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Influence of variable feeding on mesophilic and thermophilic co-digestion of *Laminaria digitata* and cattle manure

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ABSTRACT

In this study the effect of various feeding ratios on mesophilic (~35 °C) and thermophilic (~50 °C) co-digestion of brown algae *Laminaria digitata* and cattle manure was investigated. Algae input of 15% VS caused no influence on specific methane yield from mesophilic co-digester while deteriorated the process parameters such as the development of propionic acid in total volatile fatty acids (tVFA) pattern of the thermophilic co-digester. The accumulation of tVFA continued for the latter reactor as the feeding ratio of algae enhanced to 24% VS, but the specific methane yield improved dramatically. Same rise in feeding once again showed no improvement in specific methane yield from mesophilic co-digester even though the other process parameters stabilized or, enriched such as the gain in average volumetric methane yield. For the last feeding ratio at 41% VS algae, specific methane yield from mesophilic co-digester slightly increased which however was not still comparable with the ultimate methane yield from the cattle manure alone. The thermophilic co-digestion on the other hand yielded maximum specific methane, together with the improvement in different process characteristics, as the feeding of algae maximized at the final stage. The trend of methane production from this reactor nevertheless was sharply downward towards the end of the experiment suggesting that the optimum feeding ratio has already been achieved for the present experimental conditions.

1. Introduction

The ever increasing population, continuous depletion of fossil fuels and the pressing environmental issues are the prime indicators of the predicament present energy scenario [1]. Driving various sources including with the mushrooming renewables are thus critical to combat much of the challenges associated with energy and environment where the role of biomass is predicted to be significant [2]. The biomass based energy policy is already evident elsewhere, such as the one by the European Union (EU), targeting 10% share of biofuel in the total energy consumption by the year 2020 [3]. Strong awareness and stimulation of sustainable biomass are the keys to efficiently achieve this target where algae has enormous potential. The contexts in which algae has much more promises over its complementary terrestrial biomass include: growth rate, chemical composition, competition with agricultural land, impact on water, CO_2 uptake, etc. [4–6]. Furthermore, in the recent concept of bio-refinery addition of algae is a revolution [7].

Anaerobic digestion (AD) has been a popular approach for the last few decades, successfully converting range of biomass into useful products. Including with the production of biogas – a renewable fuel, the digestate from AD is a valuable source of fertilizing agricultural lands [8]. Among the various possible biomass, algae can be a promising alternative for AD owing to its attractive chemical composition and high conversion efficiencies [9]. A large amount of researches dedicated to evaluate the methane potential from several algae that include but not limited to are: *Macrocystis, Hypnea, Ulva, Laminaria, Sargassum, Gracilaria*, microalgal strains, etc. [10–13]. Those studies showed average specific methane yield from various macroalgae to lie within the range of 150–410 L/kg VS [14], intriguing special interest to the commercial biogas plants. However, the anaerobic digestion of algae alone was concluded to be problematic due to its low C/N ratio leading to the unexpected generation of total ammonia nitrogen (TAN) and ultimately to methane inhibition [15]. Co-digestion of algae with animal manure such as with the cattle manure was suggested to provide solution by reducing problems in regard of low C/N ratio, tVFA accumulation, TAN, low buffering, etc. [14]. In fact, a great deal of innovative researches reported that co-digestion can drastically improve methane yield as compared to algae digestion alone with

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a gain of over 45% in case of co-fermentation of green algae (*Ulva lactuca*) and CM [16]. Extended researches [14,16] also mentioned the financial advantages of co-digestion to overcome few long-lasting issues of the livestock industries in Denmark. Algae co-digestion hence is ever growing and welcoming in the field of renewable energy.

Marine biomass consists more than half of the primary biomass resources in the world [17] and as a part of this lion's share, *Laminaria digitata* is ubiquitous in Danish coastal areas, growing at a rapid pace every year. *L. digitata* is an attractive feedstock for hydrocolloid industries [18] and one of the largest aquaculture resources worldwide [19]. For AD and further to produce biogas, this brown macroalgae may be a suitable feedstock due to its rich carbohydrate content [20]. However, its direct application for AD alone may result the increase in TAN and other operational problems, as cited by the similar study [15] before. Present study hence focuses on co-digestion and proposes cattle manure (CM) as the co-substrate for AD with *L. digitata*. The potential of methane yield from *L. digitata* has already been investigated for various temperature treatments [21]. Additionally, the co-digestion with cattle manure was also successfully tested [14]. Moreover, an outstanding research [17] evaluated the methane yield and biofuel potential of *L. digitata* as an effect of seasonal variation in algae composition. Bearing all these studies into consideration, effort nevertheless still remains to be paid for the semi-continuous co-digestion of *L. digitata* with CM for which the present work is entirely devoted. Determining the influence of several feeding proportions on methane boosting and relevant process parameters were the other aspects of this study investigated at moderate operational periods for two temperature treatments (mesophilic and thermophilic).

2. Materials and methods

2.1. Inoculum

This study utilized both mesophilic and thermophilic inoculum. The effluent from the biogas plant Foulum, Denmark was used as thermophilic inoculum. The plant operates with a thermophilic digester maintaining temperature at 50 ± 1 °C. The measured total solid (TS) and volatile solid (VS) of thermophilic inoculum were 2.83 ± 0.5% and 1.43 ± 0.5% respectively, whereas the approximate pH value and total ammonium nitrogen (TAN) were found as 8.12 ± 0.05 and 1.82 ± 0.5 g/L respectively. The mesophilic inoculum, on the other hand, was collected from the Bårnlev biogas plant, Aarhus, Denmark, that works at 35 ± 2 °C with an average TS, VS, pH and total ammonia content of 4.4 ± 0.5%, 3.9 ± 0.7%, 8.15 ± 0.04 and 3.8 ± 0.3 g/L respectively.

2.2. Substrates

2.2.1. Dairy cattle manure

Cattle manure was derived from 54 Holstein cows fed with 55% dry matter of forage for one week. Upon receipt, cattle manure was stored in vicinity to the experimental facilities in slurry tanks each with 1 m^3 of volume, exposed to the variable ambient temperature of 15 ± 2 °C throughout the experimental period. The TS, VS and pH of the cattle manure was measured as 6.8 ± 0.9%, 5.6 ± 0.6% and 6.8 ± 0.5% respectively.

2.2.2. L. digitata

L. digitata was collected by divers from natural populations (Fornæs, Denmark). After harvesting, algae was packed in plastic bags, brought to the laboratory and preserved in freeze at −18 °C. Before utilizing for experiment, the algae was further pre-treated by washing with tap water and macerating for about 30 min with kitchen scissors to fragments of an approximate size of 10 × 10 mm. Maceration and washing prior to fermentation facilitate AD and is believed to increase the specific methane yield in the range between 180 and 271 kg/VS, as cited by [22].

2.3. Analytical methods

To perform chemical analysis, samples were collected twice in a week. Total solids (TS) were evaluated after oven-drying the samples at 105 ± 2 °C for 24 h. Dried samples were then placed into a muffle furnace at 550 ± 2 °C for approximately 5 h to convert into ashes. Volatile solid (VS) was calculated by subtracting the amount of ashes from the amount of TS, as described by the Ref. [23]. Total volatile fatty acid was determined by acidifying 1 mL of sample with 4 mL of pivalic acid and subsequently centrifuged for 20 min at 12,000 rpm. The centrifuged samples were then filtered to prepare for GC (Gas Chromatograph-Hewlett Packard 6850A) which analyzed the tVFA by using its column, flame ionization detector and career gas. The dimension of the GC column was 30 m × 0.25 mm × 0.25 μm for which Helium (He) was used as career gas. The temperature of the column was gradually increased from 110 °C to 220 °C with a rate of 10 °C/min. pH of the sample was determined by using a glass pH probe (Knick Portamess, 911 pH, Germany) whereas Total Ammonia Nitrogen (TAN) was analyzed calorimetrically at 690® nm with Merck spectrophotometer (NOVA 60). The produced biogas from each reactor was measured by using the online gas measurement system that was composed with a water bath (41 × 26 × 25 cm dimension and 27 L capacity) and data acquisition system. At the bottom of the water bath there are set of devices producing pulses each time biogas is generated. There are interconnections between the tested reactors, pulse generators and the data acquisition system through silicon tubes, allowing the generated pulses from the reactors to calibrate into the amount of corresponding biogas and further to data analysis. Gas samples were analyzed both for CO_2 and CH_4 content using another Gas Chromatograph Perkin Elmer Clarus 500 equipped with a Thermal Conductivity Detector and a Turbo matrix 16 Headspace auto sampler as described by Møller et al. [24]. Methane and carbon dioxide was isolated by a 12′ × 1/8″ Haysep Q 80/100 Column. The temperatures of the injection port, oven and detector were 110, 40 and 150 °C respectively. Helium (He) was used as a carrier gas with a flow rate of 30 mL/min. H_2S concentration in biogas was calorimetrically measured by using precision gas detector tubes (Kogyo K.,K., Kitagawa, Japan) [25]. The color of the reagent inside the detector tubes turns from pink to yellow along the tube the length of which is corresponded with the concentration of H_2S.

In order to evaluate the level of C/N ratio, the effluent from co-digestion was analyzed on an elemental analyser (Rob prep C/N, Europa Scientific Ltd., UK) coupled with a triple collector isotopic ratio mass spectrometer (Tracemass, Europa Scientific Ltd., UK), as described by [26,27].

2.4. Experimental setup of mesophilic semi-continuous reactors

Reference reactor R_1 and test reactor R_2, containing an identical capacity of 5 L, were used for this experiment. The working volume of both of these reactors was 3.2 L which was designed to operate for a hydraulic retention time (HRT) of about 22 days. The reactors were placed in a mesophilic incubator, maintaining temperature at 35 ± 2 °C. Stirring of the reactors was given semi-continuously by a metal stick connected with an electric motor (Zheng, China, 12 V) mounted on the top of the reactor lid. The frequency of the stirring was counted as 5 min in every 45 min, provided by the motor spinning at 60 rpm.