

Influence of Food Waste Composition and Volumetric Water Dilution on Methane Generation Kinetics

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Abstract- Food water composition and the amount of water addition are strong determinants of a digester's performance. Hence, the objective of this paper is to study how variations in the majoring food groups and water additions can affect digester performance. The performance of carbohydrate, protein, lipid and cellulose rich mixed food wastes, subjected to five factors of volumetric dilution, were evaluated in a controlled laboratory scale set up at 38°C and 28°C. Substrate degradation was high for all assays with 86.6 – 100% and 87.1 – 98.0% reduction in VS and COD respectively. Maximum methane (CH₄) yield varied between 362.7 (carbohydrate at 1:2 dilution) and 0.53 m³ CH₄/kg VS (protein at 1:6 dilution) at 38°C and 0.32 (lipid at 1:2 dilution) and 0.52 m³ CH₄/kg VS (protein at 1:6 dilution) at 28°C with the maximum rate of CH₄ production varying between 0.015 (lipids at 1:2 dilution) and 0.053 m³ CH₄/kg VS/day (protein at 1:6 dilution) at 38°C and between 0.006 m³ CH₄/kg VS/day (lipids a 1:2 dilution) and 0.026 (protein at 1:6 dilution) m³ CH₄/kg VS/day at 28°C. Lipid rich waste obtained the lowest yield while cellulose and protein showed interchangeably the highest yield. To successfully digest lipid rich waste a dilution no less than 1:4 was required to improve CH₄ generation and to drastically reduce retention time. Both Bo and maximum rate of CH₄ production increased as dilution factor and temperature increased while lag phase decreased. Results indicate that with sufficiently long retention time, food waste up to a dilution of 1:2 did not experience irreversible inhibition problems and achieved high substrate degradation although sufficient water additions can significantly improve a digester's lag time and CH₄ generation potential.

Keywords- Food Waste; Anaerobic Digestion; Kinetic Study; Small Scale; Methane; Organic Loading Rate

I. INTRODUCTION

Food waste forms a large component of municipal, commercial and industrial waste [1] which continues to pose an environmental and health issue in both industrial and developing countries [2]. Anaerobic digestion provides an alternative mean of disposal as oppose to conventional options such as landfilling and open dumping, and can be applied at a variety of scales. In addition, biogas generated provides a source of energy which is extremely beneficial serving people off the grid. In order to assess the performance of the digester, it is useful to understand the kinetics behind the digestion process. Methane (CH₄) generation kinetics depends largely on the relative quantity of the four major macronutrients present in food waste – carbohydrate, protein, lipid and cellulose. It is therefore important to extract a collection of kinetic coefficients to understand and predict how variations in food waste components can affect a digester's performance.

Recent studies with regard to anaerobic digestion modelling have either opted to utilize synthetic macronutrients for degradation monitoring [3,4], or relied on a sole source to act as a representative macronutrient [5,6,7] or an overall municipal solid waste sample, which varies vastly between locations and usually contains green waste [8,9,10]. Hence, this study aims to understand and predict how variations in food waste components can affect a digester's performance at mesophilic and ambient temperatures, by employing various sources of representative macronutrient food waste.

In addition, studies performed on understanding the influence of dilution on waste performance have been done from the perspective of a large plant operator with variations in percentage total solids (%TS) [11, 12]. However, with over 16 million micro-scale and community based digesters worldwide, with more than 10 million in China and India alone [13] and more than 100 thousand digesters in Nepal [14], it is important to predict a digester's performance based on information provided by an everyday user. Instead of %TS, volumetric waste to water ratio is often the "unit" of measurement used by the everyday users. Therefore, this study's second aim is to evaluate how variations of volumetric waste to water ratio can affect a digesters' performance at mesophilic and ambient temperatures.

II. MATERIAL AND METHODS

A. Waste Characteristics and Preparation

Carbohydrate, protein, lipid and cellulose rich mixed food wastes were prepared by mixing food groups representative of carbohydrate, protein, lipid and cellulose in the ratio 2:1:1:1; 1:2:1:1; 1:1:2:1 and 1:1:1:2 respectively. A mixture of potatoes, bread, rice and pasta was used to represent carbohydrates; chicken and beef was used to represent proteins; vegetable oil and animal fat were used to represent lipids, and a mixture of carrots, spinach and lettuce was used to represent cellulose. Nutrient data for each of these major food groups are detailed in Table 1. It should be noted that the definition of cellulose used and referenced in this paper refers to low lignin content cellulose such as vegetable and fruit waste, as opposed to high lignin green waste such as leaves and bark. Each majoring macronutrient group was then subjected to five dilutions with a volumetric waste to water dilution of 1:2, 1:3, 1:4, 1:5 and 1:6.

TABLE 1 FOOD COMPOSITION (%) OF CARBOHYDRATE, PROTEIN, LIPIDS AND CELLULOSE RICH FOOD GROUPS

Majoring macronutrient group	% Moisture	% Carbohydrates	% Protein	% Fats	% Fibres
Carbohydrate rich food waste	61.3	16.4	6.6	15.1	1.4
Protein rich food waste	65.1	6.1	12.4	16.1	0.7
Lipid rich food waste	44.4	6.1	6.8	42.3	0.7
Cellulose rich food waste	70.9	7.9	5.8	14.8	1.4

¹ Values obtained by working out the average nutritional value from USDA [15] of carbohydrate, protein, lipid and cellulose waste based on ratios used

Each feedstock coupled with its assigned dilution was then blended using an electric blender to homogenize the sample. The average solids COD and VFA concentration of each assay are presented in Table 2.

B. Inoculum

Anaerobic sludge collection from the Woodman Point Wastewater Treatment Plant (mesophilic) anaerobic digester in Perth, Western Australia, was used as the inoculant. The inoculant was tested for active methanogens prior to use. The chemical composition of the inoculant is detailed in Table 2.

TABLE 2 AVERAGE pH, SOLIDS CONCENTRATION AND COD CONCENTRATIONS OF MAJORING MACRONUTRIENT GROUPS TESTED AT FIVE VOLUMETRIC DILUTIONS

Majoring macronutrient group	Dilution waste: water	pH unitless	TS (g/L)	VS (g/L)	TS (%)	COD (g/L)
Majoring in carbohydrates	1:2	4.28	115.6 ± 6.4	114.3 ± 6.5	11.18 ± 0.00	76.52 ± 0.01
	1:3		90.9 ± 6.5	89.9 ± 6.3	8.18 ± 0.06	61.91 ± 0.11
	1:4		70.6 ± 1.8	70.0 ± 1.8	6.62 ± 0.01	51.64 ± 0.06
	1:5		57.9 ± 3.3	57.3 ± 3.3	5.53 ± 0.02	43.44 ± 0.01
	1:6		51.4 ± 1.2	50.7 ± 1.3	4.81 ± 0.03	36.76 ± 0.18
Majoring in proteins	1:2	3.96	112.2 ± 1.8	109.2 ± 1.0	10.92 ± 0.08	63.08 ± 0.02
	1:3		81.6 ± 0.8	80.2 ± 0.6	7.87 ± 0.01	47.64 ± 0.36
	1:4		68.5 ± 0.9	67.4 ± 1.0	6.51 ± 0.04	35.52 ± 0.09
	1:5		56.2 ± 1.2	55.6 ± 1.4	5.31 ± 0.07	28.92 ± 0.03
	1:6		46.4 ± 2.2	45.8 ± 2.2	4.47 ± 0.04	23.24 ± 0.03
Majoring in lipids	1:2	3.78	182.6 ± 8.0	181.2 ± 8.0	17.11 ± 0.47	60.2 ± 0.02
	1:3		123.4 ± 1.8	122.6 ± 2.4	12.36 ± 0.17	45.04 ± 0.15
	1:4		103.9 ± 0.5	103.0 ± 0.6	10.2 ± 0.05	34.04 ± 0.04
	1:5		88.6 ± 1.4	87.9 ± 1.7	8.42 ± 0.02	26.08 ± 0.38
	1:6		76.9 ± 4.3	76.0 ± 4.2	7.33 ± 0.07	19.52 ± 0.17
Majoring in cellulose	1:2	3.94	90.1 ± 1.9	88.0 ± 2.0	8.53 ± 0.14	53.12 ± 0.00
	1:3		66.8 ± 2.6	65.3 ± 2.5	6.54 ± 0.01	37.18 ± 0.12
	1:4		54.4 ± 3.0	53.1 ± 2.9	5.17 ± 0.04	21.6 ± 0.28
	1:5		42.7 ± 1.7	44.6 ± 1.2	4.25 ± 0.25	19.8 ± 0.06
	1:6		38.8 ± 0.6	38.0 ± 0.6	3.7 ± 0.08	17.24 ± 0.33
Inoculent	-	7.37	40.9 ± 0.573	30.4 ± 0.694	4.2 ± 0.043	3.7 ± 0.085

C. Reactor Setup

100ml serum bottles were used for the batch experiments, which were washed and soaked in 10% hydrochloric acid solution overnight and then washed thoroughly with distilled water prior to use. The working volume of 50ml in each reactor comprised of 40ml inoculum, 10ml of the assigned feedstock (waste) and 120mM of bicarbonate, to ensure an optimal pH. Each serum bottle was purged with a mixture of 90% N₂ gas and 10% H₂ gas for 30 seconds before being sealed with a rubber septum seal and aluminium crimps to ensure an anaerobic condition. Each test was performed in duplicate. Duplicates were conducted due to resource constraints. For future studies, it is recommended that additional replicates be performed. In each batch experiment, blank reactors with 10ml tap water and 40ml inoculum were also prepared to serve as the control. Experiments were conducted in two temperature controlled water baths at 38°C (mesophilic) and 28°C (ambient). All reactors were depressurized to atmospheric pressure after the first hour of incubation.

D. Experimental Procedure

All assays were tested for gas production and composition at regular intervals. Testing was done while assays were still submerged in their respective water baths. Following gas testing, each reactor was swirled gently to mix the substrate and microbes. Gas testing was performed until all significant CH₄ production ceased. This took an average of 100 days for assays at 38°C and 187 days for assays at 28°C, although the time differed between each reactor. The final substrate was then tested for pH, TS/VS, chemical oxygen demand (COD) and volatile fatty acids (VFA) to determine the conditions and extent of substrate degradation.

E. Gas Production and Analysis

The biogas accumulated in the headspace of the serum bottles was sampled regularly and the CH₄ and carbon dioxide (CO₂) concentrations were determined. Biogas composition was analysed for CH₄ and CO₂ percentage using a Varian Star 3400 gas chromatograph (GC) equipped with a thermal conductivity detector. The volume of gas produced was determined by displacement using a glass syringe. CH₄ production for each measurement was calculated using both the volume displacement and the percentage of CH₄ for any current reading and its previous reading as seen in Equation 1.

$$CH_4 = \left[\frac{(A + B) \cdot \% CH_{4,t}}{100} \right] - \left[\frac{B \cdot \% CH_{4,(t-1)}}{100} \right] \quad \text{Equation 1}$$

Where

- A is the volume of displaced gas
- B is the volume of headspace gas
- t is the day of measurement

III. KINETIC STUDY

The first order model is commonly used to describe the kinetics of complex waste [5,12]. However, the first order equation still does not factor in the lag phase (λ). In order to take λ into account, a sigmoid function will be used instead of a logistic function. By assuming that the CH₄ generation rate corresponds to the specific growth rate of methanogens, CH₄ generation can be modelled according to the modified Gompertz equation (Equation 2). Other studies that utilized the modified Gompertz equation include Olivares *et al.* [16], Lo *et al.* [17] and Li *et al.* [18].

$$B = B_o \cdot \exp \left\{ \left[- \exp \left[\left(\frac{Rm \cdot e}{B_o} \cdot (\lambda - t) + 1 \right) \right] \right] \right\} \quad \text{Equation 2}$$

Where

- B_o is the max CH₄ generation potential (m³ CH₄)
- R_m is the max CH₄ production rate (m³ CH₄/day);
- λ is the lag phase period (days).

The values of B_o, R_m and λ were determined through non-linear regression curve fitting using SigmaPlot 11.0. SigmaPlot 11.0 utilizes the Marquardt-Levenberg algorithm to estimate the values of model parameters by minimizing the sum of the squared differences between the observed and predicted values.

IV. RESULTS AND DISCUSSION

Cumulative CH₄ production for all assays at mesophilic and ambient temperatures is described in Figure 1. All assays displayed the similar behaviour with a period of lag phase, followed by peak period of CH₄ production. The duration of peak CH₄ production lasted between 12 – 18 days and 15 days respectively at 38°C and 28°C. However, peak production for the former was uniformly higher as compared to the latter for all assays. In general, B_o achieved at 28°C was similar to or slightly lower than that achieved at 38°C. Maximum CH₄ generation ranged between 0.32 – 0.58 m³ CH₄/kg VS, with lipid rich waste at 1:2 dilution having the lowest and cellulose rich waste at 1:4 dilution having the highest (Figure 1). Generally, carbohydrate rich waste had the lowest B_o ranging from 0.33 – 0.42 m³ CH₄/kg VS while protein and cellulose rich waste had interchangeably the highest range of B_o ranging between at 0.41 – 0.50 m³ CH₄/kg VS and 0.44 – 0.57 m³ CH₄/kg VS respectively. At 28°C, protein rich and cellulose rich assays achieved the highest B_o in terms of m³ CH₄/kg VS while lipids and carbohydrates obtained comparably lower B_o. Lipid rich assays had the lowest B_o ranging from 0.32 – 0.43 m³ CH₄/kg VS. Neves *et al.* [7] who also studied mixed food waste stream of major macronutrients, reported a lower range of B_o, ranging from 0.36 – 0.43 m³ CH₄/kg VS. In contrary to current findings, Neves *et al.* [7] reported waste streams with an excess in lipids to have the highest CH₄ yield and waste streams in excess of carbohydrate or cellulose to have the lowest CH₄ yield.

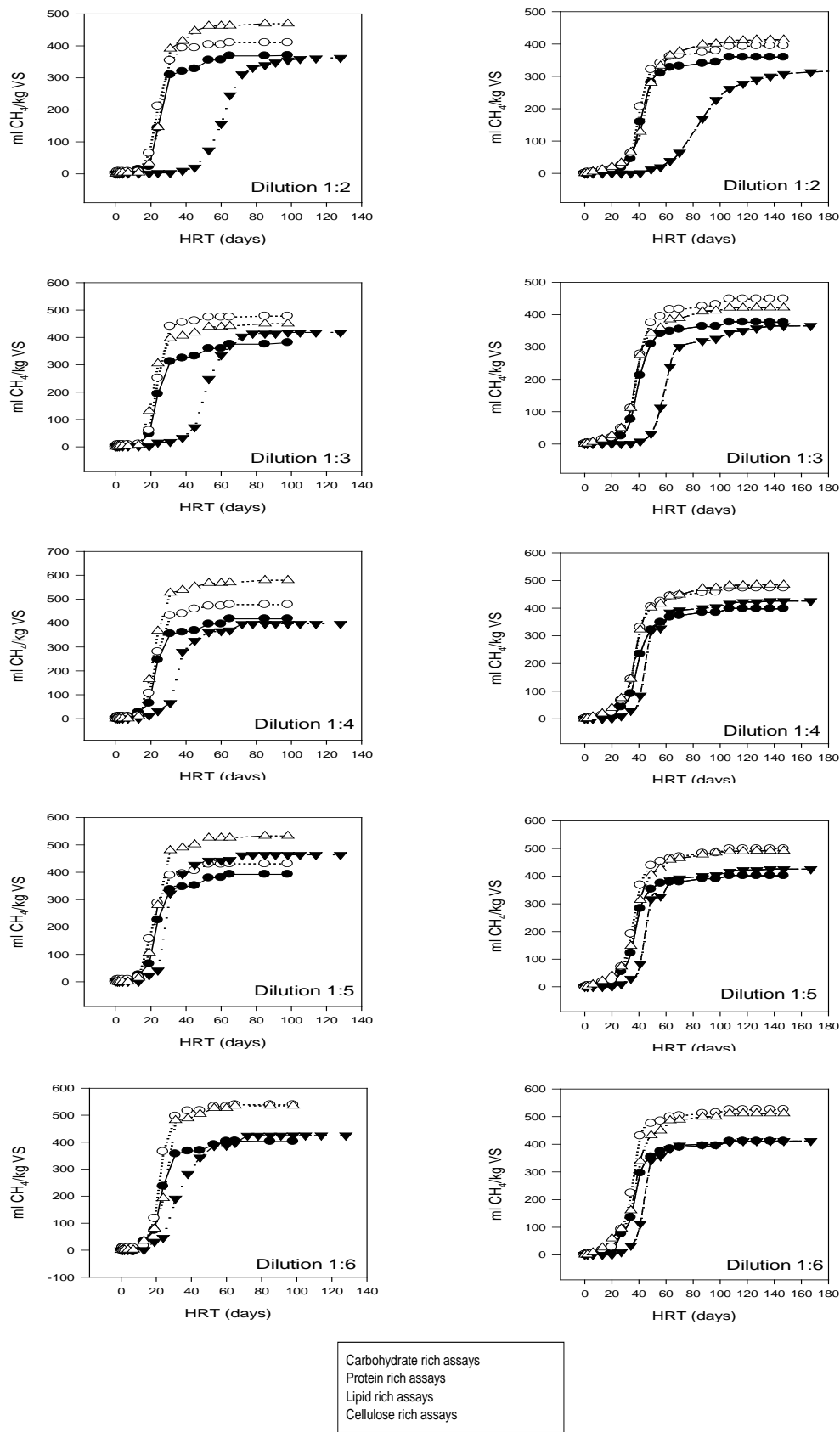


Figure 1
Cumulative CH₄ production for carbohydrate, protein, lipid and cellulose rich mixed FW at five dilution factors at 38°C (right) and 28°C (left)

Studies from Cho & Park [19] found a wide range of Bo from 0.29 – 0.48 m³ CH₄/kg VS for waste streams varying in macronutrients. Findings from Cho & Park [19] agreed with the current study in that carbohydrates had the lowest Bo but protein was found to have the highest achievable Bo. Comparative results from this study against previous similar studies are provided in Table 3. Organic loading rates tested in this study varied between 17.1 – 3.7 % TS. In general, assays with a higher dilution factor obtained a higher Bo at both 38°C and 28°C. Exception to this occurred mainly at 38°C, whereby Bo decreased for dilution above 1:5, and the specific CH₄ production decreased. The first discussed trend shadowed that of Fongsatikul et al. [11] who found that specific gas production increased as %TS decreased. Fongsatikul et al. [11] also observed a 26% increase in specific gas production when TS decreased from 15% to 8% (from 0.54 to 0.73 m³ CH₄/kg VS). However, when too much water is present, the enzymes and microbes responsible for CH₄ production may be diluted, thereby affecting the Bo. It is important to determine the appropriate amount of water additions required for food waste digestion as food waste tends to undergo rapid acidification resulting in a high VFA accumulation, causing the irreversible inhibition of methanogenesis [20, 21]. Regardless of the high concentrations at dilution 1:2 (8.5 – 17.1 %TS), there was no irreversible inhibition to any of the assays tested as evident by the reasonable specific CH₄ yield, and high degradation of VFA (87.1 – 98.1%), COD (90.4 – 96.9%) and VS (82.5 – 100%) (Figure 2).

Food waste high in protein was able to degrade effectively at low dilutions without visible signs of ammonia inhibition. Even low dilutions of lipid rich waste, despite a long lag phase, digested effectively with no irreversible inhibition as evident by CH₄ generation and high substrate degradation varying between 92.4 – 100% (Figure 1 & 2). This is important as long chain fatty acid had been reported to be the main cause of anaerobic inhibition [22, 23]. Hence care should be taken when dealing with high lipid waste. The maximum concentration of lipids prior to inhibition varied between studies – from 2.5 g/L or 0.1 – 0.5 g/L LCFA [24] to 3.5 g COD/L [25] to 20.0 g/L. Hanaki *et al.* [23] studied the inhibition effects of

oil and grease in kitchen waste and found that although 20 g/L of oil and grease concentration did not completely inhibit methanogenesis, varying degree of inhibition were shown between 5 – 20g/L where the 50% inhibition concentration occurred at 10g/L.

With the cumulative CH₄ profile, it was possible to calculate the maximum rate of CH₄ production for all assays by fitting the profile with a modified Gompertz equation. R² for all fittings were above 0.99, confirming the suitability of the modified Gompertz fitting. Caution should be made when using the long λ values presented here, as these values include the start up period, and would not normally be as long for established digesters receiving its daily input of waste [26]. However, they still provide an indication of the behaviour to be expected with each waste stream. All parameter values for the modified Gompertz equation are listed in Table 4.

With the exception of lipid rich waste, λ at 38°C varied between 19.9 – 14.9 days and between 31.5 – 22.5 days at 28°C. Furthermore, with the exception of lipid rich waste, there was no obvious difference between macronutrient groups and between dilution factors at both temperatures. As for lipid rich waste, for both temperature ranges, λ decreased substantially with increased dilution factor, from 48.7 days to 20.2 days (1:2 to 1:6) and 58.9 days to 36.9 days (1:2 to 1:6) at 38°C and 28°C respectively, but remained higher as compared to all other macronutrient mixed waste. However, the longer λ observed in lipid rich waste was only visibly obvious for higher concentration waste, L1:2 – L1:4 for reactors at 38°C and L1:2 and L1:3 at 28°C (Figure 1). The longer λ suggested bacteria needed time to acclimatize to the high concentration of lipids. McCarty [27] noted that the degradation of lipid rich waste occurred approximately 10 days after protein and cellulose. The longer lag time required by lipid rich waste could be attributed to the presence of a higher concentration of complex LCFA that required a longer time to degrade [18, 28]. It has also been reported that the possible adsorption of lipids/LCFA on cell surfaces may hinder access of simple substances, therefore delaying methanogenesis [29]. Irregardless of the long lag time, McCarty [27] revealed that lipids did not directly inhibit the growth of anaerobic microbes, and they needed time to acclimatize to the subjected concentration.

TABLE 3 COMPARITIVE RESULTS OF BO FROM SIMILAR STUDIES (m³ CH₄/kg VS)

Majoring macronutrient group	Neves <i>et al.</i> [7]	Cho & Park [19]	Current study	
			38°C	28°C
Carbohydrates rich	0.37	0.29	0.37-0.42	0.36-0.41
Protein rich	0.39	0.48	0.41-0.54	0.40-0.53
Lipids rich	0.43	-	0.36-0.46	0.32-0.43
Cellulose rich	0.36	0.36	0.50-0.58	0.41-0.51

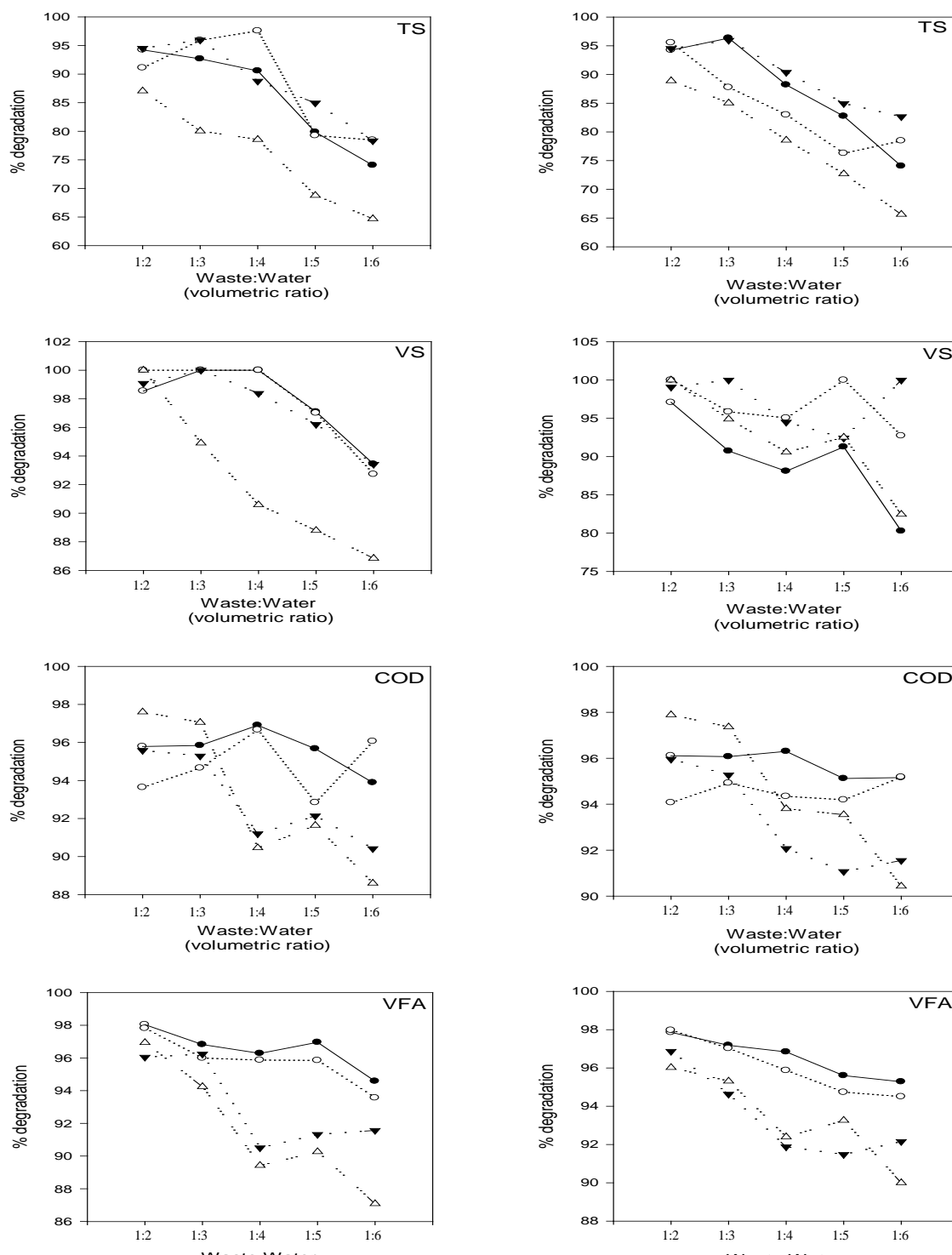


Figure 2

Substrate degradation for carbohydrate, protein, lipid and cellulose rich waste across five dilutions for 38°C (right) and 28°C (left)

The maximum rates of CH_4 production were visibly higher for assays subjected to 38°C as compared to 28°C. This was expected as lower rates of reaction are expected at reduced temperature. With the exception of lipid rich waste, all assays at 38°C achieved a minimum R_m value of $0.03 \text{ m}^3 \text{ CH}_4/\text{kg VS}/\text{day}$. Conversely, all assays at 28°C obtained R_m values below $0.030 \text{ m}^3 \text{ CH}_4/\text{kg VS}/\text{day}$, with the majority below $0.020 \text{ m}^3 \text{ CH}_4/\text{kg VS}/\text{day}$. Generally,

R_m values increased as the dilution increase. This is especially so for lipid rich waste which obtained the lowest R_m values at dilution 1:2 – 1:4 at 38°C and 1:2 at 28°C. Protein rich waste obtained the highest R_m value for almost all dilutions at 28°C, while protein rich and cellulose rich waste had interchangeable highest R_m values at 38°.

TABLE 4 SUMMARY OF KINETIC CONSTANTS FOR CARBOHYDRATE, PROTEIN, LIPID AND CELLULOSE RICH MIXED FW AT FIVE DILUTION (C1:2 – C1:6; P1:2 – P1:6; L1:2 – L1:6 & Cel:2 – Cel:6 RESPECTIVELY AT 28°C & 38°C)

Constant	Units	38°C					28°C				
		C1:2	C1:3	C1:4	C1:5	C1:6	C1:2	C1:3	C1:4	C1:5	C1:6
Bo	m ³ CH ₄ /kg VS	0.36	0.38	0.34	0.38	0.41	0.35	0.37	0.39	0.40	0.40
Rm	m ³ /day	0.03	0.03	0.03	0.03	0.04	0.02	0.02	0.02	0.02	0.02
λ	days	19.0	17.6	16.9	16.6	16.4	31.5	29.3	27.1	26.3	24.1
Bo	m ³ CH ₄ /kg VS	P1:2	P1:3	P1:4	P1:5	P1:6	P1:2	P1:3	P1:4	P1:5	P1:6
Rm	m ³ /day	0.41	0.47	0.47	0.49	0.53	0.39	0.44	0.47	0.49	0.52
λ	days	0.03	0.04	0.04	0.04	0.05	0.02	0.02	0.02	0.03	0.03
Bo	m ³ CH ₄ /kg VS	L1:2	L1:3	L1:4	L1:5	L1:6	L1:2	L1:3	L1:4	L1:5	L1:6
Rm	m ³ /day	0.36	0.42	0.39	0.46	0.42	0.32	0.35	0.36	0.414	0.40
λ	days	0.02	0.02	0.03	0.04	0.02	0.01	0.02	0.18	0.02	0.03
Bo	m ³ CH ₄ /kg VS	Ce1:2	Ce1:3	Ce1:4	Ce1:5	Ce1:6	Ce1:2	Ce1:3	Ce1:4	Ce1:5	Ce1:6
Rm	m ³ /day	0.46	0.44	0.57	0.53	0.53	0.41	0.42	0.48	0.49	0.51
λ	days	0.04	0.03	0.04	0.04	0.04	0.01	0.02	0.02	0.02	0.02
Bo	m ³ CH ₄ /kg VS	19.9	15.1	15.2	16.5	18.4	30.5	25.5	23.7	24.0	22.5

V. CONCLUSION

Results showed the influence of major macronutrients on the CH₄ generation kinetics of a digester. Increasing the dilution factor increased the Bo and Rm while decreasing the λ. CH₄ generation improved with increased dilution for lipid rich waste while cellulose rich waste and protein rich waste offered the highest CH₄ generation. To successfully digest lipid rich waste a dilution no lesser than 1:4 was required to improve CH₄ generation and to drastically reduce retention time. Substrate degradation for all waste was high with VS and VFA degradation ranging between 98.0 – 87.1% and 82.5 – 100% respectively. Maximum CH₄ yield (Bo) varied between 0.36 – 0.53 m³ CH₄/kg VS at 38°C and 0.32 – 0.52 m³ CH₄/kg VS at 28°C. Performance differences between 38°C and 28°C were not large and such digesters have shown their potential in providing users with a fair amount of energy generation throughout the year.

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