Energy Conversion and Management 174 (2018) 855–862

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Biomethane production from various segments of brown seaweed

Muhammad Rizwan Tabassum[a,d], Ao Xia[c,*], Jerry D. Murphy[a,b]

[a] MaREI Centre, Environmental Research Institute, University College Cork, Cork, Ireland
[b] School of Engineering, University College Cork, Cork, Ireland
[c] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, China
[d] Punjab Bioenergy Institute, University of Agriculture, Faisalabad 38000, Pakistan

ARTICLE INFO

Keywords:
Anaerobic digestion
Biomethane
Algae
Brown seaweed
Morphological impact

ABSTRACT

Brown seaweed may be an option as a feedstock for gaseous biofuel production. This paper proposed a detailed study on the impacts of various segments of seaweed thalli on the biomethane production. *Ascophyllum nodosum*, *Laminaria digitata*, *Laminaria hyperborea*, *Saccharina latissima* and *Saccorhiza polyschides* have shown significant variation in proximate, ultimate and biochemical composition in various segments of their thalli. The highest biomethane potential of 286 L CH_4 kg VS^{-1} was recorded from the stipe of *L. digitata*, whereas the lowest value of 118 L CH_4 kg VS^{-1} was obtained from the holdfast of *L. hyperborean*. Due to the accumulated salt in the holdfast, the biomethane performance was reduced compared with the frond and stipe. The specific yield per fresh weight of seaweed was measured in the range of 10 to 32 m^3 CH_4 t_{wwt}^{-1}. Considering the dominant role of fresh thallus, the frond was the most significant part for seaweed biogas production.

1. Introduction

Gaseous biofuel production via anaerobic digestion (AD) of seaweed is suggested as a sustainable source of renewable sustainable advanced transport biofuel [1,2]. Seaweed can be an attractive candidate as a feedstock for sustainable bioenergy systems [3,4] due to higher growth rates than land-based energy crops [5–7]. Moreover, lack of lignin in seaweeds makes the AD process more efficient [8,9]. However, the potential of such a fuel is still under investigation and has not yet been fully realised [10]. Ireland has a great potential due to a significant coastline with a temperate oceanic climate, which allows access to a large amount of seaweed resources, either from nature (present annual production of Irish seaweeds is 30,000 tons wet weight) or from mass cultivation. Development of a seaweed-based gaseous biofuel industry may allow for the production of third generation biofuel to comply with European Directives and decarbonisation of transport fuel [11]. Irish brown seaweeds such as *Ascophyllum nodosum, Laminaria digitata*, *Laminaria hyperborea, Saccharina latissima and Saccorhiza polyschides* are an important marine bioresource and are under investigation as a feedstock for biomethane production.

The body of the seaweed “plant” may be expressed as “thallus”, as it is not differentiated into true roots, stem and leaves. These parts can be classified into holdfast, stipe and frond, respectively. Brown seaweed has shown significant morphological variation in these parts which form the thallus [12]. The compositional variety in the biochemistry of various segments of the thallus may be expressed in dry solids, ash and organic contents [13]. For example, the holdfast of the seaweed was shown to contain higher salts (ash) but less organic content as compared to the stipe and frond [14]. This would greatly affect biomethane production as a high ash content can significantly reduce the performance of the AD process as stated in various studies [2,15,16]. Salt concentration (ash) can be tolerated by using acclimatized consortium of microorganisms [17] well adapted to high salt concentration [18]. Comparative studies on anaerobic digestion of different seaweed species revealed that salt concentration has a significant role on the biomethane production [1,2,19].

Variation in temperature, nutrients, sunlight, water current and flow (due to different geographical locations) generate different growth environments, which results in a significant variety in composition and in morphology of brown seaweed [1,19,20]. This difference may alter the biomethane potential as well as the AD performance when digesting seaweed. Brown seaweed has been previously reported as a potential feedstock for biomethane production [15,16,21–24]; however, significance in biochemical variation of various segments of the thallus (frond, stipe and holdfast) of the seaweeds has not yet been investigated. This is crucial in determining the exact energy yield from seaweed biomethane and the relationship to harvest methods. Crude harvest methods may include for removal of all seaweed including

* Corresponding author at: Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, China.
E-mail address: aoxia@cqu.edu.cn (A. Xia).

https://doi.org/10.1016/j.enconman.2018.08.084
Received 25 April 2018; Received in revised form 29 July 2018; Accepted 22 August 2018

holdfast, while more sustainable practices may leave the holdall in place for regrowth in following years. The innovation in this paper is in assessing the morphological variation in composition of each fragment of the thallus and in biomethane production using Irish brown seaweeds. The objectives of this paper are to: assess the variation in biomethane production for different segments of seaweed; perform kinetic analysis to study the biodegradability of each seaweed segment; identify the optimal seaweed part for biogas production; and calculate the specific methane yield of each fragment with reference to the whole thallus. This kind of study has not to the best of the authors' knowledge been reported in the literature before.

2. Materials and methods

2.1. Sample collection, processing and analysis

Samples of *A. nodosum, L. digitata, L. hyperborea, S. latissima and S. polyschides* were collected from their natural marine environment in the Roaring Water Bay, Co. Cork, in the south of Ireland (51°N, −9°E) in March 2015. All samples were washed with tap water to remove foreign particles. The weight and length of the whole thallus of all species was measured before cutting into individual fragments (such as frond, stipe and holdfast) as shown in Fig. 1. After cutting into fragments, all segments were measured and weighed again. The individual samples were macerated in a Buffalo macerator to a particle size of 4 mm and subsequently packed in transparent plastic bags. Packed samples were stored at −20 °C prior to analysis and biomethane potential (BMP) assessment. The contents of moisture, total solid (TS), volatile solid (VS) and ash were determined by using the standard method of drying of seaweed for 24 h at 105 °C and subsequently burning for two hours at 550 °C [23,25].

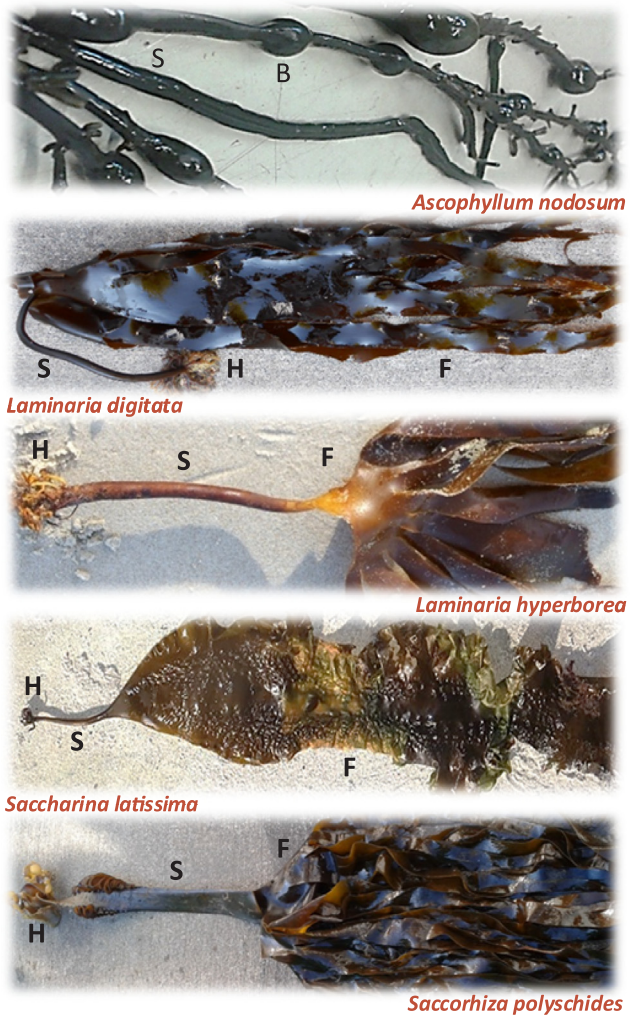

Fig. 1. Morphological difference in the thallus of various Irish brown seaweeds. F: frond; B: bladder; S: stipe; H: holdfast.

Macerated samples were dried at 105 °C for 24 h and then were grinded to pass through a 500 μm sieve for ultimate analysis. Samples were analysed for the mass ratio of C, H, N, and O (O calculated by difference) on an ash free basis using a CE 440 elemental analyser. The polyphenol content of each segment of the seaweed thallus was measured by a modified Folin Ciocalteu assay described in a previous study [26]. The protein content was calculated based on the data from ultimate analysis. The total protein content in the seaweed sample was evaluated by multiplication of the nitrogen content by 5.38 [27]. The experiments were carried out in triplicate, and the results were expressed as the mean values and standard deviations.

2.2. Inoculum collection and processing

The inoculum was collected from lab-scale continuous stirred-tank reactors (operated at 37 °C), which processed a mixture of different substrates including dairy slurry, grass silage and seaweed. Firstly, the inoculum was degassed by treating in a CSTR at the same experimental conditions (to avoid VS influence of any leftover mixed substrates) and afterwards it was sieved through a 2 mm sieve to remove any larger particles. Before batch digestion experiments, the inoculum was characterized for proximate analysis. The processed inoculum was stored at 4 °C for further use.

2.3. Biomethane yields

The theoretical yield was calculated by using the data obtained from ultimate analysis with the use of the Buswell equation (Eq. (1)). The output yields a maximum potential methane yield by conversion of the organic materials to methane and carbon dioxide [28]. The molar volume of the gases was taken as 22.14 L at 0 °C and 1 atm.

$$C_nH_aO_b + \left(n-\frac{a}{4}-\frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)CH_4 + \left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}\right)CO_2 \quad (1)$$

A computer aided automatic methane potential test system (Bioprocess AMPTS II® system) was used to determine the BMP of seaweeds. The Bioprocess AMPTS II® system consists of fifteen glass bottles, each of them serve as the batch reactor. The system has the capacity to lodge five specimens at a time in triplicate. In each experiment of batch digestion, three samples of brown seaweed, one of inoculum and one of cellulose were assessed in triplicate. The initial substrate to inoculum ratio (S:I) on a VS basis, of 1:2 was used [21]. Each bottle had a working volume of 400 mL with a head space of 250 mL. All the vessels were filled with calculated amounts of inoculum and substrate. Nitrogen gas was flushed through each bottle to create anaerobic conditions. Each reactor was maintained at 37 °C in a water bath and continuously stirred at a speed of 45 rpm by fixing an alternating time for on and off every 60 s. The produced gas was purified by 3 M NaOH solution to remove CO_2, H_2S and other impurities, and subsequently the volume was measured by a gas tipping device. The data was recorded every 15 min. To determine the specific biomethane production, biomethane produced from the inoculum was subtracted from biomethane produced by each sample. Salinity (g/L) was measured by a salinometer before and after each BMP assay to obtain the value of salinity increase (%) to evaluate the effect of biochemical composition of each segment of the thallus on the reaction performance and biomethane yield. The pH values were measured by a pH meter before and after each BMP assay.