Kinetic Evaluation of Co-Digestion of Oarweed with Simulated Food Waste (SFW) in Batch Reactors Studies

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***Abstract*— This study examined anaerobic digestion (AD) by mono and co-digestion of *Laminaria digitata* (LD) with a simulated food waste (SFW) in batch experiments. Different mix ratios of LD and SFW, namely, $LD_{100:0\%}$, $LD_{90:10\%}$, $LD_{75:25\%}$, $LD_{50:50\%}$ were assessed. Results from the batch reactors indicated the mono-digested feedstock $LD_{100:0\%}$ produced the highest cumulative methane yield at 207 ± 0.07 mL $CH_4.gVS^{-1}$ after 34 days. This was followed by $LD_{90:10\ \%}$ with a CH_4 yield of 167 ± 1.43 mL CH_4 g VS^{-1} while the 100% SFW ($LD_{0:100\ \%}$) produces the lowest BMP yield of 30 mL CH_4 g VS^{-1}. The $LD_{100:0\%}$ had the highest BI of 0.67. The co-digested mix ratios in the batch test exhibited both antagonistic ($LD_{90:10\%}$) and synergistic ($LD_{75:25\%}$) effects. The half-life (T_{50} days) for all the mix ratios was a maximum of 3 days with a T_{90} (90 % of methane production) of between 14 - 19 days.**

Keywords: **Co-digestion; batch; biogas; kinetics; biomethane; antagonistic; synergistic; biodegradability.**

I. INTRODUCTION

The societal need to develop sustainable renewable energy sources has seen a recent increase in the amount of research on anaerobic digestion technologies. Biofuels from algae, known as third generation biofuels, are taking a lead interest in this regard. The characteristics of the biopolymer components (no ligin, low cellulose and lipid content) of seaweed, particularly brown algae, make it suitable for methanogenic digestion, and brings advantages over other biofuel feedstocks which displace terrestrial food crops from agricultural production. Macroalgae have been identified as feedstock with sustainable potential for co-digestion with food waste having positive environmental and health benefits [1]. They can be converted to biofuels from thermal, fermentation and various other processes [2]. Organic waste from mainly food waste is a very attractive and potential feedstock for anaerobic digestion due to the high content [3]. Anaerobic digestion (AD) of the organic fraction of municipal solid waste (OFMSW) offers the advantage of both a net energy gain by producing methane as well as the production of a fertilizer from the residuals [4]. One of the biotechnologies developed in the last decades to utilize municipal solid wastes (MSW) for useful energy and materials recovery is anaerobic digestion [5]. Anaerobic digestion is widely applied to treat these diverse ranges of organic waste promoting better landfill management and produces a potential renewable energy source. The EU directives are geared towards diverting organic waste from landfill with energy consumption targeted from renewable energy [1]. The European landfill directive requires member state to take steps required to reduce the quantities of biodegradable municipal waste going to landfill from 75 to 50 and to 35% of the total amount of biodegradable waste produced in 1995 by weight, in periods of 5,8 and 15 years after 2001 respectively [6]. Food waste is a highly desirable substrate for anaerobic digestion with regards to its high biodegradability and methane yield [7]. Food waste is defined as materials that result from the processing, storage, preparation, cooking, handling, or food residual [8], from residences, commercial and industrial institutions. The characteristics of food waste that makes it a good co-substrate has been highlighted by Nayono, Gallert [9]: 1) The concentration of the organic substances should be comparable with biowaste, so that addition will not change significantly loading and hydraulic retention time, 2) The waste should consist of easily degradable organics with a high biogas production potential, 3) it should not contain any dangerous or poisonous substances, which hinder anaerobic digestion 4) it must be available in sufficient quantities at a reasonable price and should be storable 5) it should be pumpable without danger of clogging. Food waste has been used as a co-substrate in a biowaste digester for equilibration of biogas production because of its steady availability, similar biodegradability and high methane potential [9]. Several studies have reported co-digestion of the organic fraction of municipal solid waste with other feedstocks, such as sewage sludge [10], grease trap sludge [11], swine manure [12], energy crops manure [13]. This study utilizes brown macroalgae, Laminaria digitata in co-digestion with stimiluated organic fraction (SFW) of foodwaste for biomethane production.

II. MATERIALS AND METHODS

A. Collection, pre-treatment, 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) in January 2017. The seaweeds were transported in 30 liter bags and were immediately washed to remove marine salts and sediments which can cause mechanical problems in digesters. Sand is

known to be abrasive to moving parts such as mixers and pumps while salt removal leads to more stable digestion [21]. The reactors feedstocks were prepared using only the frond; the stipe and holdfast were discarded. This has an inherent advantage of scalable mariculture for biomass regrowth and production [23]. The fronds were roughly chopped by hand to particle size of about 10 mm using knife. To obtain the dry algal substrate the roughly chopped frond were oven dried at 70 °C for 24 - 48 hrs. This was then pulverized with a Kenwood 100 coffee blender to particle size generally < 1mm. All samples were stored at 4 °C in an airtight gas bag until required.

B. Experimental Batch reactor system

The modified assessment was carried out in a water bath at mesophilic temperature of 35^{O}C. The batch reactors consisted of 500 ml Duran bottles (actual internal volume 580 ml) fitted with rubber stoppers (Fisher brand Height 30 mm, bottom 29 mm) with a 4 mm diameter stainless steel tube (45 mm long) inserted to serve as an outlet port for biogas collection in gas bags and as a purging port for Nitrogen flushing of the headspace. The method has been fully described in [14]. Before starting the BMP test all reactor bottles were pressure tested for air leakage, and once the experiment has commenced, 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 (6 g VS / L: 2 g VS / L). This was to ensure adequate destruction of the volatile solids and overcome possible VFA inhibition [15, 16].

C. Inoculum and operation

The reactors were inoculated with a mixed methanogenic sludge from a full-scale running anaerobic digester (Cockle Park Farm, Newcastle) operating on grass silage. It had following characteristics; pH 7.50, 21.2% TS, 60% VS (%TS), 0.019 Sulphur and C: N of 0.061. All samples were carried out in duplicate and standard deviation (SD) of the data shown in parenthesis.

III. LABORATORY ANALYTICAL METHODS

A. Biogas and methane measurement

The percentage (%) methane from the biogas content was determined using a GC-FID analyser (Carlo-Erba 5160 GC) in split mode with the injector at 150°C and FID at 300°C.Using a 100 µl sample Lock syringe (Hamilton, USA), duplicate headspace samples (100ul) were injected manually every 2 minutes into the GC with the split open 5 turns (100mls min^{-1}). After the initial injection, the GC temperature programme and data acquisition commenced. Separation was performed on an HP-PLOT-Q capillary column (30m x 0.32mm id) packed with 20um Q phase. The GC was held isothermally at 35°C for 90min and heated to 250 °C at 10 °C min^{-1} and held at final temperature for 10 minutes with Helium as the carrier gas (flow 1ml min^{-1}, pressure of 50kPa, split at 100mls min^{-1}. The acquisition was stored on an Atlas laboratory data system. Methane standard were prepared prior to each analysis from 100% analytical grade CH_4 (BOC Gases, UK) by injecting duplicate sample to make a five–point standard curve in the range 20 - 100% CH_4. The volume of biogas produced was measured using a 100 ml BD Plastipak syringe from the gas bags. The % methane calculated was multiplied by the measured biogas volume giving the volume of methane produced [14, 17].

B. Synthetic food waste preparation

The synthetic food waste components, Table III-1 were selected and prepared according to methods reported by [18] and [19]. A representative sample, 50g of each food substrate was weighed, then first chopped into small sizes (1 – 5 cm) with a kitchen knife before maceration and blending for approximately 2 minutes in a kitchen blender (James martin ZX 865) to produce a homogenous mixture of approximately 0.5 - 1 mm typical size.

C. Experimental procedure

Kinetics evaluation used in this study has been fully described in [17]. The different mix ratios used for the batch reactors are given in Table III-2.

Table III-1 Selected types of food substrates used

Fruits (g)	Vegetables (g)	Meat and Fish waste (g)
Apples	Tomatoes	Pork/ham/bacon
Oranges	Onions	Beef
Peaches	Pepper	Fish / Shell fish
Melon	Potatoes	Lamb
Pears	Beans	Chicken
Kiwi	Carrots	Seafood
Water Melon	Cabbage	Sardines
Pineapples	Cucumber	Cod
Tangerines	Mushroom	Mussels
Strawberries	Broccoli	Embed
Grapes/ Lemons	Lettuce	Others/Cakes/Rice

Table III-2 Ratios of LD with SFW used in both batch and continuous reactors study

Ratios	Algae 100: 0 SFW	Algae 90: 10 SFW	Algae 75: 25 SFW	Algae 50: 50 SFW	Algae 25: 75 SFW	Algae 10: 90 SFW	Algae 0: 100 SFW
Batch test	$LD_{100\ \%}$	$LD_{90:10\ \%}$	$LD_{75:25\ \%}$	$LD_{50:50\ \%}$	$LD_{25:75\ \%}$	$LD_{10:90\ \%}$	$FW_{100\ \%}$

In the batch trials the antagonistic or synergistic effects of co-digestion on methane yields was evaluated based on the following equations Eqn III-1 and Eqn III-2.

$$Effects = CH_{4\ MY} - \sum CH_{4\ WMY} \qquad \text{Eqn III-1}$$

$$\sum CH_{4\,WMY} = LD_{CH_{4\,MY}} \times P.LD + FW_{CH_{4\,MY}} + P.FW \quad \text{Eqn III-2}$$

Where; $CH_{4\,MY}$ is experimental determined methane yield of substrates.

$CH_{4\,WMY}$ is weighted average methane yield.

$LD_{CH4\,MY}$ is methane yield for *L. digitata.*

$FW_{CH4\,MY}$ is methane yield for food waste,

P is the percentage of the substrate in the mixture

If $CH_{4\,MY} > CH_{4\,WMY}$ *(synergetic effect)* and $CH_{4\,WMY} > CH_{4\,MY}$ *(antagonist effect).*

The biodegradability index (BI) is defined as ratio of BMP_{exp} / BMP_{theo} [20, 21].

The % VS reduction efficiency is given as; [22]

$$\%\,efficiency = \%\,vs\,in - \%\,vs\,out \div [\%\,vs\,in - (\%\,vs\,in \times \%\,vs\,out)] \times 100 \quad \text{Eqn III-3}$$

Where vs is the volatile solids.

IV. Results and Discussion

A. Characterisation of macroalgae and food substrates

The chemical characteristics and elemental analysis of the macroalgae, food and inoculum samples used in the batch processes are shown in Table IV-1. Based on the elemental analysis results obtained in Table IV-1, and using methods as reported by [23], the stoichiometric equation of the algal samples were evaluated and applied in the Buswell equation to calculate the theoretical methane yield and composition shown in Table IV-2, together with the experimental BMP yield, degradation constant (k) and biodegradability index (BI). From Table IV-1, the total solids (%TS) of the algae feedstock is 86.8% with the organic fraction (% VS) constituting about 61.2 % of the TS. This indicates the biomass feedstock comprises mainly organic matter, which is the predominant precursor to methane formation during AD [24]. The methane yield is affected by the type and composition of the marine biomass [25]. The %TS of the co-substrate (FW) is 10.1% with a %VS content of 61.2 %. The C: N ratio for both the macroalgae (11.7: 1) and food substrate (11.0: 1) are quite similar as shown in Table IV-1 but are still under the ideal range of 15:1 - 30 :1 suggested as optimum conditions for AD operation [26-28]. *L. digitata* has been reported as having a range between 10.9: 1 - 31.9: 1 [29].

Table IV-1 Characteristics of inoculum, macroalgae, and food used for batch and continuous processes

Characteristics	Inoculum	Macroalgae	Food
% TS	26 (0.1)	87	10 (0.1)
% VS (% TS)	52 (0.1)	61 (0.1)	94.0 (0.1)
% Moisture	*	13 (0.1)	90 (0.1)
TKN (g/kg)	*	5.0 (0.2)	2.0 (0.2)
Ammonia (g/L)	1.8 (0.1)	1.7 (1.1)	0.4 (0.6)
Protein %TS (kg)	*	2.7 (0.2)	1.2 (0.5)
Alkalinity (g CaCO3/l)	11	*	*
TVFAs (g/L)	3.4 (0.2)	*	*
% C (% TS)		24 (0.4)	40.2 (0.30)
% H% (% TS)		5	7 (0.1)
% N% (% TS)		2 (0.4)	3.7 (0.9)
% S (%TS)		0.6 (0.2)	0.3
% O (% TS)		38	41 (0.2)
% Ash content		30	8 (0.2)
% TOC	7 (0.2)	30 (0.1)	5 (0.2)
C: N		12 (0.2)	11.0: 1 (0.1)
C:S		40.7: 1 (0.11)	134: 1 (0.2)

In brown algae, the *Laminaria* genus has the capability to take up and store nitrate, with the nitrate content accounting for a major proportion of the TAN [30]. Low C:N ratio < 15 can lead to elevated ammonia levels causing digestion instability [21]. The low C: N ratio obtained for the substrates indicates they might be problematic during the digestion process leading possibly to accumulation of toxic level of total ammonia nitrogen (TAN) [31, 32], which inhibits methanogens [33], and in turn decreases methane yields [27]. Co-digestion of anaerobic feedstocks with food waste (FW) has been proposed as a way to improve the C: N ratio [34], and help enhance stable process stability [1]. Another important factor that should be considered during anaerobic digestion of macroalgae is the production of H_2S. An elevated level of dissolved H_2S is toxic and inhibits methanogens in AD process [35]. H_2S is produced from Sulphur reduction which is proportional to the amount of biodegradable carbon in a feedstock [35]. The C: S ratio in a feedstock has been used to predict the concentration of H_2S in biogas [35]. A C: S ratio of 40 is recommended as minimum ratio for substrate below which accumulation of higher level of H_2S is observed as shown in seaweed fermentation experiments [33]. From Table IV-1, the C: S of macroalgae is 41: 1 while the foods substrate is 134: 1. A range of 29 - 60.3: 1 has been reported for *L. digitata* [29]. Co-digestion of both substrates is expected to improve the C: S and C: N ratios positively enhancing the digestion process synergistically.

Table IV-2 Kinetic analysis of the different mix ratio using the modified Gompertz equation

Parameter	Modified Gompertz						
	LD_{10} 0 %	$LD_{90:1}$ 0 %	$LD_{75:25}$ 5 %	$LD_{50:50}$ 0 %	$LD_{25:75}$ 5 %	$LD_{10:90}$ 0 %	FW_{10} 0 %
Model BMP (ml)-	215.4	179.2	183	129.1	101.9	61.0	51.9

predicted							
Max BMP (ml)- predicted	228.4	187.6	194.4	138.5	110.2	66.6	56.9
R_B (ml/day)	32.2	37.6	27.1	18.1	9.8	7.4	4.6
Lag phase (λ)	0.5	0.2	0.6	1.1	1.8	1.9	2.5
T_{50} (days)	3	2	3	3	3	2	2
R^2	0.96	0.97	0.96	0.94	0.94	0.9	0.91
RMSE	14.2	10.1	12.4	10.1	7.8	5.8	4.5

V. BATCH STUDIES: CH_4 PRODUCTION

The biomethane potential for each LD to SFW ratio was measured under controlled conditions (35 °C) for 34 days. The daily and cumulative biogas and methane production profiles are shown in Figure V-1 and Figure V-2. In assessing the data, biogas contribution from the inoculum was deducted from the cumulative yield. In all the reactors pre-acclimatization of inoculum with macroalgae resulted in negligible lag time in biogas production. The extent of cell wall degradation is known to be critical for the rate of conversion of algae biomass to biogas [36]. Pre-treatment has been shown to aid the decomposition of cells, enhancing methane productivity [37]. Pre-treatment of the macroalgae samples by maceration ensured rapid digestibility of some macroalgae components with naturally large particle size by promoting cell-wall disruption [23], since the macroalgae has a relatively thick cell walls [37] which are tough and protective making them particularly resistant to microbial attack, producing low methane yields during the AD process [36].

Figure V-2 shows the reactors with $LD_{100\ \%,}$ ratio produced the highest biogas and evaluated CH_4 yield (MY) at 619 ± 0.99 mL biogas g^{-1} VS and 207 ± 1.10 mL CH_4 g VS^{-1}, respectively. This was followed by $LD_{90:10\ \%}$ ratio at 477 ± 0.07 mL biogas g VS^{-1} with a slightly lower CH_4 yield of167 ± 1.43 mL CH_4 g VS^{-1} compared to 174 ± 1.89 mL CH_4 g VS^{-1} obtained for the $LD_{75:25\ \%}$ ratio as shown in Figure V-2. The results indicate that as the proportion of SFW ratio added to the mixture increases, the methane yield decreases with 100% SFW $(LD_{0:100\ \%})$ producing the lowest BMP yield of 30 mL CH_4 g VS^{-1}. This value is low compared to reported BMP values for FW of between 0.44 - 0.48 L CH_4 g VS^{-1} [38], 0.18 L CH_4 g VS^{-1} [1], 0.392 L CH_4 g VS^{-1} [39] and 0.18 to 0.73 L CH_4 g VS^{-1} [40]. This dissimilarity in the reported BMP values of FW can be ascribed as a function of the characteristics of the food waste mixture used, with respect to the %TS and %VS content, as the chemical composition of the FW mainly determines its degradability [41]. The approximate 3 fold difference in these BMP yields from FW could be due to the heterogeneous nature of the FW and variability in nutrient content between regions [39]. The characteristics of the FW used in this study was chosen in order to minimise operational disturbance of the process as single digestion of FW as shown to induce high VFA accumulation with low pH [42], and an elevated ammonia /ammonium ion concentrations as a results of high protein content in most FW [43].

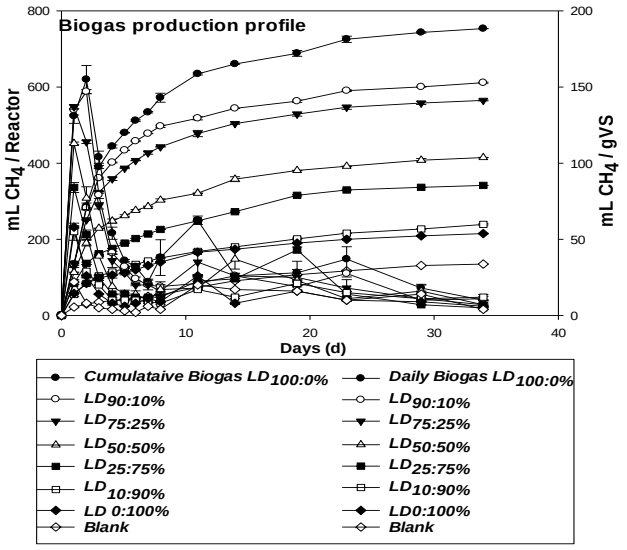

Figure V-1 Cumulative and daily biogas profile for different design mix of algae to food ratio

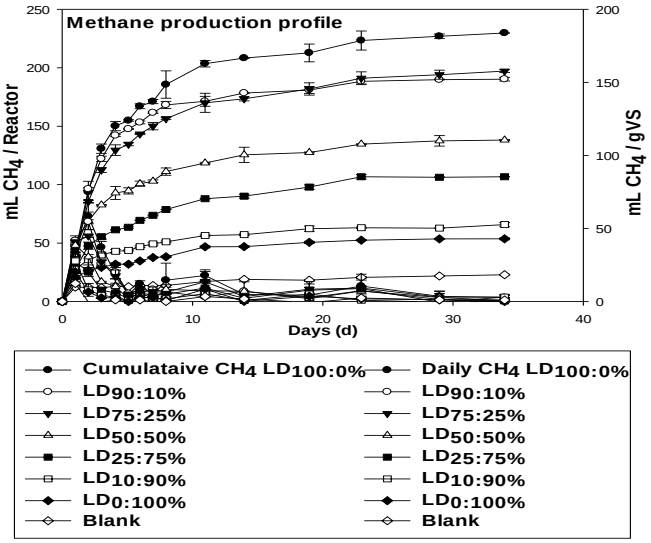

Figure V-2 Cumulative and daily methane profile for different design mix of algae to food ratio

. The BMP result for 100% *Laminaria* feedstock, $LD_{100\ \%,}$ of 207 mL CH_4 g VS^{-1} is in very close agreement with reported values of 218 ± 4.1 mL CH_4 g VS^{-1} [21], 219 mL CH_4 g VS^{-1} [44], and quite close to 184 mL CH_4 g VS^{-1} [45], but lower

than 280 mL CH_4 g VS^{-1} [46] for *L. digitata*. However, it is higher than 141 mL CH_4 g VS^{-1} reported for *L. digitata* (Membere et al., 2015), and 173 mL g VS^{-1} for *Laminaria japonica* [47]. Factors like seasonal variation, species types and geographical location influence the composition of the algae and its BMP yield [44]. All the reactors achieved between 45 - 54% CO_2 compositions in the biogas, except for the no substrate control reactor which had a maximum of 14% (data not shown). This agrees with 51 - 54% CO_2 in biogas reported for co-digestion of macroalgae with FW [1].

VI. Kinetics of CH_4 production

The theoretical methane potential (BMP_{theo}) for the different mix ratios calculated using the Buswell equation as reported in [17] is given in Table VI-1. The BMP_{theo} values are higher than all experimental BMP_{exp} yields. As the proportion of FW increased the estimated BMP_{theo} increased due to the higher percentage of carbon and hydrogen in the co-substrate (FW). Although, the Buswell equation neglects cellular synthesis [48], which involves the maintenance and anabolism of the microbial community [20], and does not account for around 12% of carbon which is consumed by the cell protoplasm [1], the BMP_{theo} yields will therefore be overestimated [20]. The difference between BMP_{theo} and BMP_{exp} ranges from 29% for $LD_{100\ \%}$, to 92% $FW_{100\ \%}$. The high variation and low yields obtained with higher proportions of FW could be due to the characteristics of the SFW feedstock, and its suitability for digestion, but could also have been due to the lack of pre-acclimatization of the microorganisms to the SFW substrate before the start of the experiment, and the pH of the inoculum used (7.5 - 7.6). Compared to other AD processes, reactors operating on FW commonly operate at high pH > 8 level [1] due to the breakdown of proteins producing elevated ammonia [49]. Table VI-1 shows the biodegradability index (BI). Since, the BI is an indication of the biomass degradation efficiency, high BI index corresponds to higher digestion efficiency [20]. The $LD_{100\ \%}$ had the highest BI of 0.67, followed by 0.53 for $LD_{90:10\ \%}$, 0.52 for $LD_{75:25\ \%}$, and $SFW_{100\ \%}$ having the lowest value of 0.08. Reported BI values range from 0.19 to 0.78 for different macroalgal species, 0.46 for *L.digitata* [21], and 0.47 – 0.54 for co-digested macroalgae substrates [33]. Generally, the BMP_{exp} profiles in Figure V-2 showed no sign of a prolonged lag phase, which can hamper the accuracy of a kinetic assessment [21], except for the mix ratios with higher content of SFW (1.06 d for $LD_{50:50\ \%}$, 1.77 d for $LD_{25:75\ \%}$,1.85 d for $LD_{10:90\ \%}$ and 2.52 $SFW_{100:0\ \%}$) compared to 6 days reported for digested brown algae [50].

Table VI-1 Design mix used in the batch reactors operations with BMP results of experimental and theoretical methane (CH_4) yields

	$LD_{100\ \%}$	$LD_{90:10\ \%}$	$LD_{75:25\ \%}$	$LD_{50:50\ \%}$	$LD_{25:75\ \%}$	$LD_{10:90\ \%}$	$FW_{100\ \%}$
C	24 (0.1)	26 (0.1)	28 (0.1)	32	36 (0.2)	39 (0.1)	40 (0.3)
H	5 (0.1)	5 (0.1)	5.5 (0.1)	6 (0.1)	6.6	6.9 (0.1)	7.1 (0.14)
N	2 (0.1)	2.3 (0.1)	2.5	3.0 (0.1)	3 (0.1)	3.5 (0.2)	3.7 (0.1)
O	38 (0.1)	38 (0.2)	39 (0.1)	39 (0.1)	40 (0.1)	41 (0.1)	41 (0.6)
S	0.6 (0.6)	0.6 (0.1)	0.6 (0.2)	0.5 (0.2)	0.4 (0.2)	0.37 (0.1)	0.34
C: N	12 (0.2)	11 (0.3)	11 (0.3)	11 (0.2)	11 (0.4)	11 (0.5)	11 (0.1)
C:S	41 (0.1)	43 (0.2)	50 (0.2)	66 (0.1)	86 (0.4)	104 (0.2)	118 (0.2)
Theo (L CH_4/kg VS)	291	306	327	359	339	401	390
Theo (L Biogas /kg VS)	403	420	444	479	509	526	536
Theo % CH_4	45	46	47	48	49	50	50
BMP (L CH4/kg VS)	207	167	174	115	84	43	31
BMP (L Biogas /kg VS)	619	477	430	280	206	104	80
Bio-degradability Index (BI)	0.8	0.5	0.5	0.3	0.2	0.11	0.08
K (d^{-1})	0.3	0.33	0.3	0.3	0.2	0.33	0.24
R^2	0.99	0.99	0.99	0.98	0.98	0.95	0.87
pH	7.6	7.5	7.6	7.6	7.6	7.5	7.5

The kinetic constant corresponds to the slope of the curve after the lag phase [51]. The almost immediate steep curve (without lag) for all the mix ratios was an indication of fast degradation rates (k), and a result of using the *Laminaria*-acclimatized inoculum [23]. The hydrolysis rate constant was obtained by fitting the data set to the first order rate model [17] using MATLAB software. All the different mix ratios had a similar kinetic decay constants (k) ranging from 0.25 for $LD_{100:0\ \%}$, 0.29 for $LD_{50:50\ \%}$, 0.24 $FW_{100:0\ \%}$, and 0.33 being the highest for $LD_{90:10\ \%}$ and $LD_{10:90\%}$ shown in Table VI-1. A k value of 0.19 [21], 0.33 - 0.36 [23] has been reported previously for *L digitata*, and a range of 0.12 - 0.17 for FW [52]. T_{50} is the substrate half-life, regarded as the time taken to produce half of the methane [53]. The half-life (T_{50} days)

for all the mix ratios was a maximum of 3 days with a T_{90} (90 % of methane production) of between 14 - 19 days, suggesting substrates were readily degradable, and a retention time of 20 - 30 days could be adequate and applied in a continuous digestion process. The modified Gompertz model evaluation used as reported in [17] also exhibited a good fit of the data set, with a correlation coefficient (R^2) ranging from 0.90 - 0.96, and the RMSE value (which represents a statistical indicator to measure the model error [54, 55] range from 4.5 - 14.2 mL CH_4 g VS^{-1}.

VII. Antagonistic or Synergistic Effects of Co-Digestion on Methane Yields

One method of evaluating the potential performance of co-digesting substrates is to determine any synergistic or antagonistic effects. In the current study, these were evaluated based on a method by Cogan and Antizar-Ladislao [1] and [48]; given as the difference between an experimentally determined methane yield (CH_{4MY}) and sum of a weighted average of the individual substrates, ($CH_{4\ WMY}$), Eqn III-1 and Eqn III-2. Labatut, Angenent [48] stated that a synergistic effect results if the CH_4 yield of the mix co-substrates is higher compared to the sum of their individual weighted average CH_4 yield, while an antagonistic effect results when the individual weighted average CH_4 yield is higher. Various factors have been attributed to causing either synergetic effects, such as trace elements, alkalinity, enzymes or other amendments not present in individual samples which can aid biodegradability of the substrate, or antagonist effects such as elevated VFA or pH inhibition and ammonia toxicity [1, 48], and rapid acidification of some component of the FW leading to methanogen inhibition [56]. Table VII-1 is a summary of the effects obtained for the different mix ratios (*LD: SFW*) used. The results indicate that synergistic effects were observed for $LD_{75:25\ \%}$ and $LD_{25:75\ \%}$. For instance, the weighted average methane yield ($CH_{4\ WMY}$) *for* $LD_{75:25\ \%}$ is 163 mL CH_4 g VS^{-1} whereas the methane yield ($CH_{4\ MY}$) of the co-digested substrate of $LD_{75:25\ \%}$ is 174 mL CH_4 g VS^{-1}. Since the positive differential in CH_4 yield is greater than the SD (1.24 mL CH_4 gVS^{-1}), then the synergetic effects of co-digestion of $LD_{75:25\ \%}$ brought about an increase of 6.5% in methane yield. However, the co-digestion of the mix ratios of $LD_{90:10\ \%}$, $LD_{50:50\ \%}$ and $LD_{10:90\ \%}$ produced antagonistic effects in methane yield. Comparing their $CH_{4\ WMY}$ and $CH_{4\ MY}$ values with the SD, shows a decrease of 13.4%, 3.1%, and 12.7% respectively in methane yield of the mixed substrate when juxtaposed with the weighted average of the individual substrate.

Table VII-1 Antagonistic or synergistic effects of co-digestion on methane yields

LD: SFW ratios	$CH_{4\ MY}$	$CH_{4\ WMY}$	Differential ($CH_{4\ MY}$ - $CH_{4\ WMY}$)	% CH_4 increase	Effects
$LD_{100\ \%}$	207 ± 0.1	207	-	-	n/a
$LD_{90:10\ \%}$	167 ± 1.5	189	-22	-13	Antagonist
$LD_{75:25\ \%}$	174.3 ± 1.2	163	11	6.5	Synergistic
$LD_{50:50\ \%}$	115 ± 0.4	119	-4	-3	Antagonist
$LD_{25:75\ \%}$	84	75	9	11	Synergistic
$LD_{10:90\ \%}$	43. ± 1.8	48	-5.5	-13	Antagonist
$SFW_{100\ \%}$	31 ± 0.81	31	-	-	n/a

VIII. Conclusion

Batch trials of mono-digestion $LD_{100:0\%}$ and co-digestion of *L. digitata* with food waste were carried out at different mix ratios. The $LD_{100:0\%}$ reactor produced the highest BMP yield while the 100% SFW ($LD_{0:100\ \%}$) produced the lowest BMP yield. The difference between estimated BMP_{theo} and BMP_{exp} ranges from 29% for $LD_{100\ \%}$, to 92% $SFW_{100\ \%}$. The high variation and low yields obtained with higher proportions of SFW could be due to the characteristics of the SFW feedstock, and its suitability for digestion, but could also have been due to the lack of pre-acclimatization of the microorganisms to the SFW substrate. $LD_{100:0\%}$ exibited highest BI index 0.67 which corresponds to higher digestion efficiency. Both $LD_{90:10\%}$ *and* $LD_{10:90\%}$ showed an antagonistic effect on the digestion process. The half-life (T_{50} days) for all the mix ratios was a maximum of 3 days. The R^2 values ranging from 0.90 - 0.96 from modified Gompertz model shows the data set exhibited a good fit. All the reactors achieved between 45 - 54% CO_2 compositions in the biogas, except for the no substrate control reactor which had a maximum of 14%. Pre-treatment and acclimatisation of the macroalgae samples greatly enhanced digestibility.

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