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Evaluation of the Biogas Productivity Potential of Fish Waste: A Lab Scale Batch Study

Gopi Krishna Kafle, Sang Hun Kim*

Department of Biosystems Engineering, Kangwon National University, Chuncheon, Korea

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Abstract

Purpose: The biogas productivity potential of fish waste (FW) was evaluated. **Methods:** Batch trials were carried out in 1.3 L glass digesters kept in a temperature controlled chambers at 36.5˚C. The first order kinetic model and the modified Gompertz model were evaluated for biogas production. The Chen and Hashimoto model was used to determine the critical hydraulic retention time ($HRT_{Critical}$) for FW under mesophilic conditions. The feasibility of co-digestion of FW with animal manure was studied. **Results:** The biogas and methane potential of FW was found to be 757 and 554 mL/g VS, respectively. The methane content in the biogas produced from FW was found to be 73% and VS removal was found to be 77%. There was smaller difference between measured and predicted biogas production when using the modified Gompertz model (16.5%) than using first order kinetic model (31%). The time period for 80%-90% of biogas production (T_{80-90}) from FW was calculated to be 50.3-53.5 days. Similarly, the $HRT_{Critical}$ for FW was calculated to be 13 days under mesophilic conditions. The methane production from swine manure (SM) and cow manure (CM) digesters could be enhanced by 13%-115% and 17%-152% by mixing 10%-90% of FW with SM and CM, respectively. **Conclusions:** The FW was found to be highly potential substrate for anaerobic digestion for biogas production. The modified Gompertz model could be more appropriate in describing anaerobic digestion process of FW. It could be promising for co-digestion of FW with animal manure.

Keywords: Biochemical methane potential (BMP), Co-digestion, Fish waste, Kinetic study, Mesophilic temperature

Abbreviations

%	Percentage
ADF	Acid detergent fiber
BMP	Biochemical methane potential
BR	Mass of biogas removed (g)
C/N	Carbon to nitrogen ratio
CF	Crude fiber
CP	Crude protein
d	Day
d.w.	Dry weight
EE	Ether extract
F/I	Feed to inoculum ratio
FW	Fish waste
g	Gram
HRT	Hydraulic retention time (days)
K	Kinetic constant (1/day)
K_{CH}	Chen and Hashimoto kinetic constant
L	Liter
mL	Milli liter
NDF	Neutral detergent fiber
NFE	Nitrogen free extract
OLR	Organic loading rate (g VS/L)
ppm	Parts per million
SD	Standard deviation
STP	Standard temperature (0℃) andpressure (1atm.)
TA	Total alkalinity (mg/L $CaCO_3$)
TCOD	Total chemical oxygen demand (mg/L)

***Corresponding author:** Sang Hun Kim
Tel: +82-33-250-6492; **Fax:** +82-33-255-6406
E-mail: shkim@kangwon.ac.kr

TS	Total solids (%)
TVFA	Total volatile fatty acids (mg/L acetate)
VS	Volatile solids (%)
w.w.	Wet weight
λ	Lag phase (day)
μ_m	Maximum specific growth rate of microorganisms (1/day)

Introduction

Energy production from biomass (biogas production) provides a renewable alternative to fossil fuels, considering the huge amount of organic waste such as food-industrial wastes and municipal solid wastes produced around the world. Many of these wastes are still unexploited and contribute to environmental pollution in both urban and rural areas. World fish consumption per capita nearly doubled over the last 45 years, leading to larger quantities of fish processing wastes (Ward and Løes, 2011). In 2005, the UN Food and Agricultural Organization has estimated the annual world fish harvest resulting from commercial fishing in wild fisheries and fish farms to be 140 million tons (FAO, 2005). Fish processing generates considerable amounts of waste in the form of edible and non-edible by-products. Assuming 45% of the live weight to be waste (Rai et al., 2010), it can be estimated that nearly 64 million tons of fish waste are generated annually. This waste is mainly composed of heads, viscera, bones and scales, and is rich in lipids and proteins. Fish processing wastes have a great potential for energy production. The increase in fish processing wastes and the expansion of the renewable energy market imply that fish processing wastes could play a part in the future of bio-fuels. Waste such as fish waste and fish sludge, which are rich in lipids and proteins, have the advantage of giving high methane yields, and can be attractive as substrates in an anaerobic digestion process (Cirne et al., 2007). Thus, anaerobic digestion could be a good approach for FW utilization and energy generation. Anaerobic digestion of this biodegradable waste will provide a solution for reducing both this environmental problem and the consumption of fossil fuels. Plant nutrients such as nitrogen and phosphorus are retained in the effluent (digestate) after anaerobic digestion, which can be used as a bio-fertilizer in agricultural production provided it meets the required standards.

The experimental data on the bio-methanization of FW are limited. Ward and Løes (2011) examined the potential of fish waste for liquid and gaseous biofuels. Kim et al. (2012) performed lab scale study on the technical feasibility of using jellyfish (*Aurelia aurita*) for biogas production. Similarly, Mshandete et al. (2004) tested the batch anaerobic digestion of fish waste obtained from the landing beach at F/I ratio of 0.05-1.6 (VS basis) and obtained highest methane yield of 0.39 L/g VS added at F/I ratio of 0.05 (VS basis). Eiroa et al. (2012) evaluated the BMP of different varieties of solid fish wastes (tuna, sardine, mackerel and needle fish waste) obtained from a canning industry. Chen et al. (2010) evaluated the BMP test on a fish farm waste at F/M ratio of 0.5-1.0 under both mesophilic and thermophilic conditions.

The main objective of this study was to investigate the feasibility of biogas production from fish waste (FW). The biogas potential of FW was determined and anaerobic digestion process was evaluated using different kinetic models.

Materials and Methods

Feed stock and inoculum

FW was obtained from a market in Korea. The FW was crushed in a blender and stored at 4°C. The anaerobic inoculum was obtained from a small lab digester with swine manure under mesophilic condition. The characteristics of FW and inoculum are shown in Table 1.

Test set up and experimental design

The experimental design for batch test is shown in Table 2. The test was carried out in 1.13-1.28 L glass bottles (liquid volume 0.4-0.8 L). The feed to inoculum (F/I) ratio was maintained 0.0-0.5. The F/I ratio was calculated based on the initial VS of the substrate and inoculum.

$$F/I = \frac{\text{Substrate added (g VS)}}{\text{Inoculum added (g VS)}} \tag{1}$$

After adding the required amounts of inoculum and substrate, each digester was filled with tap water to maintain the designated volume. The batch digesters were checked for any leakage and flushed with 100%

pure nitrogen for approximately 1.5-2.0 minutes to ensure anaerobic conditions. The anaerobic digesters were maintained at 36.5℃ in a temperature-controlled incubator. Batch test was carried out in duplicate, and the results were expressed as a mean. Each digester was mixed manually for one minute once a day just before the gas volume measurement. Assays with inoculums alone were also used as controls. Biogas and methane produced from inoculums were subtracted from the sample assays.

Table 1. Characteristics of FW and inoculum

Characteristics	units	FW	Inoculum
Moisture content	%	68.7	98.18
Total solids (TS)	%, w.w.	31.30	1.82
Volatile solids (VS)	%, w.w.	27.50	0.73
VS/TS		0.88	0.40
pH		-	8.15
Total volatile fatty acids (TVFA)	mg/L	-	1313
Total alkalinity (TA)	mg/L	-	14397
TVFA/TA		-	0.091
TCOD	mg/L	-	11627
SCOD	mg/L	-	6400
NH_3-N	mg/L	-	3320
TKN	%, TS	6.54	0.501
Crude fiber (CF)	%, TS	0.0	-
Crude protein (CP)	%, TS	40.9	-
Crude fat (CF)	%, TS	48.6	-
Ash	%, TS	5.7	-
Nitrogen free extract (NFE)	%, TS	4.8	-
Neutral detergent fiber (NDF)	%, TS	0.0	-
Acid detergent fiber (ADF)	%, TS	0.0	-
C/N		4.1	0.81

-: Not determined
CP = 6.25× TKN
C/N = TOC/TKN

Biogas volume/mass measurement and composition analysis

The daily biogas production of each digester was determined by the volume of biogas produced, which was calculated from the volume and pressure in the headspace of the digester. The pressure was measured using a WAL-BMP-Test system pressure gauge (Type 3150, Wal, Germany) (EI-Mashad and Zhang, 2010; Kafle and Kim, 2012). Daily pressure differences were converted into biogas volume using the following equation:

$$V_B = \frac{(P_f - P_i)V_H.C}{R.T} \qquad (2)$$

where,
V_B = Biogas volume (L)
P_i = Initial pressure in the reactor head space (mbar)
P_f = Final pressure in the reactor headspace after 24 hrs. (mbar)
V_H = Volume of the headspace (L)
C = Molar volume (22.41 L/mol)
R = Universal gas constant (83.14 L mbar/K/mol)

The biogas composition (CH_4 and CO_2, %) was measured using a GC-2014 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a thermal conductivity detector. Helium was used as the carrier gas in the GC. The GC was calibrated using standard gases consisting of CH_4 60% and CO_2 40% on a volume basis (v/v). The hydrogen sulfide concentration in the biogas was measured using a handy gas analyzer (BioGas Check - Geotechnical Instruments, UK) (Kafle et al., 2012a). The measured wet biogas and methane volumes were adjusted to the volumes at standard temperature (0℃) and pressure (1 atm) (VDI 4630, 2006). The corrected methane content in the biogas was calculated using equation (3) as proposed in German standard procedure (VDI 4630, 2006).

Table 2. Experimental design for batch test

	F/I	OLR(g VS/L)			Liquid volume (mL)	Head space mL	Test period (days)	Purpose
		FW	Inoculum	Sugar				
FW digesters[a]	0.50	2.5	5.0	0.0	800	380	60	Biogas potential of FW
Blank digesters[a]	0.0	0.0	5.0	0.0	800	380	60	Biogas potential of inoculum
Sugar digesters[a]	0.25	0.0	5.0	1.25	400	730	3	Methanogenic activity of inoculum

[a] Number of replications (n) = 2

$$CH_{4\ Corr} = \frac{C_{CH_4} \times 100}{C_{CH_4} + C_{CO_2}} \tag{3}$$

where,
$CH_{4\ Corr}$ = corrected methane content in the dry gas (% by volume)
C_{CH4} = measured methane content in the gas (% by volume)
C_{CO2} = measured carbon dioxide content in the gas (% by volume)

During batch digestion, the biogas production rates and methane content change considerably over the digestion time. The methane content on intermediate days was calculated using linear interpolation by the INTERP1 function in Matlab software R2011b (7.13.0.564). The weighted average methane content over the digestion period was calculated. The mass removal in the form of biogas at the end of the experiment was calculated using a formula shown in equation (4). The density of CH_4 was taken as 0.000668 g/mL, and the density of CO_2 was taken as 0.00184 g/mL (Kafle et al., 2012b).

$$\mathrm{BR} = \frac{V_0 \times \rho_{mix}}{m} \tag{4}$$

where,
BR = Mass of biogas removed per gram VS added (g/ g VS $_{\text{added}}$)
V_0 = Volume of biogas produced (ml, at STP)
ρ_{mix} = Mass concentration of CH_4 + CO_2 in the biogas (g/mL)
m = VS added (g)

Analytical methods and organic matter removal

Total solids (TS) and volatile solids (VS) were determined in the well-mixed samples in triplicate according to standard methods (APHA, 1998). The TOC (total organic carbon) was calculated using relation, TOC = VS/1.8 (Haug, 1993). Total Kjeldahl nitrogen (TKN) was analyzed using a Kjeldahl apparatus (Kjeltec 2100, Foss, Sweden). The ammonia nitrogen (NH_3-N) was measured using the Nessler method and was determined using a spectrophotometer (DR 2500, Hach, USA). The analysis of crude fiber (CF), crude protein (CP), Ether extract (EE), ash, nitrogen free extract (NFE) were done according to the methods described in AOAC (1990). The analysis of neutral detergent fiber (NDF) and acid detergent fiber (ADF) was carried out according to the methods of Goering and Van Soest (1970). The closed reflux titration method was used for total chemical oxygen demand (TCOD) and soluble oxygen demand (SCOD) analysis. pH value was determined using a pH meter (YK-2001 PH, Taiwan). TVFA (Total volatile fatty acids), TA (total alkalinity) and TVFA/TA ratio were determined using Nordman method (Kafle and Kim, 2011; Kim and Kafle 2010). The TS and VS removal of feed during the batch test were calculated based on total mass removal from the testing reactors and the blank reactors (equation (5)).

$$\text{TS or VS removal of feed (\%)} = \frac{(\mathrm{F}+\mathrm{I}) \times \mathrm{X} - \mathrm{I} \times \mathrm{Y}}{\mathrm{F}} \tag{5}$$

where,
F = Total TS or VS feed added to reactor (g)
I = Total TS or VS inoculum added to reactor (g)
X = Calculated TS or VS removal of mixture of feed and inoculum based on total initial and final gram TS or VS present in the testing reactors (%)
Y = Calculated TS or VS removal of inoculum in blank reactors (%)

Kinetic modeling

Due to the role of microbes in the anaerobic process, kinetic models (particularly first-order kinetics) were commonly applied to simulate anaerobic biodegradation. Like the phase of bacterial growth, biogas production rate showed a rising curve, and a decreasing curve indicated by exponential and linear equations (De Gioannis et al., 2009; Kumar et al., 2004). Assuming first-order kinetics for the hydrolysis of particulate organic matter, the cumulative biogas production can be described by equation (6).

$$\mathrm{G(t)} = \mathrm{G_o} \times (1 - \mathrm{e}^{(-\mathrm{Kt})}) \tag{6}$$

where,
G (t) = The cumulative biogas production at digestion time t days (mL)
G_o = Biogas production potential of the substrate (mL)
K = Biogas or methane production rate constant (first order disintegration rate constant) (1/day)
t = Time (days)

Along with biogas production, the duration of the lag phase is also an important factor in determining the efficiency of anaerobic digestion. The lag phase (λ) can be calculated with the modified Gompertz model (Kafle and Kim, 2012) as follows:

$$G(t) = G_0.\exp\left\{-\exp\left[\frac{R_{max}.e}{G_0}(\lambda - t) + 1\right]\right\} \tag{7}$$

where,
R_{max} = Maximum biogas production rate (mL/d)
λ = Lag phase (day)
t = Time (day)
e = exp (1) = 2.7183

A nonlinear least-square regression analysis was performed using SPSS program (IBM SPSS statistics 19 (2010)) to determine K, R_{max}, λ, and the predicted biogas production. At the same time, the standard error and coefficient of determination or correlation coefficient (R^2) were also obtained. The predicted biogas production obtained from the SPSS program was plotted with the measured biogas production using Matlab software R2011b (7.13.0.564). The statistical indicators R^2 and root mean square error (RMSE) were calculated (Bhattarai, et al., 2012a; Bhattarai, et al., 2012b):

$$RMSE = \left(\frac{1}{m}\sum_{j=1}^{m}\left(\frac{d_j}{Y_j}\right)^2\right)^{\frac{1}{2}} \tag{8}$$

where,
m = Number of data pairs
j = j^{th} values
Y = Measured biogas production (mL)
d = Deviations between experimental and predicted biogas production

Critical retention time

Chen and Hashimoto's model (Chen and Hashimoto, 1979; Chen and Hashimoto, 1980) was used to determine the critical retention time for FW (Tosun et al., 2004). This model is a modification of the Contois model (Contois, 1959) and is based on fundamental biochemical principles and has been found to be reliable predictive tool in applications regarding digestion of wastes with substantial TS content (Fongsatitkul et al., 2012). Chen and Hashimoto's model (equation (9)) can be described as follows:

$$\frac{C_t}{Co} = \frac{K_{CH}}{HRT \times \mu_m + K_{CH} - 1} \tag{9}$$

where,
C_t = Outlet substrate concentration (mg/L)
C_o = Inlet substrate concentration (mg/L)
HRT = Hydraulic retention time (days)
K_{CH} = Chen and Hashimoto kinetic constant (dimension less)
μ_m = Maximum specific growth rate of microorganisms (1/day)

Substrate concentration can be expressed in terms of VS or COD. VS or COD removal is an indicator of biogas production in anaerobic digestion process:

$$\frac{C_t}{Co} = \frac{G_o - G(t)}{G_o} \tag{10}$$

where,
G (t) = The cumulative biogas production at digestion time t days (mL)
G_o = Biogas production potential of the substrate (mL)

$$\frac{G_o - G(t)}{G_o} = \frac{K_{CH}}{HRT \times \mu_m + K_{CH} - 1} \tag{11}$$

The equation (11) can be converted to equation (12).

$$HRT = \frac{1}{\mu_m} + \frac{K_{CH}}{\mu_m}\frac{G(t)}{G_0 - G(t)} \tag{12}$$

When hydraulic retention time (HRT) was plotted as a function of $G(t)/(G_0 - G(t))$, a straight line was obtained with the slope K_{CH}/μ_m and the intercept $1/\mu_m$. The critical hydraulic retention time ($HRT_{Critical}$) indicating the time when the washout of micro-organisms occurs is numerically equal to the reciprocal of the maximum specific growth rate (Kafle and Kim, 2012):

$$HRT_{Critical} = \frac{1}{\mu_m} \tag{13}$$

Results and Discussion

Substrate characterization

As shown in Table 1, the TS content of FW was 31.3%

and among which around 88% was represented by biologically degradable materials, which is VS. Chen et al. (2010) reported very high VS/TS ratio (0.98) of FW compared to our study. The FW contained very high amount of protein (40.9, % TS) and fat (48.9, % TS), thus, it was expected to obtain much higher methane yields than animal manure. The theoretical yield for fat (lipids) is about 1000 mL/g VS, and for protein is about 480 mL/g VS, while the theoretical yield for carbohydrate is about 375 mL/g VS (VDI 4630, 2006). There was no fiber (CF) detected in FW. The C/N ratio, 4.1, of FW in our study was similar as reported by Chen et al. (2010) but it was very low compared to as reported by Mshandete et al. (2004), 9.0 as shown in Appendix 1. Sievers and Brune (1978) reported C/N ration in the range of 25-30 to be the optimal range for anaerobic digestion. The TA concentration (14397 mg/L) and pH (8.15) of inoculum was very high in our study so there was no need to add up external compounds such as NaOH, Na_2CO_3, and $CaCO_3$ to maintain pH and alkalinity.

Methanogenic activity of inoculum

Before the BMP test the methanogenic activity of inoculum was tested using highly degradable material (sugar, 1.25 g VS/L) (Table 2). Biogas production started in sugar digesters immediately after some hours of incubation. The average biogas volume of 110 mL/L, 223 mL/L and 93 mL/L was collected on day 1, 2 and 3 respectively (data not shown). Similalry, average methane content in the biogas produced from sugar digesters increased from 10.3% to 32.5% during these 3 days. The biogas yield from sugar digester was calculated to be around 425 mL/L (340 mL/g VS) on day 3. Thus, the biogas production and methane content in the biogas produced from sugar digesters indicates that the inoculum used was active enough for the BMP test.

Biogas productivity of FW

The biogas and methane production rate and cumulative biogas and methane production for FW are shown in Figure 1 and Figure 2, respectively. The BMP test lasted for 60 days. The biogas production started immediately from the first day of digestion in all the digesters. The biogas production rate was 30 mL/d on first day and it rapidly decreased by 1.3 mL/d till day 4. From day 8 biogas production rate increased slowly up to 45 mL/d until day 15 and thereafter it rapidly decreased till day 22 regularly. The biogas production was almost ceased during days 23-28. The reason for low biogas production during days 3-10 and days 23-28 may be because of two phase decomposition process occurring in FW due to high protein and fat content. The conversion of carbohydrates can be very rapid (a few days) but proteins and fats sometimes require several weeks (VDI 4630, 2006). From day 29 again biogas production rate increased and reached peak value of 79 mL/d on day 40. Thereafter biogas production slightly decreased and maintained in the range of 45-68 mL/d during days 41-55. From day 56 the biogas production decreased continuously and produced very low biogas production (<4 mL/d) on days 59-60. Blank digesters produced biogas production rate of 12 mL/d on first day and then decreased until day 4 (<2 mL/d). Thereafter the biogas production from blank digester remained constant (<2 mL/d) until end of the test. The BMP test was terminated after 60 days of digestion. Approximately 90% of biogas production from FW was obtained within 54 days. The specific biogas yield was calculated to be 757 mL/g VS

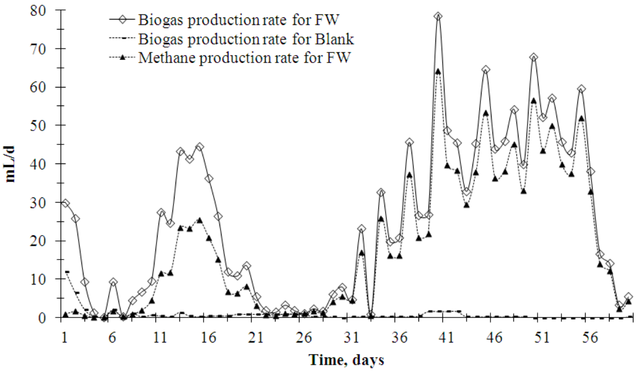

Figure 1. Daily biogas and methane production from FW.

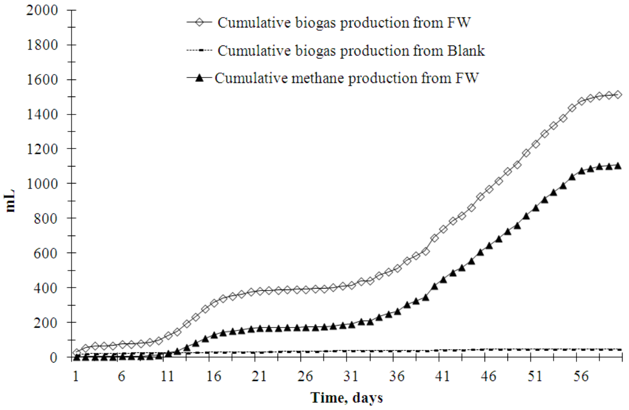

Figure 2. Cumulative biogas and methane production from FW.

after 60 days of digestion.

Figure 3 shows the methane and H_2S concentration in the biogas produced from FW digesters. The methane content in the biogas produced from FW was 2.5% on first day and it continuously increased by 82.5% until day 37 and thereafter almost remained constant until end of the test. The weighted average methane content in the biogas produced from FW was calculated to be 73% (Table 3). Thus, average methane yield from FW was calculated to be 554 mL/g VS (Table 3). The methane yield obtained for FW in our study is in the range as reported in different literatures (Appendix 1). The H_2S concentration in the biogas produced from FW was in the range of 850-2150 ppm. On the first day H_2S concentration was 1530 ppm and it remained almost constant till day 15. On day 16 highest H_2S concentration of 2150 ppm was measured and then the H_2S concentration decreased by 850 ppm until day 39 and thereafter it remained almost constant (Fig. 3).

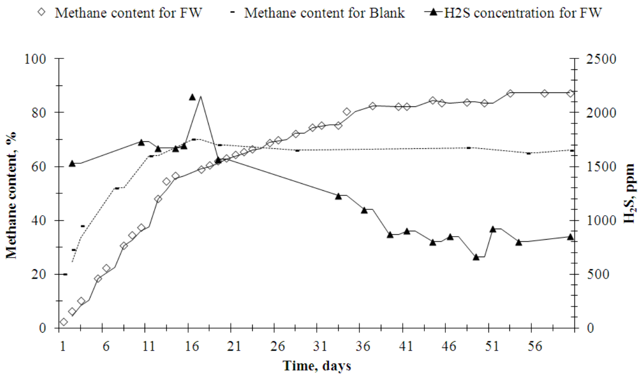

Figure 3. Methane content and H_2S concentrations in the biogas produced from FW.

Table 3. Gas yield, BR and VS removal for FW

	Units	Average value (SD)
Biogas yield	mL/g VS added	757
	m^3/ton(d.w.)	524.28
	m^3/ton(w.w.)	164.10
Methane yield	mL/g VS added	554
	m^3/ton(d.w.)	382.72
	m^3/ton(w.w.)	119.79
Methane content	%	73(21)
VS removal	%	77.3(2.1)
BR	g / g VS added	0.745(0.039)

Table 4 shows the initial and final characteristics of digesters contents. The pH of the digester contents decreased and TA increased after anaerobic digestion. The final pH value of 7.79 and TVFA/TA ratio of 0.081 showed that there was no accumulation of VFA and inhibition to methanogens due to VFA in FW digesters. Raposo et al. (2009) observed stable digestion operation for TVFA/TA ratio in the range of 0.30-0.40 or less but at around TVFA/TA ratio of 0.70 destabilization of digester was observed. Similarly, Islam et al. (2012) noticed TVFA/TA ratios as important criteria for judging stability in batch digesters during anaerobic co-digestion of food waste with SM. The VS removal for FW was found to be 77.3% which is similar as reported by Eiroa et al. (2012) but lower than as reported by Chen et al. (2010) (81%-95%) (Appendix 1). Richard et al. (1999) reported that the mass of biogas removed (BR) includes both converted substrate mass and biogas originated from water hydrolytically consumed. Thus, the calculated BR should be higher than the measured VS destructions. But in our study BR from FW was found to be lower (by 4%) than VS removal (Table 3). Similar to our results, Liu et al.

Table 4. Initial and final characteristics of FW and blank digester contents

Characteristics	Units	FW digester contents		Blank digester contents	
		Initial	Final	Initial	Final
pH		8.16(0.04)	7.79(0.02)	8.20(0.03)	8.0(0.04)
TVFA	mg/L	906(69)	720(45)	798(41)	672(28)
TA	mg/L	9570(104)	10650(73)	9862(91)	9991(85)
TVFA/TA		0.095(0.015)	0.068(0.010)	0.081(0.010)	0.067(0.011)
NH_3-N	mg/L	2210(60)	2240(29)	2300(55)	2460(38)
TKN	mg/L	3015(25)	2986(41)	-	2798(56)
TCOD	mg/L	-	7015(145)	-	7840(95)
SCOD	mg/L	-	3215(289)	-	2773(115)

(2009) also reported lower BR (up to 23%) than VS destructions during anaerobic digestion of green waste. The difference between BR and VS destructions may be due to an error in determination of VS concentration. Hayward and Pavlicick (1990) reported that the excessive loss of VFAs and other volatile compounds during the drying process of VS measurement can cause errors in determining the actual VS destruction.

Results of kinetic modeling

The kinetic parameters estimated for FW using first order kinetic model and the modified Gompertz model are summarized in Table 5. The biogas production rate constant (K) and lag phase (λ) for FW was calculated to be 0.019 and 14.1 days, respectively. High difference between measured and predicted biogas production was found when using first order kinetic model (31.1%) than modified Gompertz model (16.5%). Fig. 4 shows the relation between measured and predicted biogas production with statistical indicators (R^2 and RMSE value). The R^2 value was calculated to be 0.909 and 0.826 when using first order kinetic model and the modified Gompertz model, respectively. Similarly, RMSE value was calculated to be 0.646 and 0.417 when using first order kinetic model and the modified Gompertz model respectively. Thus based on R^2, RMSE and difference in measured and predicted biogas production, the modified Gompertz model was found to be better fitted to experimental results and first order kinetic model is not recommended for FW.

Table 5. Parameters estimated from first order kinetic model and modified Gompertz model for anaerobic digestion of FW under mesophilic conditions

	Units	Value
First order kinetic model[a]		
Biogas production rate constant (K)	1/day	0.019
Standard error		0.010
R^2		0.751
Experimental biogas production (60 days)	mL	1515
Predicted biogas production (60 days)	mL	1043
Difference between measured and predicted biogas production	%	31.1
Modified Gompertz model[a]		
Maximum biogas production rate (Rm)	mL/d	32.9
Standard error		2.4
Lag phase (λ)	days	14.1
Standard error		1.6
R^2		0.904
Experimental biogas production (60 days)	mL	1515
Predicted biogas production (60 days)	mL	1265
Difference between measured and predicted biogas production	%	16.5
T_{50}	days	41.3
T_{80}	days	50.3
T_{90}	days	53.5
$T_{80\text{-}90}$	days	50.3-53.5
T_{Ef}	days	36.2-39.4

[a] At 95% confidence interval
T_{50} = Time period for 50% of total biogas production
T_{80} = Time period for 80% of total biogas production
T_{90} = Time period for 90% of total biogas production
$T_{80\text{-}90}$ = Time period for 80-90% of total biogas production
T_{Ef} = Effective biogas production duration ($T_{80\text{-}90}$ -λ)

It took 50.3-53.5 days for 80%-90% of total biogas production ($T_{80\text{-}90}$). The effective time for biogas production (T_{Ef}) from FW was calculated to be 36.2-39.4 days. The higher difference in T_{Ef} and $T_{80\text{-}90}$ was due to longer λ. The one reason for longer λ was due higher % of CP and EE in FW which has very slow rate of degradation

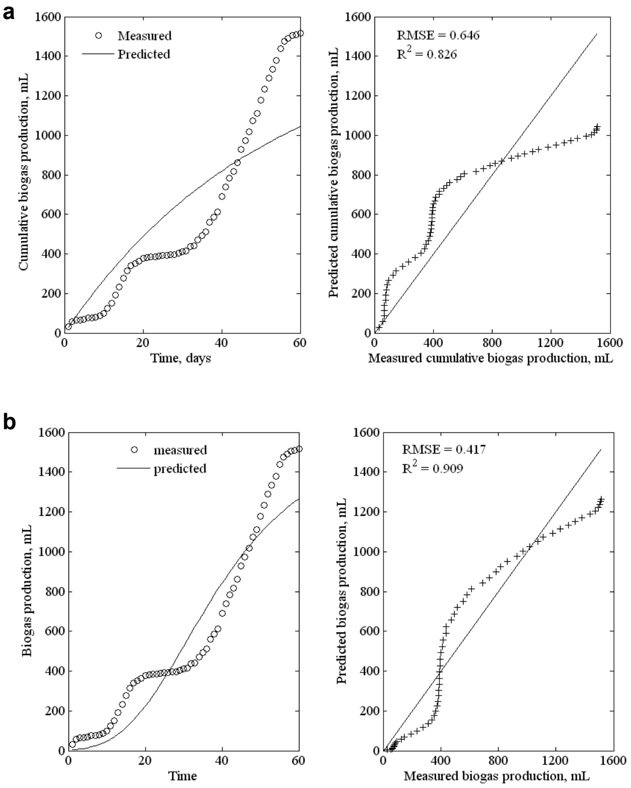

Figure 4. Plot of measured and predicted cumulative biogas production from FW using (a) first order kinetic model; (b) modified Gompertz model.

compared to other carbohydrates materials (Table 1). The other reason may be due to inhibition caused by long chain fatty acids (LCFAs). LCFAs are produced by the hydrolysis of lipids such as fats, oils and greases during anaerobic treatment (Khanal, 2008). The specific substrate utilization rate (μ_m) and critical HRT ($HRT_{Critical}$) for FW under mesophilic conditions was calculated to be 0.075 per day and 13.3 days, respectively, using Chen and Hashimoto model as shown in Figure 5.

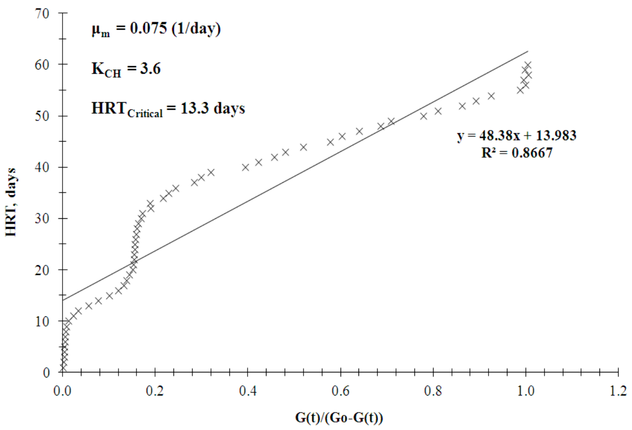

Figure 5. Critical HRT ($HRT_{Critical}$) determinations for FW using Chen and Hashimoto model.

Comparing FW, SM and CM digestion

Appendix 1 summarizes results of previous studies on anaerobic batch digestion of FW, swine manure (SM) and cow manure (CM) under different experimental conditions. The previous studies showed much lower methane yield from SM and CM than FW thus; it showed large scope for co-digestion of FW with SM and CM to improve the methane production from SM and CM digesters. Figure 6 shows the predicted methane yield that could be obtained from SM and CM digesters at addition of different % of FW to respective digesters. The methane potential for FW, SM and CW were taken to be 554, 243 and 206 mL/g VS, respectively (Appendix 1) for predicting methane yield from co-digestion of FW with SM and CM (Fig. 6). The methane production from SM digester could be improved by 13%-115% (Fig. 6) by addition of 10%-90% of FW as co-substrate to SM digester. Similarly, the methane production from CM digester could be improved by 17%-152% (Fig. 6) by addition of FW as co-substrate to CM digester. Mshandete et al. (2004) reported increased in methane yield by 94% when 33% of FW was co-digested with sisal pulp. Callaghan et al. (1999) reported increased in methane yield from 0.28 to 0.38 L/g VS removed from co-digestion of fish offal with cattle slurry (Cattle slurry: fish offal: inoculum = 70:20:10, % w/w). Similalry, Bouallagui et al. (2009) reported improvement in gas production (8%) and digester process when FW was co-digested with fruits and vegetable waste (FVW) compared to FVW alone. Li et al. (2009) reported 106%-121% increased in methane production when 50%-75% of kitchen food waste was co-digested with CM. Kaparaju and Rintala (2005) reported that mixture of potato waste (20%) and SM (80%) increased methane yield up to 30% compared to swine manure alone at OLR of 2.0 g VS/L.d. Similarly, specific methane yield was increased by 19.2% when 25% of herbal extraction residues was co-digested with 75% of SM (VS basis) compared to SM alone (Li et al., 2011).

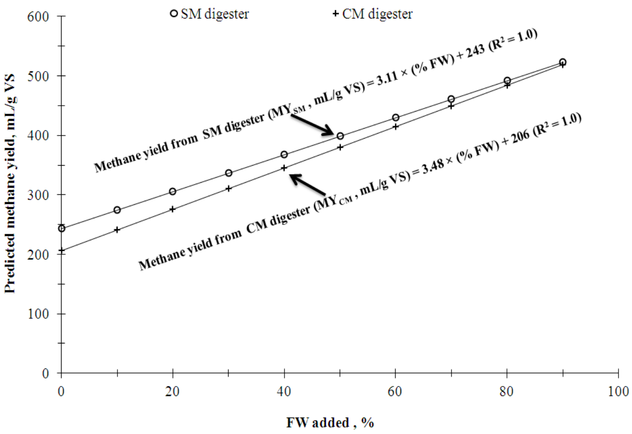

Figure 6. Predicted methane yields from swine manure (SM) and cow manure (CM) anaerobic digesters with addition of different % of fish waste (FW).

Conclusions

In the present study, the biogas productivity of fish waste (FW) was evaluated using batch anaerobic digesters under mesophilic conditions. FW showed very high biogas and methane potential of 757 and 554 mL/g VS, respectively. The modified Gompertz model was found to be best for describing the anaerobic digestion process of FW. The minimum HRT of 13 days is recommended to prevent the washout of biomass for continuous anaerobic digestion of FW. Similalry, total HRT of 50-54 days is suggested for maximum recovery of biogas from continuous FW digesters. Methane production from biogas plant working with animal manure (SM and CM) could be enhanced by addition of FW as co-substrate.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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Appendix 1. Batch test results on fish waste, swine manure and cow manure in different literatures

Feed	Feed name	Feed characteristics					Experimental conditions						Results			Literature
		TS (%)	VS/TS	TKN (% TS)	C/N	Fat (%TS)	F/I	Loading (g VS/L)		DP (days)	DT (℃)	DV (L)	mL CH_4/ gVS	CH_4 (%)	VSR (%)	
								I	F							
Fish waste	FW	31.3	0.88	6.54	4.1	48.6	0.5	5.0	2.5	60	36.5	0.8	554	73	77	This study
	FFW	55.8	0.98	-	3.0	28.6	0.5,1.0	1.5,3.0	3.0	30	36.5	0.5	510,920	59,69	81,82	Chen et al. (2010)
		55.8	0.98	-	3.0		0.5,1.0	1.5,3.0	3.0	30	55	0.5	860,380	69,54	84,95	
	FW	41.2	0.86	5.78	-	-	-	12	-	33	37	0.5	828	-	-	Nges et al. (2012)
	FS	37.7	0.83	6.92	-	-	-	12	-	33	37	0.5	742	-	-	
	FW	28-37	0.74-0.85	9.0-10.2	-	6.8-36.9	1.1-1.3	-	-	70-80	37	-	250-350	-	74-84	Eiroa et al. (2012)
		28-37	0.74-0.85	9.0-10.2	-	6.8-36.9	2.8-3.3	-	-	70-80	37	-	70-250	-	49-72	
		28-37	0.74-0.85	9.0-10.2	-	6.8-36.9	5.7-6.5	-	-	70-80	37	-	40-180	-	49-70	
	FW	32.2	0.55	5.85	9.0	12.6	0.05,1.6	57	-	29	27	0.6	390	-		Mshandete et al. (2004)
	FPW	-	-	-	-	-	1.0	-	-	36	28	0.36	560	-	-	Gumisiriza et al. (2009)
Swine manure	SM	5.64	0.65	13.0	4.8	-	-	-	-	-	-	-	242	-	-	Zhang et al. (2011)
	SM	12.6	0.74	4.3	-	-				90	35	0.80	280	-	61	Xie et al. (2011)
	SM	29.2	0.80	19.3	14.4	-	-	-	-	30	35	0.375	207	-	-	Li et al. (2011)
Cow manure	CM	13.8	0.80	4.9	-	-	2.4	2.1	5.0	30	35	0.50	241	66	45	Ei-Mashad and Zhang (2010)
	CM	6.5	0.76	4.15	-	-	1.0	-	-	100	35	1.5	233	-	-	Lehtomäki et al. (2009)
	CM	23.4	0.59	4.80	5.8	3.5	-	-	8.4	35	35	-	144	-	-	Li et al. (2009)

I: Inoculum; F: Feed; DP: Digestion period; DT: Digestion temperature; VSR: VS removal; DV: Digester volume; FW: Fish waste; FS: Fish sludge; FFW: Fish farm waste; FPW: Fish processing waste; SM: Swine manure; CM: Cow manure