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Energy-efficient methane production from macroalgal biomass through chemo disperser liquefaction

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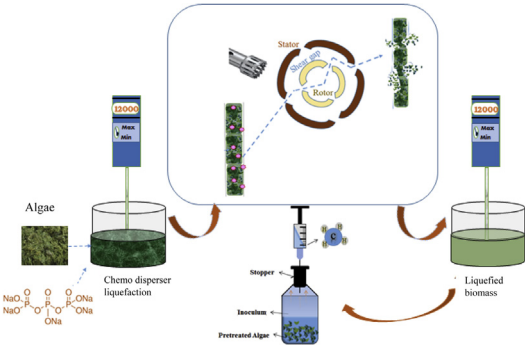
HIGHLIGHTS

- Chemo disperser liquefaction boost up disintegration synergistically.
- This modernistic method induces solubilization at DSE of 3312.6 kJ/kg TS.
- Kinetic study represents rapid disintegration rate by this incentive process.
- Chemo disperser liquefaction archived a higher biodegradability (0.14 g COD/g COD).
- Net profit of about 4 USD/per ton of algae biomass was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an effort has been made to reduce the energy cost of liquefaction by coupling a mechanical disperser with a chemical (sodium tripolyphosphate). In terms of the cost and specific energy demand of liquefaction, the algal biomass disintegrated at 12,000 rpm for 30 min, and an STPP dosage of about 0.04 g/g COD was chosen as an optimal parameter. Chemo disperser liquefaction (CDL) was found to be energetically and economically sustainable in terms of liquefaction, methane production, and net profit (15%, 0.14 g COD/g COD, and 4 USD/Ton of algal biomass) and preferable to disperser liquefaction (DL) (10%, 0.11 g COD/g COD, and -475 USD/Ton of algal biomass).

1. Introduction

Seaweed (*Chaetomorpha antennina*), the macroscopic multicellular marine algae, is the most broadly distributed weed in the marine ecosystem. Serious hygienic and environmental problems may arise because of the massive algal growth in the coastal areas due to eutrophication (Xia et al., 2016). Such seaweed contains protein, amino acids, inorganic salts, vitamins, alginate, a small amount of enzymes, plant hormones, polyphenols, and polysaccharides (Manimuthu et al., 2015). Given the need for renewable energy resources, research focused on renewable and eco-friendly green energy has gained much attention in recent years (Suganya et al., 2016). Anaerobic digestion (AD) is the technology that promises to provide nutrient recycling, production of biogas, a sustainable bioenergy process, and minimalization of waste materials (Oliveira et al., 2014). The macroalgae is more suitable as a substrate for AD, owing to its high carbohydrate content and

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low lignin (Xia et al., 2015). The anaerobic digestion process has four phases, namely: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Hydrolysis refers to breakdown of the crystalline structure of seaweed biomass into a soluble substrate, which is a rate-limiting step that determines the overall reaction rate (Xia et al., 2016). The bioavailability of the organic matter present in seaweed biomass is limited by its structural intricacy and the inflexibility of its particles resulting in inefficient degradation (Jung et al., 2015). Hence pretreatment prior to AD is crucial for increasing the rate of hydrolysis. There are various methods for algal pretreatments, such as thermoacidic pretreatment (Barbot et al., 2014), mechanical pretreatment (Tedesco et al., 2013), and chemical pretreatment (Yazdani et al., 2011). Among them, the mechanical pretreatment disintegrates the biomass efficiently and increases the surface area for a subsequent biodegradability process (Karray et al., 2015). Even though mechanical disintegration of macroalgal biomass is advantageous, it has some limitations such as high energy requirement and treatment cost, which still restrict its application, as the incessant increase of energy cost is not compensated for by an increase in methane production. The energy requirement of disperser disintegration (DD) can be minimized by coupling the DD with other methods. In the present study, the chemical surfactant, STPP (sodium tripolyphosphate) has been used, as it is known for its ability to lower surface tension (Reinhold, 2013). Lowering the surface tension of the medium resulted in efficient disintegration. For instance, Poornima et al. (2014) achieved a greater degree of sludge disintegration through surfactant- mediated dispersion. However, the effect of combined chemo mediated dispersion disintegration on macroalgal biomass has not been documented in the literature so far. In addition, many researchers have reported that *Chaetomorpha antennina* contains higher organic content, such as proteins, carbohydrates, and lipids (Premalatha et al., 2011; Manimuthu et al., 2015). The presence of higher levels of proteins and carbohydrates in the *Chaetomorpha antennina* biomass makes it a good feedstock for biogas generation. Keeping all this in mind, a novel attempt has been made in the present study to disintegrate the macroalgal biomass (*Chaetomorpha antennina*) through chemo (STPP) mediated disperser liquefaction (CDL). Thus, to overcome the above-mentioned shortcomings, the purpose of this research is (1) to optimize the disintegration condition for chemodisperser liquefaction for cost-effective performance; (2) to explore the kinetic study of chemodisperser liquefaction and to analyze its efficiency; (3) to evaluate the synergistic effects of this combined pretreatment; (4) to assess the effectiveness of this combined pretreatment on anaerobic biodegradability and methane generation; (5) to evaluate the economic feasibility of implementing the CDL process.

2. Materials and methods

2.1. Collection and processing of macroalgae

Chaetomorpha antennina was collected from Manapad beach, on the southern coastal region of Tuticorin, Tamilnadu, India (8°22′39″N, 78°3′8″E). The collected macroalgal samples were shade dried for 3 days. After 3 days, sand- free samples were used for further analysis. The components of macroalgal biomass, measured by elemental and compositional analysis, with measurements as a percentage based on dry wt, were: carbon- 28.7%; hydrogen – 4.9%; nitrogen – 3.2%; protein – 48%; carbohydrate – 16%; lipids – 2.2%; volatile solids – 72%.

2.2. Disperser-mediated liquefaction (DL)

DL was carried out by using a laboratory disperser (IKA T25 Ultra Turrax Digital disperser) equipped with a biomass cutting rod (S 25, N 25, G ST). A sequence of experiments was performed at various rpm (4000 to 24,000) with 2 g/100 mL of macroalgal biomass taken in 1L beakers. Samples were collected and analyzed at regular time intervals.

2.3. Chemodisperser-mediated liquefaction (CDL)

The CDL was carried out with 2 g/100 mL of macroalgal biomass taken in 1L beakers, by varying the STPP dosage from 0.005 to 0.5 g/g COD at the optimized DL conditions. During the course of the experiment, the samples were collected and analyzed at regular time intervals.

2.4. Fermentation experiment

To evaluate the effects of combinative chemo disperser liquefaction (CDL) on hydrolysis and acidification, a fermentation assay was performed, following the methods detailed in Poornima et al. (2014). The assay was carried out for 3 days, and the ratio of sample and seed slurry was maintained as 9:1. The sample was heated for 30 min at 102 °C. Then, 50 mM concentration of Bromo ethane sulphonic acid (BESA) was added to each bottle in order to get rid of methanogens. Each serum bottle was purged with nitrogen to eliminate the oxygen content, and then the bottles were wrapped with air-tight stoppers and placed in a shaker at 120 rpm for 72 h at 35 °C.

2.5. Biochemical methane potential (BMP) assay

A biochemical methane potential assay was conducted by following the methods detailed in Uma Rani et al. (2012). The inoculum (bovine rumen fluid) and substrates control (untreated), DL and CDL pretreated, were taken in the ratio 3:1. The samples were purged with nitrogen gas to provide anerobic conditions. Then the samples were shaken at 150 rpm in an orbital shaker (Digital IKA KS 130). The methane content in the biogas was estimated by using a gas chromotograph. The cumulative methane production and the kinetics of methane production were evaluated by first-order kinetics based on Eq. (1):

$$M(t) = M(fd) * (1 - e^{kt}) \quad (1)$$

where *M (t)* is the cumulative methane yielded at digestion time *t* days (g COD/g COD added), *M (fd)* is methane potential of the substrate (the fraction of the degradable substrate that can be converted to methane (g COD/ g COD added)), *k* is the first-order disintegration rate constant (day^{-1}), and *t* is the time (days). The model was executed in a Mat lab 2012a Version. The parameter calculation, and unpredictability with 95% confidence region, was calculated based on the work of Kavitha et al. (2016a).

2.6. Analytical methods

TCOD, SCOD and Volatile Fatty Acids (VFA) were analyzed by Standard methods (APHA, 2005). The biopolymers (protein and carbohydrates) were measured based on the method implemented by Kavitha et al. (2015a). The contents of carbon, hydrogen, and nitrogen were determined by an elemental analyzer (Exeter Analytical CE 440, UK).

2.7. Statistical analysis

The experimental outcomes were analyzed by one-way analysis of variance (ANOVA) ($\alpha = 0.05$). The ANOVA was done based on F-testing and was followed by comparisons between averages. If the *p* values were less than 0.05, then the differences between the