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Recovery of Sustainable Renewable Energy from Marine Biomass

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Marine biomass is considered an important substrate for anaerobic digestion to recovery energy i.e. methane. Nevertheless, marine biomass has attracted little attention by researchers compared to terrestrial feedstock for anaerobic digestion. In this study, biochemical methane potential (BMP) test was used to evaluate generation of renewable energy from starfish. A cumulative biogas yield of 748±67 mL g^{-1} VS^{-1} was obtained after 60 days of digestion. The cumulative methane yield of 486±28 mL CH_4 g^{-1} VS^{-1} was obtained after 60 days of digestion. The methane content of the biogas was approximately 70%. The calculated data applying the modified Gompertz equation for the cumulative CH_4 production showed good correlation with the experimental result obtained from this batch study. Since the result obtained from this study is comparable to results with other substrates, marine biomass can be co-digested with food waste or swine wastewater to produce CH_4 gas that will help to reduce the gap in global energy demand.

Key words: Biogas, Co-digestion, Marine biomass, Renewable energy

Introduction

Per capita energy consumption is considered as one of the major determinant for wealth and quality of life as energy is a fundamental input for social and economic activities (Bauen, 2006; Katuwal and Bohara, 2009). The current global energy demand is heavily relied on non-renewable energy sources especially oil and natural gases, in which more than 80% of the global energy demand has been met by this sector (IEA, 2011; Weiland, 2010). However, the use of fossil fuel is not sustainable due to their depleting nature and also confronted with a number of issues and challenges such as degradation of environment including air, water and soil (Bauen, 2006). In addition, most of the fossil fuels are stocked in politically unstable regions that can threaten the global energy security in coming years (Bauen, 2006; Weiland, 2010). Therefore, alternative sustainable energy sources have to be developed to replace the conventional fossil fuels-based energy sources.

In recent years, the efforts have been in developing new technological processes to generate clean and sustainable energy mainly through the utilization of renewable energy sources (Chynoweth et al., 2000; Vindis et al., 2007). In this regard, recovery of renewable energy (i.e. biogas from waste biomass including crops residue, food waste, swine manure and swine wastewater) plays a pivotal role in meeting the increasing global energy demand (Cho et al., 1995; Weiland, 2010; Zhang et al., 2007). Biogas is a versatile renewable energy sources which are produced through anaerobic digestion (AD) which is a microbial process that provides the opportunity to convert biodegradable organic substrates to biogas consisting mainly of methane (CH_4) and carbon dioxide (CO_2) (Katuwal and Bohara, 2009; Liu et al., 2009; Weiland, 2010). AD is a complex process, which is usually divided into four phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Oslaj et al., 2010; Weiland, 2010).

Biogas has important advantages of being relatively low cost and sustainability, and it has wide substrate choices. Therefore, it has become a rapidly emerging research topic within the field of renewable energy (Angelidaki et al., 2009; Behera et al., 2010; Heo et al., 2004; Lee et al., 2009; Weiland, 2010). The biochemical methane potential (BMP) test was developed as a standardized method to quantify the CH_4 yield from an organic substrate under specific conditions (Kim et al., 2003; Owen et al., 1979; Rincon et al., 2010). In recent years, a number of different feedstocks

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including organic wastes and energy crops such as maize and wheat has been used to evaluated the CH_4 yield from these substrates (Behera et al., 2010; Gunaseelan, 2004; Hansen et al., 2004; Oslaj et al., 2010; Rincon et al., 2010).

Compared to terrestrial-based feedstocks for CH_4 production, marine biomass has attracted little attention by researchers (Yokoyama et al., 2007). However, marine biomass is an effective feedstock for CH_4 production since it consists of easily hydrolysable sugars with zero lignin and low cellulose content (Bird et al., 1990; Vergara-Fernandez et al., 2008). Furthermore, marine biomass offers significant advantages over the other forms of bioenergy production since its cultivation does not require arable land and biomass productivities are greater (Klass, 1974). Therefore, from BMP tests, in this study we determined the potential of star fish for CH_4 production in batch digestion.

Materials and Methods

Feedstock Fresh sample of starfish was collected from the sea shore of Korea and provided to the laboratory by a local fisherman. The sample was ground in a blender, passed through a 2 mm sieve and used for BMP tests the same day. Thereafter, excess sample was frozen at -20ºC for later use. The general characteristic of the sample is shown in Table 1.

Inoculum Digested sludge was used as the inoculum to the BMP tests and collected from the anaerobic sludge digesters at Anseong Biogas plant, South Korea. Prior to use, the inoculum was sieved through a 1 mm mesh to remove large suspended particles and grit. After sieving, the inoculum had a pH of 8.2 ± 0.15, alkalinity of 23,025 mg $CaCO_3$ L^{-1}, electrical conductivity (EC) of 34±0.14 mS cm^{-1}, total chemical oxygen demand (TCOD) of 38,280±35 mg L^{-1}, soluble chemical oxygen demand (SCOD) of 25,200±42 mg L^{-1}, total solids (TS) of 3.2±0.1% and volatile solids (VS) of 2.8±0.1%.

Table 1. Characteristics of substrate.

Parameter	Unit	Star fish
Total solids	%	11
Volatile solids	%	8.9
Moisture content	%	81
VS/TS	%	89
pH		7.5±0.12
EC	mS cm^{-1}	57.8±0.28
COD	mg L^{-1}	19600±140

BMP tests Before the BMP tests, the inoculum was acclimated using star fish for approximately 20 days in batch mode using a 250 mL media bottle. During acclimatization, the media bottle was filled with the inoculum and nutrient mineral buffer (NMB) solution in the ratio of 1:1, i.e. 100 mL digested sludge and 100 mL NMB solution. The composition of the NMB used in this study was as follows (g L^{-1}): $NaHCO_3$ (3.13), NH_4Cl (0.31), $NaH_2PO_4 \cdot H_2O$ (0.75), KCl (0.13), NaH_2PO_4 (4.22), Na_2HPO_4 (2.75). The mixed solution of digested sludge and NMB was supplemented with 0.5 g of glucose and 5 g of star fish. The test was conducted in duplicate and in all the culture bottles pH was maintained at 7.5 using 0.1 N sulfuric acid. Finally, the mixed culture was cultured for 20 days in an incubator (SI-600R, Korea) at 35℃ and agitated at 100 rpm. The main purpose of acclimatization was to deplete the residual biodegradable organic material present in the digested sludge (Angelidaki et al., 2009).

Finally, BMP tests were conducted in batch mode using 285 mL media bottles. The media bottles were seeded with acclimatized sludge (20 mL) and star fish was added separately at the final concentration of 2.5 g VS L^{-1}. Tests were conducted in duplicate with two controls (NMB and inoculum only) for a total of 4 tests. After addition of the inoculum and the substrate, 230 mL of NMB solution was added to the serum bottles to make a final liquid volume of 250 mL. The initial pH was kept at 7.5 using 0.1 N sulfuric acid and after homogenization; 50 mL of sample was taken from each bottle for analysis. The tests were purged with N_2 for 5 min to achieve anaerobic conditions, capped with natural rubber sleeve stoppers, incubated at 35℃, and agitated at 100 rpm. The BMP tests were operated for 60 days. Then, 50 mL of solution was taken from each bottle for analysis.

Analytical Methods

Physicochemical analysis Physicochemical parameters such as TS, VS, COD, alkalinity, ammonium ion (NH_4^+), total nitrogen (T-N), and total phosphate (T-P) were analyzed according to standard methods (APHA, 1998). TCOD and SCOD were determined through the closed reflux titration method. T-N and T-P were analyzed at 220 and 880 nm, respectively using a UV-spectrometer (Rayleigh, UV-9200, Beijing, China). The pH and EC were measured manually using portable pH (Orion 91-05/06, Thermo, USA) and EC (Inlab 737 Mettler Toledo, Switzerland) meters. The concentration of NH_4^+-N was measured by an ammonia-gas sensing electrode (Orion 9512, Thermo, USA) connected to a multimeter (Orion 5 Star Bechtop).

Elemental analysis Sample was dried at 105℃ for 24 h and ground to a particle size of less than 0.5 mm. Then the elemental analysis (C, N, and H) was conducted by an elemental analyzer (Flash EA112, Thermo Electron, Corporation, USA).

Biogas composition The BMP tests were periodically analyzed for gas production and composition for 60 days. Biogas production was measured daily for the first 30 days and then at 2 day intervals using the method developed by Owen et al. (1979). The composition of the biogas was analyzed every 2 days using a gas chromatograph (GC) (SRI 8510C, USA) equipped with a thermal conductivity detector (TCD) and helium as the carrier gas. The injector, oven, and detector temperatures were 120℃, 60℃, and 250℃, respectively. Gas samples (1 mL) were taken from the headspace of the reactors through a septum with a gas-tight syringe (Hamilton, USA). The GC was calibrated by injecting 1 mL of a standard gas mixture containing CO_2, CO, N_2, O_2, CH_4, H_2, and He at a ratio of 1:1:1:1:0.8:0.8:0.8 (v/v), respectively (Matheson Tri- Gas, USA). Generation of CH_4 was calculated using Eq. 1 (Van Ginkel et al., 2005) and the volume of the CH_4 produced was obtained by multiplying the headspace volume by the CH_4 percentage in the headspace as determined by the GC:

$$V_{M,i} = V_{M,i-1} + C_{M,i}\,(V_{G,i} - V_{G,i-1}) + V_H\,(C_{M,i} - C_{M,i-1}) \quad (1)$$

where, $V_{M,i}$ and $V_{M,i-1}$ are the cumulative CH_4 gas volumes at the current (i) and previous (i-1) time intervals, respectively, $V_{G,i}$ and $V_{G,i-1}$ are the total biogas volumes in the current and next time intervals, $C_{M,i}$ and $C_{M,i-1}$ are the fraction of CH_4 in the current and previous intervals in the headspace of the bottle measured using GC, and V_H is the total volume of headspace in the reactor (85 mL).

Data analysis The modified Gompertz equation (Gompertz, 1825; Zwietering et al., 1990) was fitted to the observed cumulative CH_4 production curves to determine the maximum CH_4 production potential (*P*), CH_4 production rate (R_{max}), and lag phase (λ) as shown in equation 2:

$$M(t)=P\cdot \exp\{-\exp[\frac{(R_{max}\cdot e)}{P}(\lambda-t)+1]\} \quad (2)$$

where, *M* (*t*) is the cumulative CH_4 production (mL CH_4 g^{-1} VS^{-1}) at time *t*; *P* is the maximum CH_4 potential (mL CH_4 g^{-1} VS^{-1}) at the end of incubation time; t is time (d); R_{max} is the CH_4 production rate (mL CH_4 g^{-1} VS^{-1}); λ is the lag phase (d) and e is exp (1), i.e. 2.71828. The three parameters *P*, R_{max}, and λ were estimated by curve-fitting using the Solver program in MS Excel 2007 by minimizing the residual sum of squared errors between the experimental data and the modeled curve.

Results and Discussion

Table 2 shows the physicochemical characteristics of the substrate used in this study. The analyzed physicochemical characteristics showed that the main differences were in pH, alkalinity, NH_4^+-N, and COD. The final pH in the reactor (star fish) was found 7.42±0.2, which was almost similar to the initial pH. During the process of AD, pH plays vital role in the production of biogas (Agdag and Sponza, 2005; Chandra et al., 2012). The optimum pH for the methanogens ranges between 6.5 and 8.2 (Agdag and Sponza, 2005). Thus, adequate alkalinity is required to maintain stable pH and biosynthesis during the AD processes (Lee et al., 2009).

The elemental analysis showed that star fish had relatively higher content of carbon as compared to hydrogen and nitrogen. It contained 27±0.62% of carbon, followed by 3.74±0.16% nitrogen and 3.34 ± 0.1% hydrogen, respectively. The C/N ratio of the substrate was 7.2. C/N ratios <20 can lead high NH_4^+-N concentrations and the accumulations of volatile fatty acids (VFAs) during the process of AD (Sialve et al., 2009; Speece, 1996). On the other hand, higher C/N ratio may limit the CH_4 generation due to potential nitrogen limitations (Sialve et al., 2009). Ehimen et al. evaluated the generation of CH_4 at different concentrations levels of 1, 10, 20, 30, 40 and 50 kg VS m^{-3}, respectively, and found no improvement in the CH_4 recovery with C/N ratios more than 12.44 for all loading concentrations (Ehimen et al., 2011).

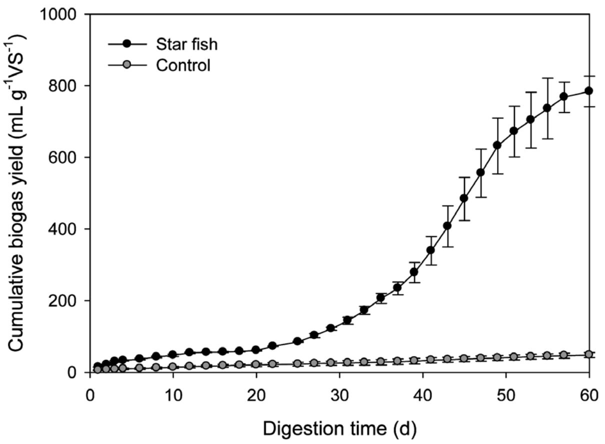

Fig. 1. Cumulative biogas yield after 60 days of digestion.

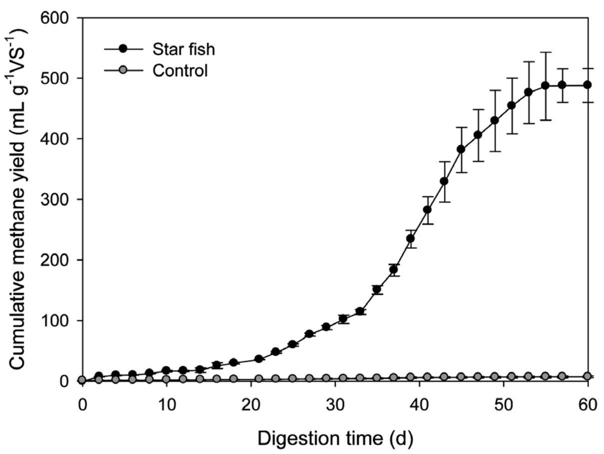

Fig. 2. Cumulative methane yield after 60 days of digestion.

Fig. 1 and Fig. 2 showed the cumulative biogas and CH_4 yield, respectively, as a function of digestion time. All these cumulative biogas and CH_4 values were expressed as dry gas flow at standard temperature and pressure (STP) conditions as mentioned elsewhere (Raposo et al., 2006). Biogas production started after a short period of lag phase. Fairly higher biogas production rate was observed from the 30 days of digestion time period. The cumulative biogas yield of 784±67 mL g^{-1} VS^{-1} was obtained after 60 days of digestion.

The cumulative CH_4 yield was 486±28 mL CH_4 g^{-1} VS^{-1} after 60 days of digestion period. The composition of the biogas was monitored throughout the experiment and the final CH_4 percentage of more than 70% was observed with star fish. As observed the plateau phase was reached after~55 days of digestion when the cumulative methane yield was 428±40 mL CH_4 g^{-1} VS^{-1}. This accounts for approximately 90% of the total CH_4

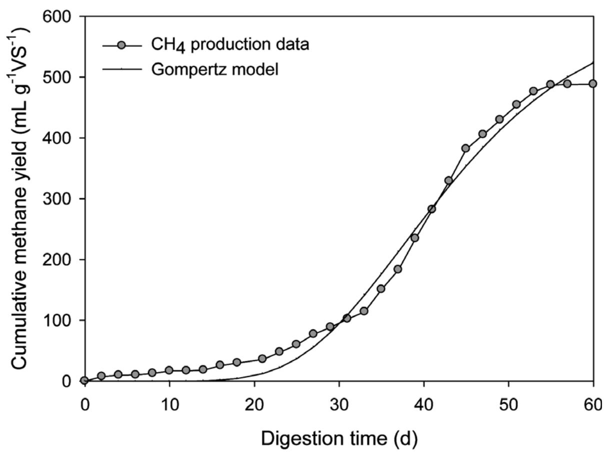

Fig. 3. Parameter estimation from Gompertz model after 60 days of digestion.

Table 2. Physiochemical characteristics of the tested sample.

Parameters	Control		Star fish	
	Initial	Final	Initial	Final
pH	7.5±0.1	7.34±0.04	7.50±0.1	7.42±0.2
EC (mS cm^{-1})	8.3±0.1	7.65±0.01	10.7±1.2	14.1±0.6
Alkalinity (mg $CaCO_3$ L^{-1})	2600±35.4	2900±45.9	3520±150	3750±120
NH_4^+-N (mg L^{-1})	300±28.3	270±14	690±85	270±125
TCOD (mg L^{-1})	2540±197	1840±28	5106±95	2440±141
SCOD (mg L^{-1})	1520±57	1440±255	3760±622	2140±226
T-N (mg L^{-1})	450±8.9	447±4.9	842±10	838±16
T-P (mg L^{-1})	651±1.7	430±13.3	560±20	331±13

yield during 60 days of digestion. As observed from Fig. 3, the experimental data obtained in the current study was in good agreement with the result predicted by Gompertz model. The maximum CH_4 potential of 617 mL CH_4 g^{-1} VS^{-1} was obtained at the end of incubation time. Similarly, a λ of 25.44 days and R_{max} of 18.43 mL CH4 g^{-1} VS^{-1} were obtained, respectively.

The result from this study demonstrated that marine biomass can be used for generation of sustainable green energy i.e. CH_4. The result obtained in this study is comparable to a result obtained elsewhere, who reported a CH_4 yield of 435 mL CH_4 g^{-1} VS^{-1}added from food waste after 28 days of digestion (Zhang et al., 2007). The cumulative methane yield of the current study is comparable to the previous study by Lee et al., who reported a CH_4 yield of 478 mL CH_4 g^{-1} VS^{-1} after 28 days of digestion using food waste leachate in a lab-scale BMP test (Lee et al., 2009). In another BMP study by Cho et al., reported a CH_4 yields of 482, 294, 277 and 472 mL CH_4 g^{-1} VS^{-1} for cooked meat, boiled rice, fresh cabbage and mixed food wastes, respectively, digested at 37℃ and 28 days hydraulic retention time (Cho et al., 1995). Heo et al., evaluated a CH_4 yield of 490 mL CH_4 g^{-1} VS^{-1} from a mixture of traditional Korean food consisting of boiled rice (10-15%), vegetables (65-70%) and meat and eggs (15-20%) at 35℃ after 40 days of digestion (Heo et al., 2004).

Conclusions

The result obtained from this study highlight the importance of using star fish as a feedstock for generation of renewable energy through anaerobic digestion. A cumulative biogas yield of 784 ± 67 mL g^{-1} VS^{-1} was obtained in the BMP tests after 60 days of digestion. The cumulative methane yield of 486 ± 28 mL CH_4 g^{-1} VS^{-1} was obtained after 60 days of digestion. The result obtained in this is comparable to other BMP studies with different feedstocks such food wastes, vegetables, leachate and so on. Based on the result obtained from this study, a field-scale pilot test is required to re-evaluate star fish as a suitable feedstock for recovery of sustainable renewable energy. In addition, utilization of marine biomass can control marine eutrophication. Thus, energy recovery from waste biomass can become vital for meeting future energy demand.

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