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Effect of temperature on kinetics of biogas production from macroalgae

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ABSTRACT

An assessment was carried out on the effect of temperature on the anaerobic digestion of *Laminaria digitata biomass*, in batch reactors (25, 35, 45 and 55 °C) with a hydraulic retention time of 40 days. The first order, modified Gompertz and logistics models were used to obtain the kinetic parameters of the biogas production process. Results indicate the chemical composition of the algae substrate could be written as $C_{316}H_{613}O_{289}N_{13}S_1$, with a theoretical methane yield of 336 ± 0.86 L CH_4 kg VS^{-1}. Experimental methane yield obtained from the reactors for 25, 35, 45, and 55 °C were 318 ± 1.58, 293 ± 1.11, 271 ± 0.98 and 352 ± 0.63 mL CH_4/gVS respectively. Their R^2 > 0.90 indicate both models fits well for predicating kinetics of methane production. The lowest k_h (0.31), high biodegradability index (0.96) and lag time (9.3–11.7 days) were obtained for 55 °C.

1. Introduction

Biofuel production from algae is known as third-generation biofuel (Allen et al., 2013a), to differentiate first and second generation biofuels produced from terrestrial biomass which is less sustainable for their production (Jung et al., 2011). Macroalgae or microalgae are photosynthetic organisms growing in aquatic environments (Demirbas, 2010). Their biomass can be degraded biologically (Park, et al., 2009). Whereas microalgae, which are unicellular and have been the focus of intensive research to various products; bioethanol and biodiesel (Hughes et al., 2012), production of methane gas (Ras et al., 2011) and hydrogen (Melis and Happe, 2001), seaweed (marine macroalgae), sometimes known as marine plant crop (Santelices, 2007) has received little attention as a prospective feedstock (Hinks et al., 2013). Hence, their utilization globally is low (Park et al., 2009). Algal biomass are known energy crops because they can trap and store solar energy as expressed by Demirbas (2010); that algae are photosynthetic aquatic organisms that convert water, sunlight and carbon-dioxide into algae biomass.

Many researchers have pointed out the inherent benefit seaweed has over other feedstocks, namely; use of large land mass for cultivation is avoided (Park et al., 2009), no competition with conventional agricultural resources (Schwede et al., 2011), large scale mariculture (Titlyanov and Titlyanova, 2010), high coastal biomass (Hinks et al., 2013), contains sulfated fucans and proteins (Kloareg et al., 1986) and high carbohydrate content (the polysaccharides of alginate, laminarin and mannitol), with zero lignin and low cellulose content making them biodegradable as biofuels during anaerobic processes (Hinks et al., 2013), and they undergo a more complete hydrolysis than terrestrial biomass (Hughes et al., 2012). For brown algae, alginates form the dominant cell wall/intercellular structural matrix making them a good potential source of methane and hydrogen production as a result of the high carbohydrate content (Park, et al., 2009).

The process and application of anaerobic digestion is a robust low-tech/low-cost process that is well understood in generating bioenergy as biogas (Hinks et al., 2013). It has been identified as a viable means of producing carbon neutral energy (Batstone et al., 2002), while also reducing uncontrolled greenhouse emissions (Møller et al., 2004). Other advantages are energy recovery, pollution control (Chen et al., 2008), destruction of pathogens (Lo et al., 1985), and the production of nutrient rich sludge that can be used as an agricultural fertilizer.

Kinetic analysis is an effective way in determining the key steps in anaerobic digestion process (Fang, 2010), which helps in pilot plant studies to provide better data for reactor designs and operation, leading to more efficient process performance and reduced reliance on skilled operators (Page et al., 2008). Mathematical models (kinetics) are used to demonstrate the effects of changing certain design parameters (Horton and Hawkes, 1981). They help to describe the kinetic behaviour of biologically mediated processes with digesters. To operate an anaerobic system effectively, and predict how the system will respond to changes in feed and other operating conditions, appropriate models need to be developed (Lyberatos and Skiadas, 1999). Mathematical modeling of anaerobic digestion process was motivated by the need for efficient operation of AD systems in the early 1970's (Donoso-Bravo et al., 2011). Models using the kinetics of microorganisms growth and chemical reactions to predict the behavior of systems have long been

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reported (Kythreotou et al., 2014). Various models have been used to estimate the kinetic parameters; first order hydrolysis constant k_h (Angelidaki et al., 2009), maximum specific growth rate μ_{max}, lag time λ, methane production time and rate (Zwietering et al., 1990). Fang (2010) stated that the modified Gompertz model has been used to describe the kinetics of methane production in anaerobic digestion process. One common feature among the models is that they predict and calculate biogas and methane production rate, which are both very important parameters for design of an efficient biogas plant (Kythreotou et al., 2014). Kinetic models are divided into two classes; structural and un-structural models (Fang, 2010), whereas the former considers metabolic pathways making it generally complicated, the latter is simpler (Mu et al., 2007). The application of un-structural models such as Gompertz and Monod equation has been previously used to describe anaerobic digestion of lignocellulose waste with rumen microorganisms (Fang, 2010).

The aim of this research was to demonstrate the application of un-structural models such as the first order, Gompertz equation and logistics model on anaerobic digestion of macroalgae feedstock to estimate and predict the kinetic parameters at different temperatures. Although, reported studies on the influence of digestion temperature on *L. digitata* is scare and or limited, similar laboratory-scale study has been carried out at 20, 35 and 45 °C to demonstrate the feasibility of biogas production at different temperatures and how it influence the cumulative and methane concentration but did not take into account the kinetics of the digestion process (Vanegas and Bartlett, 2013). Hence, this study intends to add and broaden the knowledge of this substrate to already existing literature.

1.1. Materials and methods

1.1.1. Algae collection, pretreatment, and storage

Algal biomass *Laminaria digitata* (LD) used in the batch reactor experiments were collected from shallow water during low tide at Seaton Sluice, 55.0836° N, 1.4744° W, Northumberland UK (NZ 3350) on 5th July 2015. The seaweed was transported in 30 L bags and was immediately washed to remove marine salts and sediments. The reactors feedstock were prepared using only the frond; the stipe and holdfast were discarded as reported elsewhere (Membere et al., 2015). The fronds were roughly chopped by hand to a particle size of about 10 cm using a knife, and to obtain the dry algal substrate, the roughly chopped frond were oven dried at 70 °C for between 24 and 48 hrs. This was then pulverized with a Kenwood 100 coffee blender to particle size generally < 1 mm. All samples were stored at 4 °C in air tight gas bag until required.

1.1.2. Inoculum

The batch reactors were inoculated with a mixed methanogenic sludge from a full-scale running anaerobic digester (Cockle Park Farm, Newcastle), operating on grass silage, pig and cow manure. It had following characteristics; pH 7.5, 21.2 %TS, 60 %VS (%TS), 0.019 sulphur and C: N of 0.061.

1.1.3. Substrate characterization and analysis

Characterization of the macroalgae feedstock used in this study are summarized in Table 1.

The dried macroalgae prepared had a TS content of approximately 94%, and a VS content of about 65%, giving a fairly high VS/TS ratio of 0.69, indicating mostly organic digestible matter in the feed. The C: N ratio was 21.6: 1 which is close to the optimal range (25–30:1) for stable anaerobic digestion (Kafle and Kim, 2013). C: N values as high as 27.5:1 (Tabassum et al., 2016), and 22.3:1 (Allen et al., 2015) have been reported for *L. digitata*. It has a very low lignin content (0.67%), indicating the storage carbohydrates should be accessible to fermentation since a high lignin content results in reduced biodegradability of the biomass by microbial processes, hence limiting digestibility and gas production (Ward et al., 2014).

Table 1
Physiochemical characteristics of *Laminaria digitata* macroalgal feedstock.

Physical analysis		Fibre analysis		Elemental composition	
% Moisture	6.3%	Neutral Detergent Fibre	7.0%	Carbon ©	30.8%
%TS	93.7%	Acid Detergent Lignin	0.7%	Hydrogen (H)	5.0%
%VS	65.0%	Acid Detergent Fibre	20.3%	Nitrogen (N)	1.4%
TOC	36.1%	Oil A (Ether Extract)	0.5%	Oxygen (O)	37.6%
C/N RATIO	21.6	Total Oil (Oil B)	1.4%	Sulphur (S)	0.26%

The pH was measured using a Jenway 3010 pH meter. The total solids (TS) and volatile solids (VS) were determined gravimetrically using methods described in (APHA, 2005). %TS was obtained by placing the sample in triplicate into an oven for 24 hrs at 104 °C and subsequently placed in a furnace at 550 °C between 1 and 2 h to obtain the volatile solids content (APHA, 2005). Samples were analysed for carbon, nitrogen and sulphur content using an Elementar VarioMAX CNS analyser. Fibre analysis was carried out using standard methods in Elemental microanalysis laboratory, UK.

1.2. BMP studies at different temperatures

1.2.1. Batch studies

The batch test was divided into four different temperatures range and carried out according to Membere et al. (2015), briefly described below; The incubation was carried out in a water bath at temperatures of 25 °C, 35 °C, 45 °C, and 55 °C. The batch reactors consisted of 500 mL Duran bottles (actual internal volume 580 mL) fitted with rubber stoppers inserted to serve as an outlet port for biogas collection in gas bags and as a purging port for nitrogen flushing of the headspace. Before starting the BMP test, all reactor bottles were pressure tested for air leakage, and once the experiment has commenced, for nitrogen or methane leakage using a Thermo-Scientific GLD ProLeak detector used to check any CO_2, NO_2, and CH_4 leaks. The required amount of inoculum and substrate was evaluated for each reactor on a VS basis using a ratio of 3: 1 (3 g VS_i/L: 1 g VS_f/L). This was to ensure adequate destruction of the volatile solids and overcome possible VFA inhibition (Angelidaki et al., 2009). The inoculum and substrate were then placed inside the reactor and the solution was made up to 500 mL with deionized water. The rubber stoppers were then used to close the bottles, and the headspace (approx. 80 mL) was flushed for 5 min with pure (99.99%) N_2 gas to establish anaerobic conditions. The tube clamp was used to close the PVC tube ensuring all the bottles were gas-tight without the gas bags. Triplicates reactors were used to overcome inoculum variability, sample heterogeneity and allow statistical significance (Angelidaki et al., 2009). Each digester was mixed manually by shaking for 15–30 s once a day.

Biogas collection and methane measurement was done as described in (Membere et al., 2015). The methane potential and production rate from biogas production were studied in this experiment. Assays with inoculum alone were used as controls and the methane produced from this inoculum were subtracted from the sample assays (Kaparaju et al., 2010).

1.2.2. Kinetic study on batch experiment

From the experimental elemental analysis determination, the empirical formulae ($C_aH_bO_cN_dS_e$) of the macroalgae composition was calculated (Raposo et al., 2011). This was used to develop a stoichiometric equation using the Buswell Equation, Eq. (1-1) (Allen et al., 2013b), to obtain the theoretical methane potential (BMP_{theo}), ammonium yields and carbon dioxide (CO_2) volumes that can be produced when the macroalgae feedstock is broken down by a consortium of microorganisms present in a batch reactor (Montingelli et al., 2015).