



VALORIZATION OF FOOD WASTE FOR BIOGAS PRODUCTION; EFFECT OF CO-ENSILING WITH MAIZE STRAW AT DIFFERENT C/N RATIOS

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Abstract

Food waste (FW) contribute to emission of greenhouse gases as well as environmental pollution. One way of reducing the impact of FW on the environment is by using it for biofuel production. The yield of biofuel from FW can be improved if the substrate is pretreated. In this study, ensiling was used as a cost effective method of pretreating FW for biomethane production. Co-ensiling of FW and maize straw (MS) was carried out at carbon to nitrogen ratios (C/N) of 20, 25, 30 and 35 for 210 days at ambient temperature. Thereafter, the biomethane potential (BMP) of the silages was determined using an automatic biomethane potential test system. Results showed that ensiling reduced both structural and non-structural carbohydrate components of the silages. BMPs of 385.58, 497.39, 520.53, 551.37, 542.16 and 517.29 mL/gVS from the unensiled FW, ensiled FW without MS, co-ensiled FW at C/N ratio of 20, co-ensiled FW at C/N ratio of 25, co-ensiled FW at C/N ratio of 30 and co-ensiled FW at C/N ratio of 35 respectively were obtained. A kinetic evaluation showed that the dual pool model gave a better prediction of the experimental BMP of all substrates than the first-order model and the modified Gompertz model.

Keywords: Anaerobic digestion, Ensiling, Kinetic study.

1.0 INTRODUCTION

Every year, 40% of Nigeria's total food production is wasted, thereby increasing the country's greenhouse gas emissions by 5% [1]. Indeed, food waste (FW) is a major component of most municipal solid wastes that contribute to environmental pollution [2]. Due to its high pollution potential, many methods have been devised to handle FW with some of the methods generating further polluting streams into the environment. Some of the commonly used methods for the handling of FW include incineration, composting, landfilling and anaerobic digestion (AD). A life cycle assessment by Gao et al [3] shows that AD produces the lowest pollution stream when used to handle FW.

Besides its ability to produce the least polluting streams compared to other FW handling processes, AD also produces biogas which is a form of renewable energy. The yield of biogas from FW varies with the composition of the FW. FW that contains a high

percentage of fats and lipids produces more quantity of biogas compared to FW that contains more carbohydrates and proteins [4]. Besides operating parameters like pH, temperature and organic loading rate, the carbon to nitrogen ratio (C/N) of FW can also significantly affect biogas yield from AD. It has been reported that a C/N of 25 – 30 is the optimum for biogas yield [5]. A low C/N of a substrate is an indication of a high nitrogen content and could lead to ammonia inhibition that may result to poor gas yield. On the other hand, a high C/N (>30) is an indication of inadequate nitrogen that is required for the growth of anaerobic microbial community. In order to overcome the effect of a low or high C/N during the AD of FW, it is necessary to co-digest it with an appropriate substrate.

In order to increase biogas yield from the AD of FW, pretreatment is often required. During pretreatment, the rigid structure of a substrate is disrupted, thereby enhancing enzymatic hydrolysis. Such pretreatment

processes could be thermal, mechanical, chemical, biological or a combination of some or all of the processes. Amongst these pretreatment processes, thermal pretreatment has been reported to be the most efficient method of FW pretreatment [6]. However, thermal pretreatment is associated with a high energy input [7], making it less attractive. One method that has been scarcely used for FW pretreatment is ensiling.

Ensiling is a process in which the water soluble carbohydrates content of a substrate is converted to organic acids under anaerobic conditions [8]. The organic acids formed during ensiling can disrupt the rigid structure of the substrate and make it more susceptible to microbial hydrolysis. Recently, Valentino et al. [9] demonstrated that biomethane yield can be improved from organic fraction of municipal solid waste by enhancing the formation of organic acids in a two-phase AD process. If ensiling is properly done, organic acids that can enhance the production of biogas can be formed in good quantity [10]. To the best of our knowledge, there is no evidence in literature that ensiling has been used to pretreat food waste for biogas production. Therefore, the objectives of the present study were to (i) investigate the effect of ensiling on the structural carbohydrate component of FW (ii) investigate the effect of ensiling on the biomethane potential of FW (iii) investigate the effect of co-ensiling with maize straw on the BMP of FW (iv) carryout a kinetic study of biomethane production from FW.

2.0 MATERIALS AND METHODS

2.1 Substrates and Inoculum

The FW was obtained from some major restaurants in Port Harcourt, Nigeria and consisted mainly of vegetable, *eba*, meat, fish and bones. The FW, after the removal of hard bones, was blended using a kitchen blender (7000 series, Philips, Germany). The

inoculum used was digestate from an anaerobic digester producing biogas. The maize straw (MS) used was the same as the one used in the study of Undiandeye et al. [11]. The characteristics of the FW, MS and inoculum are listed in Table 1.

Table 1: Mean values (n=3, ± standard deviation) of parameters of substrates and inocula

Parameter	Unit	FW	MS	Inoculum
Total solids	%	18.49 ± 2.78	95.13 ± 1.11	6.97 ± 1.13
Volatile solids	%TS	66.37 ± 2.16	90.71 ± 2.37	65.74 ± 2.39
pH	-	6.94 ± 1.38	5.63 ± 0.33	7.38 ± 0.59
WSC	g/L	30.27 ± 3.92	27.84 ± 1.39	ND
Lactic acid	g/L	1.98 ± 0.13	3.29 ± 0.03	ND
Butyric acid	g/L	0.19 ± 0.03	0.02 ± 0.00	ND
Acetic acid	g/L	1.28 ± 0.07	1.48 ± 0.15	ND
Ethanol	g/L	0.42 ± 0.01	0.75 ± 0.01	ND
Total carbon	%TS	50.14 ± 3.69	42.15 ± 4.74	ND
Total nitrogen	%TS	2.89 ± 0.17	0.93 ± 0.41	ND
C/N	%TS	17.35 ± 1.67	45.32 ± 3.97	ND

WSC: water soluble carbohydrate;

ND: not determined

2.2 Ensiling Process

Ensiling was carried out by mixing different proportions of FW and MS to obtain a C/N of 20, 25, 30 and 35. These ratios were labelled S1, S2, S3 and S4 respectively. The mass ratio of FW to MS required to obtain the stated C/N were determined using Equation 1. In addition to these mixtures, a batch consisting of only FW was also prepared and labelled S0. About 300 g of each mixture was put into airtight bags and sealed under vacuum as previously described [12]. The samples were stored at ambient temperature for 210 days. The characteristics of the mixtures at the time of ensiling are listed in Table 2. All samples were prepared in triplicates.

$$\frac{C}{N} = \frac{m_{FW}(TS \times TC) + m_{MS}(TS \times TC)}{m_{FW}(TS \times TN) + m_{MS}(TS \times TN)} \quad (1)$$

where m_{FW} = mass of food waste, m_{MS} = mass of maize straw, TS = total solids, TC = total carbon, TN = total nitrogen.

Table 2: Mean values (n=3, ± standard deviation) of parameters of substrates mixture before ensiling

Parameter	Unit	Substrate				
		S0	S1	S2	S3	S4
Total solids	%	18.49 ± 2.78	20.72 ± 3.28	38.83 ± 4.12	42.49 ± 5.67	48.74 ± 3.91
Volatile solids	%TS	66.37 ± 2.16	69.17 ± 4.23	79.63 ± 6.29	82.16 ± 3.64	85.14 ± 3.22
pH	-	6.94 ± 0.38	5.26 ± 0.14	5.17 ± 0.29	5.09 ± 0.17	5.02 ± 0.25
WSC	g/L	30.27 ± 2.64	29.89 ± 1.93	28.97 ± 3.28	28.64 ± 2.49	28.15 ± 1.92
Lactic acid	g/L	1.98 ± 0.13	2.07 ± 0.13	2.38 ± 0.09	2.46 ± 0.26	2.49 ± 0.06
Acetic acid	g/L	1.28 ± 0.07	1.32 ± 0.21	1.37 ± 0.17	1.39 ± 0.38	1.42 ± 0.13
Butyric acid	g/L	0.19 ± 0.03	0.14 ± 0.06	0.11 ± 0.01	0.08 ± 0.03	0.07 ± 0.01
Ethanol	g/L	0.42 ± 0.01	0.45 ± 0.03	0.49 ± 0.31	0.54 ± 0.17	0.57 ± 0.26
Cellulose	%TS	15.89 ± 2.08	19.46 ± 1.76	27.19 ± 4.39	29.68 ± 3.99	31.89 ± 2.12
Hemicellulose	%TS	6.29 ± 0.15	10.46 ± 1.39	17.32 ± 2.16	19.41 ± 1.79	22.53 ± 3.849
Lignin	%TS	1.76 ± 0.07	2.08 ± 0.03	5.44 ± 0.19	5.92 ± 0.13	6.13 ± 0.16
FW/MS	g/g	N/A	17.16:1	4.55:1	2.06:1	1.00:1
C/N	-	17.35	20	25	30	35

WSC, water soluble carbohydrate; FW/MS, mass ratio of food waste to maize straw; N/A, not applicable



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Table 3: Silage characteristics after 210 days

Parameter	Unit	Substrate				
		S0	S1	S2	S3	S4
Total solids	%	17.62 ± 1.49	19.93 ± 1.18	37.67 ± 2.24	41.47 ± 1.38	47.77 ± 4.01
Volatile solids	%TS	63.05 ± 3.21	66.40 ± 2.39	76.84 ± 4.07	79.78 ± 2.96	83.18 ± 3.94
pH	-	4.91 ± 0.46	4.03 ± 0.34	3.26 ± 0.43	3.16 ± 0.37	3.04 ± 0.21
WSC	g/L	39.95 ± 3.08	35.67 ± 2.29	38.67 ± 2.35	38.91 ± 1.53	39.26 ± 2.04
Lactic acid	g/L	5.24 ± 0.28	7.31 ± 0.48	10.03 ± 1.62	10.93 ± 2.63	11.05 ± 1.72
Acetic acid	g/L	3.46 ± 1.27	3.89 ± 1.47	5.28 ± 1.90	5.75 ± 0.71	6.42 ± 1.19
Butyric acid	g/L	ND	ND	ND	ND	ND
Ethanol	g/L	1.89 ± 0.41	2.09 ± 0.73	2.97 ± 0.57	3.14 ± 0.62	3.26 ± 0.26
Cellulose	%TS	14.78 ± 2.16	17.71 ± 1.08	23.93 ± 2.25	25.23 ± 2.46	26.79 ± 3.02
Hemicellulose	%TS	5.47 ± 0.19	8.89 ± 0.96	13.86 ± 1.28	14.56 ± 1.06	16.45 ± 2.09
Lignin	%TS	1.71 ± 0.16	2.04 ± 0.13	5.36 ± 0.25	5.85 ± 0.27	6.06 ± 0.42
FW/MS	g/g	N/A	17.16:1	4.55:1	2.06:1	1.00:1
C/N	-	17.35	20	25	30	35

WSC, water soluble carbohydrate; ND, not detected; N/A, not applicable

2.3 Batch Anaerobic Digestion

The biomethane potential (BMP) of the substrates after 210 days of ensiling as well as that of unensiled FW was determined using the automatic biomethane potential test system (AMPTS II, Bioprocess Control, Sweden) shown in Figure 1. Each reactor consisted of inoculum to substrate ratio of 3:1 based on the study of Okoro-Shekwa et al. [13]. A positive control consisting of 4.26 g of microcrystalline cellulose and the inoculum, as well as a negative control consisting of only inoculum and distilled water were also set up. To keep the systems in anaerobic condition, the headspace of each reactor was flushed with nitrogen for 2 minutes. Daily methane production of each reactor was recorded by the software of the AMPTS.

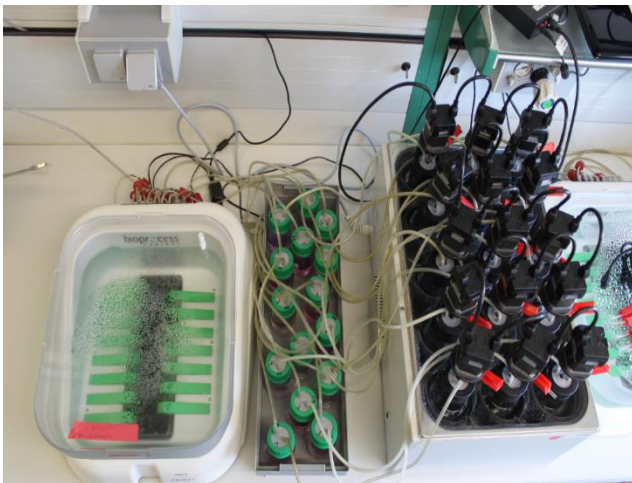


Figure 1: Automatic methane production test system used for anaerobic digestion.

2.4 Kinetics of Biomethane Potential of Silages

The kinetics of biomethane production was determined using three kinetic models including the first-order model, the modified Gompertz model and the dual pool model given in Equations 2, 3 and 4 respectively. The correlation coefficient (R^2), as well

as the root mean square error (RMSE) and the Bayesian Information Criterion (BIC) given in Equations 5 and 6 respectively were used as statistical indicators to determine the fitness of the models.

$$G(t) = G_0(1 - e^{-kt}) \quad (2)$$

$$G(t) = G_{(0)} \cdot \exp\left\{-\exp\left[\frac{R_{max} \cdot e}{G_{(0)}}(\lambda - t) + 1\right]\right\} \quad (3)$$

$$G(t) = G_{(0)}[1 - \alpha e^{-k_1 t} - (1 - \alpha)e^{-k_2 t}] \quad (4)$$

$$RMSE = \sqrt{\frac{SS}{n}} \quad (5)$$

$$BIC = n \ln\left(\frac{SS}{n}\right) + c \ln(n) \quad (6)$$

where $G(t)$ = cumulative methane potential (mL/gVS), G_0 = maximum possible methane potential (mL/gVS), R_{max} = maximum methane production rate (mL/gVS/d), λ = lag phase (d), k_1 = kinetic constant of fast degradable substrate (1/d), k_2 = kinetic constant of slow degradable substrate (1/d), α = fraction of readily degradable material, t = duration of digestion (d), k = reaction rate constant (1/d), n = number of experimental data, SS = squared sum of residuals, and c = number of parameters in the model.

2.5 Analytical Methods

Standard methods were used for the determination of total solids (TS) and volatile solids (VS) contents as previously described [14]. Briefly, about 30 g of sample was placed in a ceramic crucible and dried in an oven at 105 °C for 24 hours. The sample remaining were then further heated in a furnace at 550 °C for 2 hours. TS was determined from the mass of sample remaining after heating at 105 °C while the VS was determined from the fraction remaining after heating at 550 °C. In order to avoid overestimation of methane yield, TS and VS were corrected for organic acid loss using the Equation of Weissbach and Strubelt [15]. The pH, WSC, organic acids, ethanol, total carbon (TC), total nitrogen (TN), cellulose, hemicellulose and



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lignin contents were determined using standard methods [16].

3.0 RESULTS AND DISCUSSION

3.1 Effect of Ensiling on Structural and Non-Structural Carbohydrate Components

The ensiling effect on the structural carbohydrates (cellulose, hemicellulose and lignin) as well as non-structural carbohydrate (WSC) of the silages is shown in Table 3. In all silages, there was a significant decrease ($p < 0.05$) in all lignocellulosic as well as WSC components of the silages. This can be explained by the fact that during ensiling, WSC are converted to organic acids like lactic acids and acetic acids, as well as ethanol. The organic acids have been reported to disrupt the lignin structure of lignocellulosic biomass [17], thereby exposing the cellulose and hemicellulose contents to microbial hydrolysis. Similar reports on lignocellulosic components degradation during ensiling have been reported by other authors [18, 19]. In the present study, the most degraded structural carbohydrate in all silages was hemicellulose while lignin was the least degraded.

The dominant organic acid in all silages was lactic acid as is the case for all good silages [20]. The presence of lactic acid ensures that the pH of the systems are kept low to prevent clostridial fermentation which are usually not desired in a silage. An evidence of the absence of clostridial activity is the absence of butyric acid production which can lead to a higher loss in TS content [12]. In the present study, butyric acid was below detectable limit in all silages. There was a loss in TS and VS in all silages, a phenomenon that is common during ensiling. A loss in TS and VS is usually associated with the formation of fermentation products and has also been reported in the ensiling of sugar beet leaves [10] and rice straw [21]. In all silages, pH was significantly lower than it was before ensiling due to the presence of a higher concentration of lactic acid.

3.2 Effect of Ensiling on Biomethane Potential

The batch anaerobic digestion of the unensiled FW and silages lasted for 33 days. Digestion experiments were terminated when the daily biomethane production for 3 consecutive days was less than 1% of the cumulative biomethane production in line with the VDI 4630 guidelines [22]. The daily biomethane production of the substrates is shown in Figure 2. The results of the daily biomethane production from the unensiled FW (Figure 2a) shows three peaks, an indication of the difference in the biodegradability of

the components of the substrates. The less number of peaks, observed on days 1 and 6, in the other substrates could be explained by the fact that most of the VS components of the substrates were converted to fermentation products during ensiling and therefore degraded faster. As also shown in Figure 2, the maximum rate of daily methane production occurred on day 1 in the silages but occurred on day 3 in the unensiled FW. This can be explained by the fact that hydrolysis, which is the rate limiting step of biogas production [23], was enhanced by ensiling.

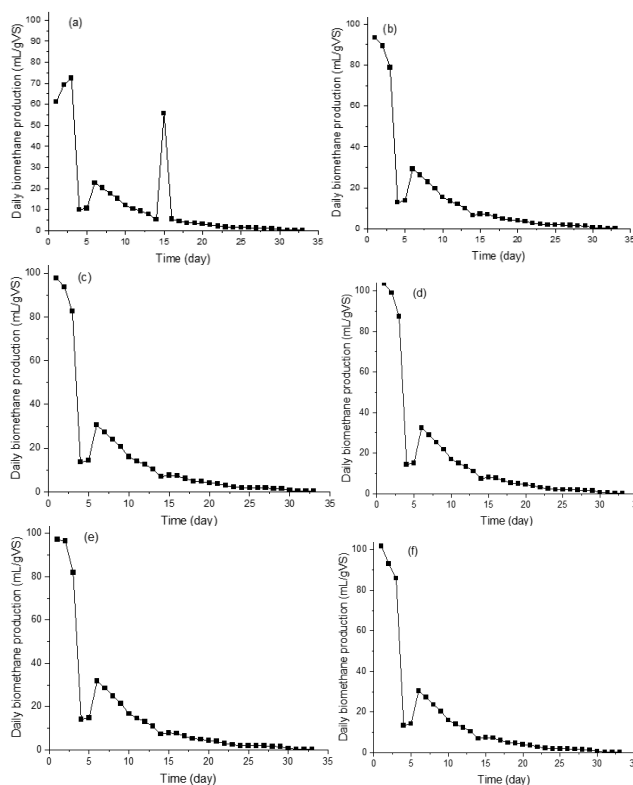


Figure 2: Daily biomethane production of (a) unensiled food waste, (b) S0, (c) S1, (d) S2, (e) S3 and (f) S4 during the period of investigation.

The cumulative BMP of the substrates is shown in Figure 3. Clearly, ensiling significantly increased ($p < 0.05$) the BMP of FW by 29%. The increase in BMP due to ensiling could be attributed to the pretreatment effect of the process. Since the fermentation products that were produced during ensiling disrupted the lignocellulosic structure of the substrates, hydrolysis was enhanced, leading to more methane production. Co-ensiling with MS also significantly increased the BMP of FW with the highest BMP obtained at a C/N ratio of 25 (551.37 mL/gVS). However, there was no significant difference ($p > 0.05$) in the BMP of the silages with C/N ratio of 20, 25, 30 and 35. Other authors have also reported that a C/N range of 20 – 30 is required for



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efficient biogas production [5, 24]. Above a C/N ratio of 30, the BMP dropped slightly ($p > 0.05$) probably due to lower nitrogen content. Generally, the BMP obtained in the present study are higher than 344 mL/gVS from the co-digestion of non-pretreated FW and wheat straw [25] and 444.7 mL/gVS from the co-digestion of non-pretreated municipal FW and cattle slurry [26]. The higher BMP obtained in the present study could be as a result of the pretreatment effect of ensiling on the substrates.

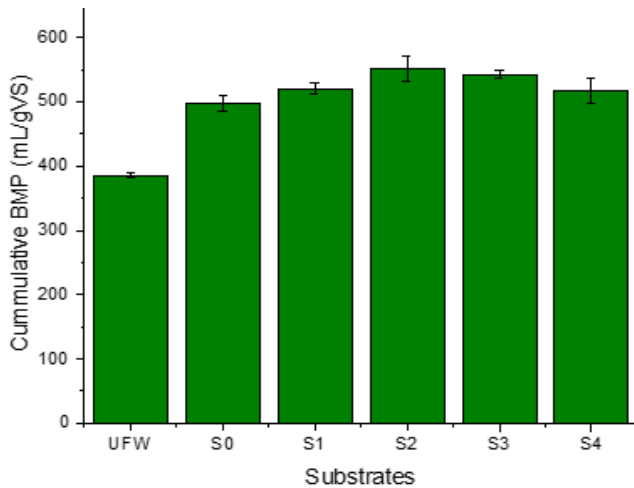


Figure 3: Cumulative biomethane production of the substrates (UFW, unensiled food waste; Error bars indicate standard deviation between replicates)

3.3 Kinetics of Biomethane Production

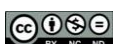
Three kinetic models were used to predict the experimental data of the BMP of the silages. As seen in Table 4, all kinetic models gave a reasonably good fit to the experimental BMP of all silages with high R^2 values (≥ 0.84), which is an indication of the feasibility of the models. However, the model with the

best fit is usually the one with the least RMSE and BIC values [27]. Therefore, for all substrates, the model that gave the best fit was the dual pool model probably because (i) it was the only model formulated with the assumption that substrates for AD could contain both fast and slow degradable components and (ii) it contain the highest number of parameters to be estimated. The fitness of the models to the experimental data is shown in Figure 4.

The first-order kinetic constant (k) is a measure of how fast a product is formed during a given reaction [28]. As also shown in Table 4, k from the first-order model was not significantly different ($p < 0.05$) among all silages despite the difference in the concentration of fermentation products. This is because (i) all AD were performed at the same temperature and pH, and (ii) factors like organic acid concentration have little or no significant effect on k [28]. However, co-ensiling significantly ($p < 0.05$) increased k , which is an indication that k is substrate-specific [29]. From the modified Gompertz model, higher maximum rate of methane production (R_{max}) was obtained from the silages compared to the unensiled substrate. Although a high R_{max} does not necessarily translates to a high biogas yield, it provides an information on the ease of biodegradability of a substrate [30]. The lag phase in all reactors was zero as also estimated from the modified Gompertz model primarily because the inoculum used was from an active biogas reactor and was therefore rich in methanogenes. Ensiling and co-ensiling with MS also significantly increased the fraction of biodegradable component (α) of the substrates, which may have led to an increase in BMP.

Table 4: Estimated model and statistical parameters for experimental BMP of substrates

Model	Parameter	UFW	S0	S1	S2	S3	S4
FOM	G_0	347.02	432.73	473.68	490.72	477.10	439.69
	k	0.21	0.24	0.37	0.35	0.39	0.36
	R^2	0.91	0.89	0.91	0.87	0.86	0.84
	RMSE	30.68	54.44	37.27	48.25	51.76	61.73
	BIC	54.89	59.68	44.38	38.02	46.38	67.32
MGM	G_0	362.44	457.60	494.50	529.32	515.05	496.60
	R_{max}	72.42	93.42	97.77	103.56	101.83	97.16
	λ	0.04	0.00	0.00	0.00	0.00	0.00
	R^2	0.94	0.93	0.95	0.96	0.90	0.92
	RMSE	18.41	31.66	20.71	17.55	21.57	16.46
BIC	37.85	34.49	23.29	14.78	29.06	37.59	
DPM	G_0	397.14	507.34	536.14	556.89	542.16	527.63
	α	0.72	0.81	0.89	0.88	0.90	0.89
	k_1	0.23	0.31	0.35	0.32	0.33	0.34
	k_2	0.05	0.09	0.10	0.08	0.07	0.09
	R^2	0.98	0.97	0.98	0.99	1.00	0.96
	RMSE	9.20	7.91	12.42	4.39	0.00	8.23
BIC	17.38	22.78	11.38	9.36	2.38	13.56	



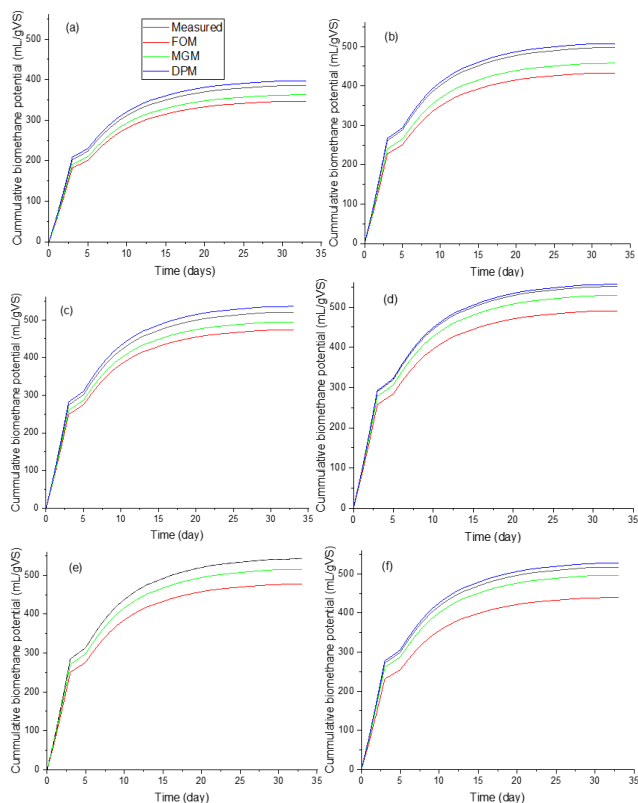


Figure 4: Fittings of experimental data of BMP from (a) unensiled food waste (b) S0 (c) S1 (d) S2 (e) S3 (f) S4 to the kinetic models (FOM, first-order model; MGM, modified Gompertz model; DPM, dual pool model. The DPM superimposed the measured data in (e).

4.0 CONCLUSION

Ensiling could be considered as an effective method of pretreatment since it significantly degraded the hemicellulose and cellulose content of food waste after 210 days. The high lactic acid formed during ensiling inhibited unwanted clostridial activities resulting in the absence of butyric acid throughout the period of ensiling. An increase in the C/N ratio of up to 25 resulted in an increase in the biomethane potential of food waste. Beyond a C/N ratio of 25, the biomethane potential reduced. Out of the three kinetic models that were used to fit the experimental biomethane potential of the silages, the dual pool model gave the best fit as indicated by lower values of root-mean-square error and Bayesian information criterion as well as higher values of coefficient of determination. In conclusion, ensiling could be used to pretreat food waste for a sustainable biogas production. Co-ensiling food waste with maize straw such that the C/N is 25 can improve the biogas yield.

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