Waste paper and macroalgae co-digestion effect on methane production

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Abstract

The present study investigates the effect on methane production from waste paper when co-digested with macroalgal biomass. Both feedstocks were previously mechanically pretreated to reduce their particle size. The study was planned according two factors: the feedstock to inoculum (F/I) ratio and the waste paper to macroalgae (WP/MA) ratio. The F/I ratios checked were 0.2, 0.3 and 0.4 and the WP/MA ratios were 0:100, 25:75, 50:50, 75:25 and 100:0. The highest methane yield (386 L kg^{-1} VS_{added}) was achieved at an F/I ratio of 0.2 and a WP/MA ratio of 50:50. A biodegradability index of 0.87 obtained in this study indicates complete conversion of feedstock at an optimum C/N ratio of 26. Synergistic effect was found for WP/MA 25:75, 50:50 and 75:25 mixing ratios compared with the substrates mono-digestion.

Keywords: Algae, Anaerobic co-digestion, Biomass, Renewable energy, Waste paper

Abbreviations: AD, anaerobic digestion; ANOVA, analysis of variance; F/I, feedstock/inoculum; KDP, potassium dihydrogen phosphate; MC, moisture content;

RSM, response surface methodology; TS, total solids; VS, volatile solids; WP/MA, waste paper/macroalgae.

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1. INTRODUCTION

EU and UK Government have tightened their waste disposal regulations, landfill disposal of organic waste will be no longer available after 2020 [1], so alternatives to waste disposal on landfills are required for an efficient and profitable recycling. By the same year of 2020, EU aims to get the 20 % of energy consumption from renewable resources, 10 % coming specifically from biofuels [2,3].

Waste management and energy recovery can be effectively combined in the anaerobic digestion process. Anaerobic digestion performed under controlled conditions also allows pollution reduction and emissions control, reducing greenhouse gas emissions compared to fossil fuels by the utilization of local resources [4]. Biogas is obtained from waste materials through the anaerobic digestion process. In the same process, a by-product with fertilizer value is obtained (the digestate) [5–7]. Upgraded biogas, named biomethane, with a concentration greater than 97 % can substitute natural gas in Combined Heat and Power Plants (CHPP) and may be injected into the gas grid or compressed and used as transport fuel [8].

Paper and cardboard account for 25-30 % of municipal solids waste (MSW) [9,10]; the biggest source of waste paper is industry and businesses with the 52 % of the total [11]. Anaerobic digestion of waste paper is usually studied as part of the anaerobic digestion of MSW. In some cases, the study was carried out on the MSW different fractions that resulted in methane yields for newsprint paper from 58 to 100 L kg^{-1} VS_{added} [9,12]; for office paper 208-369 L kg^{-1} VS_{added} [9,12–15] and for cardboard 96 and 217 L kg^{-1} VS_{added} [9,15].

The ratio carbon/nitrogen (C/N) is one of the most important factor in anaerobic digestion nutrients balance. Carbon is the source of energy for the process and nitrogen is needed for the formation of enzymes that perform metabolism. A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production, while a low C/N ratio causes ammonia accumulation and pH rises excessively. Most authors consider an optimal C/N ratio needs to be in the range 10-30 [4,16,17]. Considering other macronutrients, the C:N:P:S ratio in the reactor should be 600:15:5:3 [16]. Paper materials have a carbon-to-nitrogen (C/N) ratio ranging from 173/1 to greater than 1000/1 [18], these values are very high for anaerobic digestion so a balance of nutrients can be achieved through co-digestion with biomass that contains nitrogen and lower the C/N ratio. Digestion of nitrogenous substrates (C/N ratio less than 15) can lead to problematic digestion caused by excess levels of ammonia, increasing the pH levels in the digester leading to a toxic effect on methanogens population [19,20].

Co-digestion is the simultaneous digestion of a mixture of two or more substrates and offers many advantages, including ecological, technological, and economic benefits, compared to digestion of a single substrate [21]. The purpose of co-digestion is usually to balance nutrients (C/N ratio and macro- and micronutrients) and dilute inhibitors/toxic compounds. Moreover, the co-digestion of two or more complementary substrates may induce a synergetic effect on their biodegradability, causing an increase in the methane yield and production rate [22]. Zhong et al achieved maximum methane yield in co-digestion of algae and corn straw at C/N ratios between 20-25 [23]. Co-digestion of waste paper with *Scenedesmus spp*. and *Chlorella spp*. achieved a maximum methane yield at a C/N ratio of 18 [24].

Further advantages of co-digestion include the unification of feedstock's management by sharing treatment facilities, reducing investment and operating costs. Successful examples of co-digestion include: cow dung and water hyacinth [25]; algal sludge and waste paper [26]; cattle manure and crude glycerine [27]; grass and sludge and [28]; municipal sludge, microalgae and waste paper [4]; algae biomass residue and lipid waste [29] and hay and soybean [21].

Co-digestion can result in a positive effect (synergistic effect) on the degradation of each individual substrate in the mixture and/or an increase in the methane yield kinetics [30]. This improvement may arise from the contribution of additional alkalinity, nutrients, enzymes and trace elements that a feedstock by itself may lack and an increased buffering capacity. Evenly allocated nutrients in co-digestion would support microbial growth for efficient digestion, while increased buffering capacity would help maintain the stability of the anaerobic digestion system [31]. Antagonistic effects may result from low C/N ratios resulting in high total ammonia nitrogen (TAN) released and high volatile fatty acids (VFAs) accumulated in the digester leading to a suppression in the cellulase activity and a decrease in the methane yields. Antagonistic effects can come also from other several factors, such as pH inhibition and ammonia toxicity [32].

Synergistic effects were found on the co-digestion of primary sludge and paper pulp reject with an improvement of 32 % on methane yield [33] and the co-digestion of Taihu blue algae with corn straw (up to 60 % extra methane) [31].

The innovation in this study is that it is the first to assess the optimised conversion of waste paper to biogas through co-digestion with macroalgae (*P. canaliculata*) as a source of nitrogen to balance the C/N ratio in the process. Macroalgae is a great source of biomass in Scotland and its optimization as a feedstock for anaerobic digestion is being addressed. The optimization include both pretreatment and co-digestion for a final improved methane potential. Both feedstock were previously mechanically pretreated in a Hollander beater according to [34,35]. The study was planned to check different levels of feedstock/inoculum ratio (F/I) and waste paper/macroalgal (WP/MA) mixing percentages. A statistical analysis through Response Surface Methodology (RSM) is presented to provide a more comprehensive evaluation of the interaction between the process parameters on the methane production.

2. MATERIALS AND METHODS

2.1. Feedstock and inoculum

Pelvetia canaliculata, a brown macroalgae commonly known as channelled wrack, was collected on-shore (55°55' N 5°09 W) in the Isle of Bute, Scotland in March 2016, refrigerated at 4 ºC and used within 4 days. Mature specimens were chosen of minimum length size of tufts of 10 cm. Small contaminants like plastic or stones were removed but the algae was not washed as the algae is considered in this study a waste material to be used as found in the shore. Waste paper was collected from recycle bins at the School of Computing and Engineering at the University of West of Scotland (UWS) in Paisley, Scotland. Feedstock characterization was shown in Table 1. Both feedstocks were previously mechanically pretreated in a Hollander Beater, the optimized time of pretreatment for macroalgae was 50 min and for waste paper was 55 min. During the pretreatment, the biomass is mixed with water and a pulp is produced, this pulp is directly fed the reactor to help to fluidizer the process. Table 1 details the characterization of the macroalgae and the waste paper.

The sludge used as inoculum was provided by the Strathendrick Biogas Plant (Balfron, Scotland) which used dairy farm cow slurry, distiller's draff and pot ale syrup from local whisky distilleries and some grass silage as feedstock. The inoculum was refrigerated at 4 °C and used next day of collection (total solids (TS): 7.59 %, volatile solids (VS): 88.63 %, ash content: 11.37 %). Total and volatile solids (TS, VS) of both feedstocks and sludge were calculated in duplicate and were obtained submitting random samples of pretreated biomass at 105 °C (for TS) and 550 °C (for VS) until constant weight. The VS are expressed as percentage of TS.

Table 1. Feedstock characterization.

Parameters	Macroalgae	Waste paper
Total Solids (%)	6.17 ± 0.13	2.55 ± 0.02
Volatile Solids (% of TS)	80.18 ± 0.05	97.30 ± 0.07
Ash content (%)	19.82 ± 0.05	2.70 ± 0.03
Carbon (% of TS)	38.15 ±	36.87 ±
Hydrogen (% of TS)	5.48 ±	3.61 ±
Nitrogen (% of TS)	2.63 ±	0.30 ±
Oxygen (% of TS)	34.32 ±	56.52 ±

2.2. Biomethane potential test

The biomethane potential test were set according [36,37]. Erlenmeyer flasks of 0.5 L with a working volume of 0.4 L were used as bioreactors; the biogas was collected in airtight Linde PLASTIGAS bags. Nitrogen was flushed into the headspace of each reactor to preserve the anaerobic conditions and clear up any trace of oxygen from the system. The bioreactors were placed in a water-bath to maintain the mesophilic temperature at 37 °C.

Reactors were fed with a fixed amount of 200 g of sludge (inoculum) and the quantities of macroalgae and waste paper pulp required to meet the feedstock/inoculum (F/I) ratios (0.2, 0.3 and 0.4) and the waste paper/macroalgae (WP/MA) ratios (0:100, 25:75, 50:50, 75:50 and 100:0). The F/I and WP/MA ratios are represent in terms of VS. Control batches were prepared in the same way except for the feedstock addition to assess the inoculum contribution of the methane production. The pH was adjusted to 6.95 ± 0.40 with potassium dihydrogen phosphate (KDP) as a buffer solution. To facilitate the contact biomass-inoculum and degasification of the substrate, flasks were daily shaken during the process. The gas volume was measured with an upside-down cylinder connected to a bubbling flask to maintain anaerobic conditions; the methane content was test with a gas analyser (Drager X-Am 7000). Average results were reported in this paper from duplicated tests in terms of mL of methane per g of VS added of feedstock. Methane yields are given for a dry gas in standard conditions of temperature (0 °C) and pressure (1 atm).

2.3. Kinetics modelling

The methane production is simulated with a first order model as described as follows:

$$M(t) = F(1 - e^{-kt}) \tag{1}$$

where M(t) is the cumulative methane yield (L kg^{-1} VS$_{added}$), F is the maximum methane production (L kg^{-1} VS$_{added}$), k is the methane production rate constant (d^{-1}), and t is the time (d). Biodegradability results were compared after a significance statistical analysis by using analysis of variance (ANOVA) for a single factor. Statistical significance was established at $p < 0.05$ level.

2.4. Methane production potential

Buswell equation provides stoichiometric calculation on the products from the anaerobic breakdown of a generic organic material of chemical composition $C_nH_aO_bN_nS_s$, calculated based on the yield estimates of carbohydrates, lipids, and proteins [38]:

$$\begin{aligned} &C_cH_hO_oN_nS_s + \frac{1}{4}(4c - h - 2o + 3n + 2s)H_2O \rightarrow \\ &\frac{1}{8}(4c - h + 2o + 3n + 2s)CH_4 + \frac{1}{8}(4c + h22o - 3n - 2s)CO_2 + nNH_3 + nS_2N \end{aligned} \tag{2}$$

The equation is derived by balancing the total conversion of the organic material mainly to CH_4 and CO_2 with H_2O as the only external source as under anaerobic conditions. Note that the methane potentials from (Equation 2) do not consider the nutrients required for cell maintenance. From this equation, the biodegradability index could be determined. The biodegradability index (BI) is defined as the ratio of the experimental methane yield to the theoretical methane yield. Higher biodegradability index correspond to higher digestion efficiency.

2.5. Response surface model

A response surface methodology (RSM) with a hexagonal design is used to detects the interactions between the different factors (WP/MA and F/I ratios) and develop a predictive model for the response (methane yield). RSM sets an empirical relation between inputs and outputs variable sets, designing the model that best fit this relation [39]. In the two factors hexagonal design, one factor has 5 levels and the other factor has 3 levels. In this study, the 5 levels factor is the WP/MA ratio (0:100, 25:75, 50:50, 75:25 and 100:0) and the 3 levels factor is F/I ratio (0.2, 0.3 and 0.4). The model was developed with Design Expert v9 software and because of the software configuration, the WP/MA factor was introduced as waste paper percentage in terms of VS (noted as WP) and not as a ratio. The adequacy of the model was verified using the determination coefficient R^2, the adjusted R^2 and the predicted R^2, all of them close to 1 indicating good regression model. The statistical significance was supported by an F-test and their corresponding P-value at the 5 % significance level. Additionally verification through validation points was carried out experimentally (section 3.5).

3. RESULTS AND DISCUSSION

3.1. Feedstock elemental composition

The feedstock composition was carried out by elemental analysis of carbon, nitrogen and hydrogen components. The oxygen content was calculated by subtracting C, N, H and ash content to the sample total solids [40]. Carbon content is similar for both feedstock (Table 1), macroalgae contents 52 % more hydrogen and 776 % more nitrogen than waste paper. Nitrogen content in waste paper is at a trace level (0.3 % of TS). As the contribution to methane from inoculum is less than 10 %, the study of C/N ratio is based on the feedstock [23,31,32]. C/N for macroalgae mono-digestion was 15 while for waste paper the C/N ratio was 123 (Table 2). Highers methane yields were obtained at WP/MA 50:50 (386 L kg^{-1} VS_{added} for F/I 0.2, 369 L kg^{-1} VS_{added} for F/I 0.3 and 357 L kg^{-1} VS_{added} for F/I 0.4) which correspond to a C/N ratio of 26, these findings corroborate the optimum levels given for anaerobic digestion process. Methane yields from reactors at WP/MA 25/75 and 75/25 (C/N ratios 18 and 42 respectively) are similar with differences less than 13 %. C/N ratio of 18 (correspondent WP/MA 25/75) achieved 15 % and 27 % extra methane than mono-digestion of algae for F/I ratios of 0.2 and 0.4 respectively, compared with waste paper digestion these values were around 8 %. Smaller increases were found for C/N ratio of 45 (correspondent WP/MA 75/25), where for the lowest F/I ratio, the increase on methane yield compared to macroalgae digestion was 9 % and for the highest F/I ratio was 13 %. Compared with a C/N of 123 (waste paper), a C/N of 42 achieved similar methane yields. The salinity in the fed samples was below 1 kg m^{-1} as the unwashed algae was dilute during the pretreatment with 40 L of water. This sodium concentration if far lower than the considered toxic level for anaerobic microflora [41].

3.2. Methane production rate and yield

Experimental conditions and results of methane potentials are shown in Table 2.The inoculum contribution to biogas production was never higher than 10 % and was previously subtracted from final methane yields. Reactor with a WP/MA ratio 50:50 produced the highest methane yields for the three F/I ratios studied over a 28-day period, with a maximum value of 386 L kg^{-1} VS_{added} (F/I 0.2) which represents an increase of 30 % compare with mono-digestion of algae and 22 % with mono-digestion of waste paper. At higher F/I ratios the increase in methane yield of WP/MA 50:50 compared with digestion of single substrates is even higher (58 % and 33 % compared with WP/MA 0:100 and 100:0 respectively for an F/I ratio 0.4). For an F/I ratio of 0.3, a 50:50 mixing ratio achieved a 48 % and 50 % extra methane compared with the digestion of only macroalgae and only waste paper respectively. At higher F/I ratios, microorganisms population is small and the anaerobic degradation is more influenced by the process parameters and the effect of a specific parameter can be easily notice.

Although the effect of 50:50 co-digestion is more perceptible at higher F/I ratios, the methane yield increased with decreasing F/I ratios regardless the ratio of substrates mixture. An optimum F/I ratio ensures the presence of the microorganisms population required for the complete anaerobic degradation of the substrate. Knowing the optimum F/I ratio allows a better exploitation of the feedstock. Feeding the reactor with high quantities of biomass that the inoculum is not able to process lead to a loss of feedstock, that is not digested [42]. A decrease in methane yield in the range of 4 % (WP/MA 50:50) to 22 % (WP/MA 100:0) was found when comparing F/I 0.3 to F/I 0.2. This decrease in methane yield is higher when comparing F/I 0.4 to F/I 0.2, -33 % methane yield for WP/MA 50:50 and -45 % methane yield for WP/MA 0:100.

Table 2. Experimental results obtained at the end of the biodegradability tests.

F/I	WP/MA	C/N	CH_4 yield (ml/gVS)	k (s^{-1})
0.2	0:100	15	297 ± 14	0.16 ±0.01
	25:75	18	341 ± 20	0.18 ±0.01
	50:50	26	386 ± 25	0.23 ±0.01
	75:25	42	325 ± 19	0.13 ±0.01
	100:0	123	316 ± 14	0.17 ±0.01
0.3	0:100	15	250 ± 12	0.10 ±0.01
	25:75	18	294 ± 5	0.15 ±0.01
	50:50	26	370 ± 13	0.18 ±0.01
	75:25	42	280 ± 25	0.15 ±0.01
	100:0	123	247 ± 23	0.14 ±0.01
0.4	0:100	15	163 ± 19	0.11 ±0.01
	25:75	18	207 ± 15	0.16 ±0.01
	50:50	26	257 ± 22	0.16 ±0.01
	75:25	42	185 ± 11	0.15 ±0.01
	100:0	123	193 ± 16	0.08 ±0.01

Results from kinetic modelling of waste paper and macroalgae co-digestion are shown in Table 2; faster degradation rates, indicated by higher methane production rate (k) were achieved for co-digestion test compared with mono-digestion. WP/MA of 50/50 achieved the highest methane production rate for the three different F/I ratios with a maximum k of 0.23 d^{-1} at an F/I ratio of 0.2, which stands for an increment of 43 % compared with only macroalgae and 35 % compared with only waste paper (Figure 1).

At higher F/I ratios, similar increments on kinetic constant were forum between 50:50 co-digestion ratio and mono-digestion systems. Higher methane production rate constants were achieved from WP/MA of 15/75 and 25/75 compared with the mono-digestion test even though the increase in methane yields was not significantly high. Constant rates increased with decreasing F/I ratios for feedstock mono-digestion and co-digestion at 50:50. For WP/MA ratios of 25:75 and 75:25, no evident trend can be noticed on kinetic constants with F/I variation, the values maintain constants around 0.16 ± 0.2 s^{-1}.

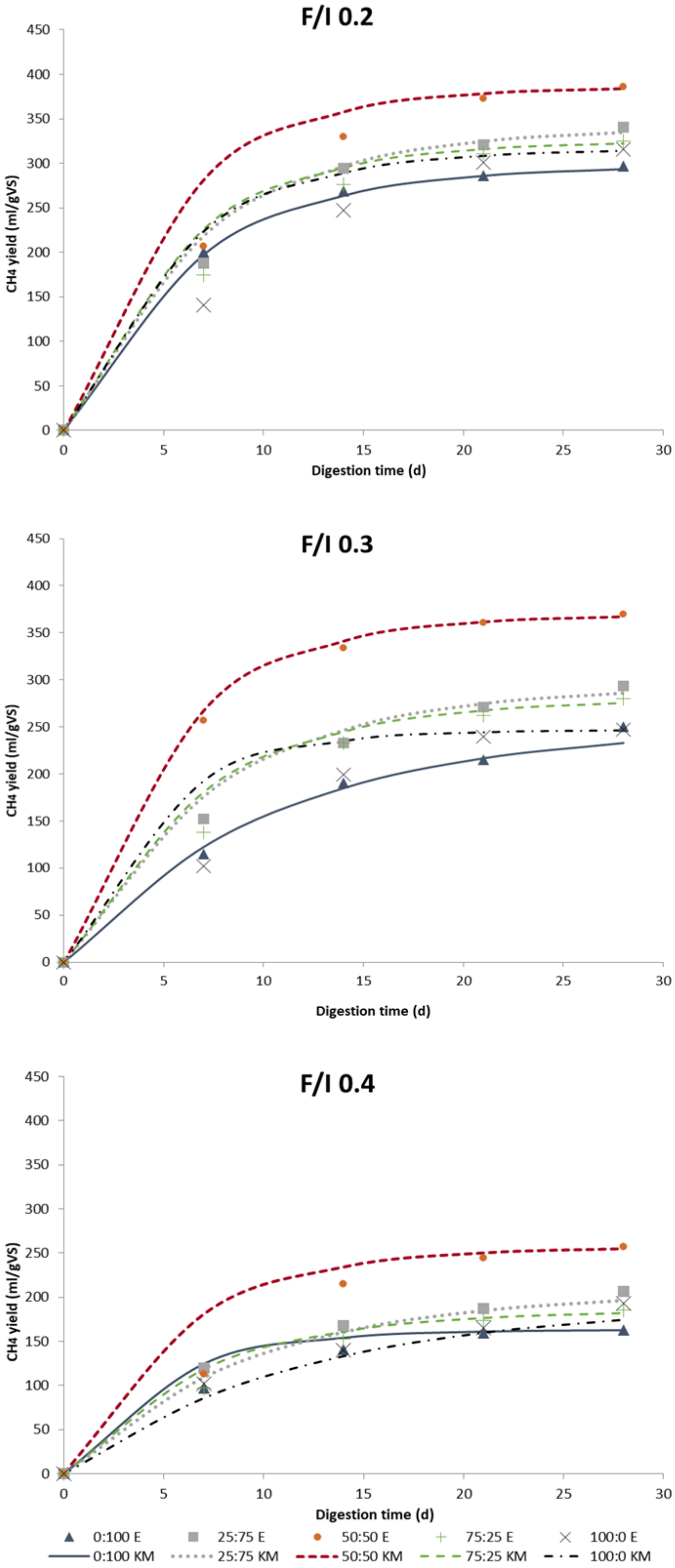

Figure 1. First order model fitting at various co-digestion and F/I ratios, E: experimental points; KM: first order kinetic model.

3.3. Synergistic or antagonistic effect

Synergistic effect is evaluated based on the weighted methane yield from the mixture co-digestion (Equation 3), calculated as the sum of the products of the methane yield of each individual substrate multiplied by its percentage in the mixture in terms of VS.

$$\text{Wieghted } CH_4 \text{ yield} = CH_4 \text{ yield (WP)} * \%\text{WP} + CH_4 \text{ yield (MA)} * \%\text{MA} \qquad (3)$$

Table 3 summarizes this analysis for co-digestion mixtures of waste paper with macroalgae *P. canaliculata*, showing the differences between the methane yields from co-digestion samples and the weighted methane yields calculated from Equation 3. A synergistic effect was found for co-digestion ratio of WP/MA 50:50 at the three different F/I ratios, with an improvement of 31 % on methane yield for high F/I ratio while a 21 % on low F/I ratio. Although no evidence was shown in the present study, it was suggested that the presence of waste paper in the digestion might induce cellulase excretion by bacteria such as *Clostridium themocellum*, facilitating the degradation of cellulosic materials [43]. Further research is required to determine the presence of celluase-secreting microorganisms in the culture. Smaller increases in methane yield were found on samples WP/MA 25:75 and 75:25 compared with their weighted methane yields. Increasing in methane yield and the synergistic effect increased with increasing F/I ratio for WP/MA 25:75 (11 % increase on methane yield for F/I 0.2 and 17 % for F/I 0.4). While for WP/MA 75:25 the synergistic effect was null for F/I ratios of 0.2 and 0.4 and an increase on methane yield of 12 % was achieved for F/I 0.3.

Table 1. Co-digestion effect for waste paper and macroalgae and biodegradability index.

F/I	WP/MA	Theoretical CH_4 yield	BI	Weighted CH_4 yield	Increasing on CH_4 yield (%)	Effect
0.2	0:100	436	0.68	297	0	n/a
	25:75	441	0.77	302	11	Synergistic
	50:50	446	0.87	307	21	Synergistic
	75:25	450	0.72	311	4	Synergistic
	100:0	455	0.69	316	0	n/a
0.3	0:100	436	0.57	250	0	n/a
	25:75	441	0.67	249	15	Synergistic
	50:50	446	0.83	249	33	Synergistic
	75:25	450	0.62	248	12	Synergistic
	100:0	455	0.54	247	0	n/a
0.4	0:100	436	0.37	163	0	n/a
	25:75	441	0.47	171	17	Synergistic
	50:50	446	0.58	178	31	Synergistic
	75:25	450	0.41	186	0	n/a
	100:0	455	0.42	193	0	n/a

3.4. Theoretical methane yield and biodegradability index

Table 3 summarizes the theoretical methane yields obtained from the Buswell equation (Equation 3) the BI for the co-digestion of waste paper and macroalgae.

Biodegradability index increases with decreasing F/I ratios, with a maximum percentage of degradation of 87 % at a F/I 0.2 and WP/MA 50:50. Studies have shown that the Buswell formula does not account for around 12-15 % of the organic matter fed to the reactor as this is consumed by the cell protoplasm [32,44], so the 87 % of degradation for a 50 % mixture waste paper and macroalgae means a complete degradation of the substrate. For a F/I of 0.3, the BI of WP/MA 50:50 reactor is still high (0.83), but a big decreased is found for F/I 0.4 (0.58). For mono-digestion of macroalgae, BI range from 0.68 for low F/I and 0.37 for high F/I. Similar values were found for mono-digestion of waste paper, with a BI of 0.69 for 0.2 F/I and 0.42 for 0.4 F/I. Reactors with WP/MA of 27:75 and 75:25 showed comparable behaviour on their BI, ranging from 0.44±0.3 for high F/I to 0.74±0.02 for low F/I.

It must be noted that the theoretical methane yield from Buswell equation is subject to some uncertainty due to sample heterogeneity. Heterogeneity in the sample may have resulted in a difference between the sample characterized and in turn the calculated theoretical methane yield and the tested substrate.

3.5. Process Modelling

The mathematical model associated with the response in terms of actual factors is shown in Equation 4 and the response surface is showed in Figure 2 (right).

$$CH_4\ yield = -239 + 4.98 \cdot WP + 3955 \cdot F/I - 0.61 \cdot W \cdot F/I - 0.05 \cdot WP^2 - 7683 \cdot F/I^2 \qquad (4)$$

By considering the coefficients of the model, it was possible to see the extent of impact of each term on methane yield, the highest impact correspondent to F/I and quadratic F/I, while the waste paper percentage in the co-digestion had a relative minor impact on methane yield.

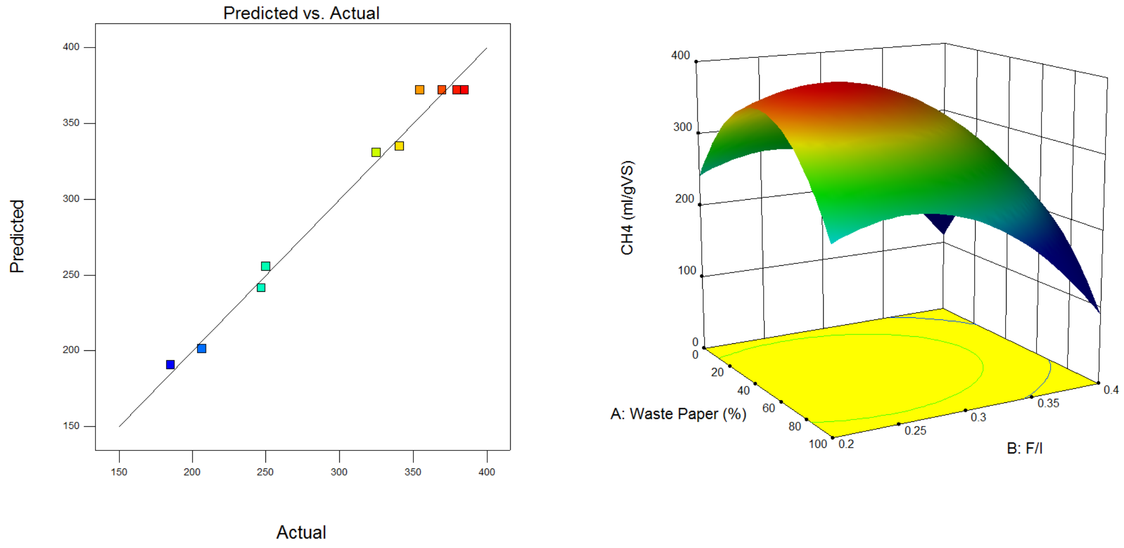

Figure 2. Scatter (left) and response surface (right) plot for methane yield model.

The adequacy of the model was verified using the determination coefficient R^2, the adjusted R^2 and the predicted R^2, all of them close to 1 indicating good regression model. The statistical significance was supported by an F-test and their corresponding P-value at the 5 % significance level (Table 4).

Table 2. ANOVA test for anaerobic process modelling.

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	
Model	49919.85	5	9983.97	55.46	0.0009	significant
A-Waste Paper	155.63	1	155.63	0.86	0.4051	
B-F/I	18773.25	1	18773.25	104.28	0.0005	
AB	9.28	1	9.28	0.052	0.8315	
A^2	20356.10	1	20356.10	113.07	0.0004	
B^2	13993.71	1	13993.71	77.73	0.0009	
Residual	720.12	4	180.03			
Lack of Fit	195.12	1	195.12	1.11	0.3685	not significant
Pure Error	525.00	3	175.00			
Cor Total	50639.97	9				

R^2 =0.9858; Adj. R^2 =0.9680; Pred. R^2=0.8429; Adeq. Precision=17.45

The scatter plot (Figure 2 (left)) shows that the predicted and actual values are distribute near to a straight line and a satisfactory correlation between them is observed. This demonstrates that the model on Equation 4 can be effectively applied. Surface plot (Figure 2 (right)) showed that higher methane yields were obtained where the F/I ratio was below 0.3 and the waste paper percentage was around 50 %. A strong decrease in methane yield is observed for F/I ratios above 0.3, also showed by line B in the perturbation plot (Figure 3 (left)). Perturbation plot also shows that both factors have a quadratic behaviour, factor A (waste paper percentage) followed a symmetric curve with its maximum at 50 %, this effect of the waste paper percentage on the methane yield is similar for low and high F/I (Figure 3 (right)). The maximum methane yield for factor B (F/I ratio) is achieved at around 0.25, decreasing abruptly after that point. Based on the response surface model showed in Equation 4, an optimization study was conducted using Design-expertV9 software. The optimization criterion was to maximize the methane yield within the design space. A maximum methane yield of 387 L kg^{-1} VS_{added} was found at waste paper percentage of 48 % and an F/I ratio of 0.26. At this optimum point allowed 30 % extra methane compared with the maximum macroalgae mono-digestion and 22 % more methane that the maximum correspondent to mono-digestion of paper.

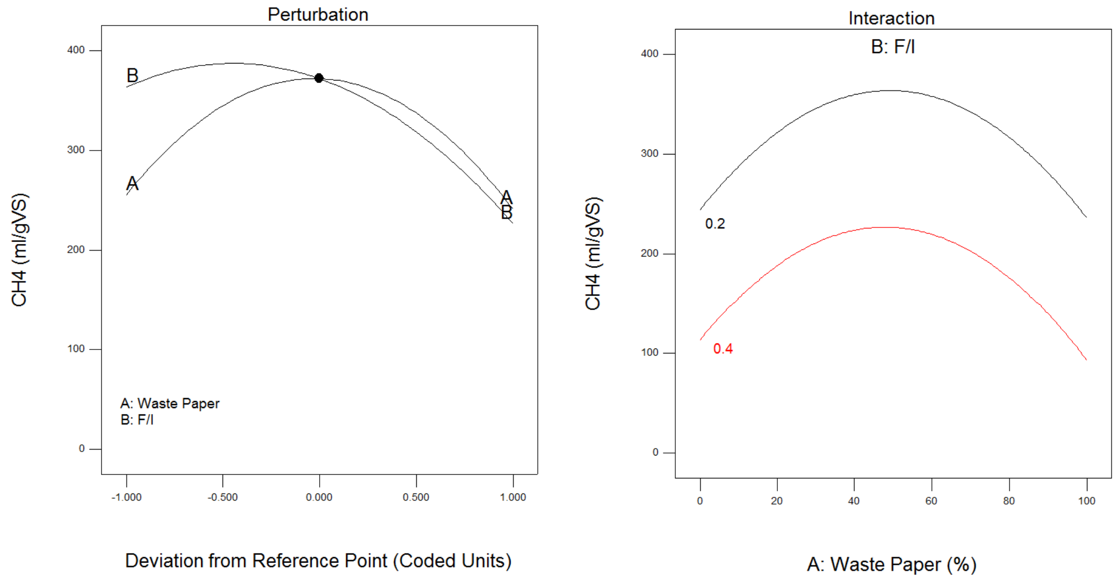

Figure 3. Perturbation (left) and interaction (right) plots for methane yield model.

To check the validity of the proposed model, two validation experiments were carried out in duplicate using different input parameters from the design matrix within the experimental range. The validation experiments were performed under the same experimental conditions that the points used to build the model. These results were compared with the predicted results from the model and found to be in good agreement (Table 5).

Table 3. Validation points for methane yield model.

Experiment	F/I	WP/MA		Methane yield (ml/gVS)
1	0.4	50	Experimental	257 ± 0.10
			Model	226
			Error (%)	12
2	0.2	50	Experimental	386 ± 0.15
			Model	363
			Error	6

4. CONCLUSIONS

A maximum methane yield of 386 L kg^{-1} VS_{added} was found for a mixing ratio of 50:50 achieving an improvement of 30 % and 22 % compared with the mono-digestion of macroalgae and waste paper respectively. Synergistic effect was found for macroalgae and waste paper co-digestion compared with the mono-digestion due to a balance in the C/N ratio. A maximum biodegradability index of 0.87 indicates a complete biodegradation of the feedstock during co-digestion at C/N of 26. F/I ratio had an enormous influence on the methane yield with maximum values achieved at F/I of 0.2. Overall the results showed that co-digestion of waste paper with macroalgae at low F/I ratios is an efficient option for methane production and waste management.

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