgae, commonly known as seaweed, are considered a potential feedstock for biomethane production with a biochemical methane potential evaluated between 0.39 and 0.41 NL g^{-1} of volatile solids (VS) [11]. This marine biomass shows the prospect of high yields without requiring the use of arable land [12]. In terms of carbon capture during photosynthesis, macroalgal primary productivity rates are much higher than the global net primary productivity of crop land [13]. A negligible or low amount of lignin makes them less resistant to degradation than lignocellulosic feedstocks, and avoids the need for energy-intensive pretreatments before fermentation [14]. Among macroalgae, the *Laminaria* spp. and *Ulva* spp. are most recommended for the production of biogas. In Ireland, it is possible to find five kelp species such as *Laminaria digitata*, *Laminaria hyperborea*, *Saccharina latissima*, *Sacchorhiza polyschides* and *Alaria esculenta*. Several reports have evaluated the feasibility of such application [15–17]. They concluded that the conversion of marine biomass to methane is feasible; however some obstacles need to be overcome. Efficient cultivation, harvesting, and conversion technologies are prerogatives in order to exploit the full potential of macroalgae. In some recent reviews [18,19] the need has emerged for the pursuance of algal biomass application for biogas production, with a focus on pretreatment technologies and conditioning of algal biomass. Since the hydrolysis is considered the rate limiting step of the AD process [20], several studies demonstrated that pretreatment can enhance the hydrolysis rate by increasing the final methane yield and speed up biogas production [20–24]. It is worth noting that a pretreatment method must be simple and the products must be highly fermentable [25,26], thus most studies investigated the use of physical pretreatments mainly because of their simplicity. Maceration pretreatment gave good results when applied to *Ulva lactuca* [21,22]. The authors recorded a methane yield of 68% more when compared to untreated biomass, with a final yield of 255 Nml CH_4 g^{-1}VS. On the contrary, maceration did not have a positive effect on

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http://dx.doi.org/10.1016/j.enconman.2015.11.008
0196-8904/

S. latissima, which showed a lower methane yield than the untreated samples [22]. Studies by Otsuka and Yoshino [24] showed an improvement of methane yield after washing and grinding of harvested sea lettuce biomass. A beating pretreatment was used to treat *Laminaria* spp. by Tedesco et al. [27]. The pretreated sample produced 425 Nml CH_4 g^{-1} of Total Solids (TS), which corresponded to 53% more methane with respect to raw seaweed. Steam explosion showed positive results on *S. latissima* [23], enhancing the methane yield up to 20%. However, the authors concluded that despite the methane yield improvement, the effects were not significant enough to justify such a harsh pretreatment.

While the benefits of the pretreatment have been largely recognized, the literature lacks data regarding the energy balance of such treatments, a crucial factor for the economics and sustainability of the process [28,29]. Besides, few studies investigated the effect of different pretreatments on macroalgae considering similar AD conditions [19]. As far as author's knowledge, there is no previous study which compared the methane yields resulting from AD of *Laminaria* spp. when BT, BM and MW pretreatment are used respectively.

Thus, the objective of this investigation is to evaluate the effect of three physical pretreatments; beating (BT), ball milling (BM) and microwave (MW) on the methane yields of the Irish macroalgae *Laminaria* spp. at pre-selected digestion parameters. Also, an energy balance study was carried out based on the energy consumption of the pretreatments.

2. Materials and methods

2.1. Substrate and inoculum

Laminaria spp. was collected on shore in Howth (Dublin, Ireland) in early November, 2013 in order to reproduce the case of harvesting readily biomass available on the beach. There was no selection of a particular Laminaria species. In the mixture harvested from the beach, three main species were identified, namely *L. digitata*, *S. latissima,* and *L. hyperborea*. The TS content was found at 19.0 ± 2.2% Wt on wet basis, while the VS content was at 84.1 ± 0.3% Wt on dry basis. Before pretreatment, fresh seaweed was roughly cut and immediately used without washing.

On the same day, treated and untreated seaweed were inoculated and subject to anaerobic conditions. The used inoculum was sewage sludge from a wastewater treatment plant (Celtic Anglian Water Ltd., Ringsend, Dublin) operating at mesophilic condition. The TS content of the inoculum was found equal to 3.6 ± 0.5% Wt on wet basis, while the VS content was equal to 79.5 ± 4.0% Wt on dry basis. The pH was measured equal to 8.0 ± 0.1. Once collected from the plant, the inoculum was immediately used and not allowed to degasify in order to reproduce the operating conditions of a co-digestion system for further studies. Hence, sludge only reactors in duplicate were also incubated in order to estimate the biogas production of the inoculum which was then subtracted from the seaweed-sludge yields.

2.2. TS and VS analysis

The TS fraction was determined by drying the seaweed at 105 °C to constant weight. VS amount was determined by igniting a known weight of dried sample at 575 ± 25 °C to constant weight, according to standard methods (NREL/MRI LAP 1994, 2008) [30,31]. Both TS and VS analysis were carried out in triplicate.

2.3. Batch experiments

The bioreactors consisted of borosilicate glass flasks of 500 ml in capacity. Each bioreactor was filled with a solution of 200 ml of tap water at 5% TS concentration of treated seaweed for each pretreatment. Then 200 ml of inoculum was added for a total working volume of 400 ml. These were performed in duplicate. The untreated seaweed sample was composed of a similar solution (200 ml of tap water at 5% TS concentration of untreated seaweed and 200 ml of inoculum). These were performed in duplicate. The reactors were prepared with 8 g of VS of seaweed and 6 g of VS of sewage sludge. After inoculum addition, the pH for each sample was measured by using a Hanna precision pH meter, model pH 213. Table 4 reports the pH values detected before digestion. They were found to be between 7 and 7.6; no adjustment of pH was applied. The reactors were then sealed with borosilicate glass adapters equipped with controlled gas opening valves. Each reactor was connected to an airtight Linde plastigas bag, where the biogas produced during all the incubation time was collected. The whole system was purged with nitrogen flow for 5 min in order to achieve anaerobic conditions. Water baths were used to incubate the reactors at an operating mesophilic temperature of 38 ± 1 °C. During incubation, the bioreactors were shaken manually once a day. The incubation time was set at 25 days. Biogas collections for analysis were performed at 3, 13, and 25 days after the start of incubation. The biogas volume was measured by using gas sampling tubes which were installed in a gas jar with confining liquid according to procedure VDI 4630 [32]. The entire experiment set-up is represented in Fig. 1. A biogas analyser, model Drager X-am 7000, was used to verify that the system was anaerobically isolated, and to measure the percentage of CH_4 in the biogas.

2.4. Pretreatment methods

2.4.1. Beating (BT)

The equipment used for the BT pretreatment was a Hollander beater, model Reina. This kind of machine is originally built for the pulp and paper industry. It is equipped with a crank handle which allows adjustment of the gap between the drum's blades and the bed-plate. The minimum gap achievable is 76 μm, which corresponds to one single turn of the crank handle. The machine performs two main actions; a – cutting action caused by the grooves located on the bed-plate, and a – high pressure beating action of the feedstock against an inclined plate placed at the exit-out of the drum. The drum of the machine permits a constant rotational speed of 580 rpm. Even though, the machine is able to operate both wet and dry biomass, it was necessary to add water in order to allow the recirculation of the feedstock. The amount of water was chosen in order to obtain a final solution of 5% of TS of seaweed biomass.

The result was a pulp of different consistencies according to the gap and the processing time applied. In this experiment, the minimum gap was 76 μm with a processing time of 10 min, according to a previous optimisation [27]. The BT experiment was performed in duplicate.

2.4.2. Ball milling (BM)

Due to the consistency of the seaweed, a ball milling of fresh seaweed was not possible to perform. Thus, the seaweed was previously dried for 24 h at 80 °C and then milled in a conventional ball milling for a period of 18 h in a ceramic cylinder (130 mm height, 140 mm diameter) with 20 aluminia balls (15 mm diameter). The resulting powder was sieved in order to obtain two different particle sizes of 1 mm and 2 mm respectively. Tap water was added in order to obtain a final solution of 5% TS for each particle size. The BM experiments were performed in duplicate.

2.4.3. Microwave (MW)

Roughly cut seaweed together with tap water was subject to microwave pretreatment. The pretreatment was performed in