



ORIGINAL RESEARCH ARTICLE

**KINETICS OF THE VALORIZATION OF FOOD WASTE FOR MEDIUM CHAIN
CARBOXYLATES PRODUCTION; EFFECT OF ENSILING AND INOCULUM SOURCE**

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**ARTICLE
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ABSTRACT

Higher yields of medium chain carboxylates (MCC) can be obtained from the anaerobic fermentation of complex feedstocks like food waste if pretreatment precedes fermentation. However, many conventional pretreatment processes produce inhibitors that could affect downstream processing in addition to increasing the cost of the overall process. In this study, ensiling was used as a cost effective and sustainable pretreatment method to instigate the formation of electron donors like lactic acid and ethanol in food waste for MCC production. Food waste was ensiled for 120 days and thereafter subjected to batch anaerobic fermentation using two different inocula including leachate and rumen fluid. Results show that ensiling degraded the cellulose and hemicellulose component of food waste and converted the water soluble carbohydrate content to lactic acid, acetic acid and ethanol. Ensiled substrates had a total MCC yield of 990.44 g/kgVS and 878.68 g/kg VS when leachate and rumen fluid was used as inoculum respectively, while the unensiled food waste had a total MCC yield of 522.80 g/kgVS and 430.88 g/kgVS when leachate and rumen fluid was respectively used as inoculum. In order to predict the MCC production, two kinetic models were used including the first-order model and the modified Gompertz model. Statistical indicators including the coefficient of determination, R^2 , the root-mean-square-error and the Akaike Information Criterion show that the first-order model predicted the experimental MCC better than the modified Gompertz model.

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1.0 Introduction

According to the United Nations, as much as 17 % of the global food production is lost between the farm and the consumer's table (UNO 2022), resulting in an estimated economic loss of USD 680 billion (Usmani *et al.* 2021). Being a greenhouse gas emitter, food wastes including left-overs from restaurants, homes and hotels, contribute to environmental pollution. Since the complete elimination of food waste is impossible, their valorization for the production of biofuels and platform chemicals has become the most attractive method of reducing their impact on the environment. Depending on their sources, the composition of food wastes varies greatly, with carbohydrate, protein and oils/lipids being the major component (Paritosh *et al.* 2017). For food waste with a high composition of scraps of vegetables and peels from fruits, valorization by anaerobic digestion (AD) has to be preceded by pretreatment for an enhanced biodegradability (Gallipoli *et al.* 2020) as a result of their lignocellulosic structure. Many conventional pretreatment methods are either too expensive or are prone to the formation of inhibitors that often affect downstream processing (Amin *et al.* 2017). One pretreatment process that reduces the drawbacks of conventional pretreatment processes is ensiling.

Ensiling is an anaerobic fermentation process whereby the water-soluble carbohydrate (WSC) component of a system is converted to organic acids that reduce the pH of the system, such that microbial activities is inhibited and the system remains at steady state. The strong acidity of some of the organic acids like lactic acid ($pK_a = 3.86$) and butyric acid ($pK_a = 4.82$) enhances the hydrolysis of lignocellulosic biomass (Cui *et al.* 2020). Although the literature is very rich as far as ensiling for biofuel production is concern, studies on ensiling of food waste is limited, especially for medium chain carboxylates (MCC) production.

MCC are carboxylic acids having carbon chain lengths of 6 – 12 with a wide range of application in the field of medicine, agriculture and corrosion prevention (Watanabe and Tsujino 2022). They can be produced by the fermentation of waste biomass through a process called chain elongation (CE), using electron donors like lactic acid and ethanol in the presence of dedicated microbial communities. The most popular MCC in literature is caproic acid, whose productivity from food waste varies between 0.12 – 16 gCOD/L/day depending on the process parameters, inoculum type and feed composition (Stamatopoulou *et al.* 2020). In most of such studies, the addition of ethanol (or lactic acid) as electron donor is required for an improved yield of MCC. However, a life cycle assessment shows that the addition of ethanol to a system for an improved yield of MCC comes with economic and environmental consequences (Chen *et al.* 2017).

Since CE takes place in the presence of dedicated microbial community, it is necessary to use an inoculum with a high concentration of microbial community that are adapted to the process. So far, the highest yield of MCC have been produced when pure cultures are used (Cavalcante *et al.* 2017). However, when complex feedstocks like food waste are to be used as substrates, cultures containing a large spectra of microorganisms are preferred (Groof *et al.* 2019).

In order to improve the understanding of CE processes, kinetic models are required. Parameters obtained from such models are often used to control and optimize the yield of a desired product. Although kinetic models are common for the fermentation of simple substrates like glucose, models based on complex substrates like food wastes are limited in literature (Groof *et al.* 2019). Therefore, the purpose of this study was to (i) investigate the effect of ensiling on the lignocellulosic component of food waste, (ii) investigate the effect of ensiling on MCC production from food waste, (iii) investigate the effect of inoculum source on MCC production from food waste and (iv) carryout a kinetic study on MCC production from food waste.

I. Materials and Methods

1.1 Substrate and Inocula

The only carbon source used was food waste which was collected from some major restaurants in Choba, Port Harcourt, and consisted mainly of rice, *eba*, vegetables, meat, fish and bones. The hard bones were removed from the mixture after which the waste was blended using a kitchen blender. The charactersitics of the blended food waste is shown in Table I. Two different inocula were used for the anaerobic fermentation including rumen fluid and leachate. The rumen fluid was obtained from freshly slaughtered goats in an abator in Port Harcourt. The leachate was generated from food waste as previously described (kefas and Undiandeye 2022). The inocula,

whose characteristics are also shown in Table I, were pretreated at 90 °C for 30 minutes to deactivate methanogenes and then stored at 4 °C until required.

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

Parameter	Unit	Food waste	Leachate	Rumen fluid
Total solids	%	16.27 ± 2.16	6.75 ± 1.12	2.92 ± 0.15
Volatile solids	%	13.98 ± 1.95	3.49 ± 0.68	2.11 ± 0.07
pH	-	4.27 ± 0.28	4.37 ± 0.21	6.94 ± 0.47
WSC	g/L	59.19 ± 4.27	ND	ND
Lactic acid	g/L	1.25 ± 0.18	ND	ND
Butyric acid	g/L	0.15 ± 0.06	ND	ND
Acetic acid	g/L	1.02 ± 0.03	ND	ND
Ethanol	g/L	0.36 ± 0.07	ND	ND
Cellulose	%TS	15.89 ± 2.08	ND	ND
Hemicellulose	%TS	6.29 ± 0.15	ND	ND
Lignin	%TS	1.76 ± 0.07	ND	ND

WSC, water soluble carbohydrate; ND, not determined

1.2 Silage Preparation

Ensiling was carried out as previously described (Undiandeye et al. 2022a). Briefly, about 300 g of the grinded food waste were sealed under vacuum in airtight bags and stored at ambient temperature for 120 days. The experiment was setup in triplicates in order to account for experimental variation.

1.3 Anaerobic Fermentation Set-up

Batch reactors were used for the anaerobic fermentation of food waste before and after ensiling using Schott bottles of 500 mL total volume and working volume of 200 mL. Each reactor contained 2.7 gVS of substrate, 100 mL of inoculum, and anoxic distilled water to make up the working volume. The initial pH in all reactors was adjusted to 5.5 (± 0.2) using 10 M HCl or 10 M NaOH solutions. Thereafter, the reactors were sealed using butyl rubber stoppers and aluminium caps and transferred to biological incubators operated at 38 °C and 150 rpm. The fermentation process lasted for 30 days with samples collected for analysis on days 0 (5 hours after start of experiment), 3, 5, 12, 19, 26 and 30.

1.4 Analytical Methods

Total solids (TS) and volatile solids (VS) of substrates and inocula were determined as described previously (Undiandeye et al. 2022b) and corrected using the Equation of Weissbach and Strubelt (2008) so as to avoid overestimation of the product yield. WSC of food waste was measured using an Azura high-performance liquid chromatography (HPLC) system (Knauer GmbH, Germany) equipped with degasser, binary pump system, auto sampler, column oven and refractive index detector (RID) set at 40 °C. Ethanol and volatile acid contents were measured by analysis on a 7890A gas chromatograph with a flame ionisation detector (FID) (Agilent Technologies, USA) as described previously (Undiandeye et al. 2023b). The head space gas composition in each bottle was measured by withdrawing 1 mL of gas sample using a syringe and transferred into 20 mL glass vials that had been flushed with argon. Measurement was then carried out using gas

chromatography equipped with an autosampler in a Perkin Elmer GC. Cellulose, hemicellulose and lignin contents were determined by measuring the neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin (ADL) of the substrates using the methods described by van Soest and Wine (2020). The difference between ADF and ADL was taken as cellulose while hemicellulose was calculated as the difference between NDF and ADF. The yield (Y) and productivity (P) of each MCFA was calculated using Equations 1 and 2 respectively.

$$Y = \frac{cv}{m_s} \quad (1)$$

$$P = \frac{c}{t} \quad (2)$$

where c = maximum concentration of a given MCC (g/L), v = working volume of reactor (L), m_s = mass of added substrate (kg VS), t = time at which maximum c was achieved (d).

1.5 Kinetics of MCC Production and Statistical Analysis

Two kinetic models were used to fit the production of MCC including the first-order model and the modified Gompertz model given in Equations 3 and 4 respectively.

$$c_t = c_{max}[1 - \exp(-k \times t)] \quad (3)$$

$$c_t = c_{max} \exp\left\{-\exp\left[\frac{R_{max}e}{c_{max}}(\lambda - t) + 1\right]\right\} \quad (4)$$

where c_t = concentration of a carboxylate at any time (g/L), t ; c_{max} = maximum concentration of carboxylic acid (g/L); k = kinetic constant (/d); R_{max} = maximum rate of carboxylic acid production (g/L/d), λ = lag phase (d).

All data were analysed using analysis of variance (ANOVA) in OriginPro software (OriginLab corporation, Northampton, USA). Tukey's test was used to compare significant difference at 95% confidence level. Three statistical parameters including the coefficient of determination (R^2), the root-mean-square-error, RMSE (Equation 5) and the Akaike Information Criterion, AIC (Equation 6) were used to determine the model that gave a better description of a given MCFA production.

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

$$AIC = N \times LN\left(\frac{SS}{N}\right) + 2C \quad (6)$$

where N = number of experimental data, SS = sum square of residuals, C = number of parameters in a model.

3 Results and Discussion

3.1 Ensiling Characteristics

The physico-chemical parameters of ensiled food waste after 120 days is shown in Table 2. Compared to the food waste before ensiling, there was a significant decrease ($p < 0.05$) in the concentration of WSC. A decrease in WSC has also been reported during the ensiling of Alfalfa (Gao *et al.* 2021) and Napiergrass (Zhang *et al.* 2022). The major reason for the reduction of WSC during ensiling is because they are converted to organic acids which are subsequently

required to maintain the quality of the silage. This explains why substrates with a low WSC content like cattle manure are not suitable for ensiling (Franco *et al.* 2020). Conversely to the concentration of WSC, the concentration of lactic and acetic acids increased significantly ($p < 0.05$) after the duration of ensiling. The increase in lactic acid led to a significant reduction ($p < 0.05$) in the pH of the system. A decrease in pH is desired in silages to inhibit microbial activities. One evidence of microbial inhibition in silages is the absence of butyric acid (Undiandeye *et al.* 2022a). Butyric acid formation in silages leads to a significant loss in VS. In the present study, a VS loss of 6.65% was observed, which is within acceptable range (Steinbrenner *et al.* 2019).

Table 2. Mean values of physico-chemical parameters of food silage after 120 days

Parameter	Unit	Ensiled Food waste
Total solids	%	15.38 ± 1.43
Volatile solids	%	13.05 ± 0.83
pH		3.19 ± 0.9
WSC	g/L	14.04 ± 0.38
Lactic acid	g/L	18.96 ± 3.04
Butyric acid	g/L	0
Acetic acid	g/L	9.26 ± 1.93
Ethanol	g/L	4.67 ± 0.31
Cellulose	%TS	12.27 ± 1.84
Hemicellulose	%TS	2.48 ± 0.09
Lignin	%TS	1.98 ± 0.16

WSC, water soluble carbohydrate

The most degraded lignocellulosic component was hemicellulose (about 61%). Ren *et al.* (2007) have also reported a preferential degradation of hemicellulose relative to cellulose during the ensiling of corn stover due to its less rigid structure. Three reasons have been attributed to the degradation of cellulose and hemicellulose during ensiling by Ren *et al.* (2007) and Undiandeye *et al.* (2023a); (i) the availability of hemicellulase and cellulase that are naturally present in food waste, (ii) production of degrading enzymes during ensiling and (iii) hydrolytic effect of the acids produced during ensiling. These lignocellulosic components (hemicellulose and cellulose) are usually degraded to WSC, which are in turn, converted to fermentation products like lactic acid, acetic acid, and ethanol. The degradation of cellulose and hemicellulose is an indication that ensiling disrupted the rigid structure of the substrate, thereby making it less recalcitrant to enzymatic fermentation for MCC production. The perceived increase in lignin content as also shown in Table 2 was solely due to the degradation of cellulose and hemicellulose.

3.2 Products of Anaerobic Fermentation

3.2.1 Effect of Ensiling

The fermentation profile of organic acids from food waste before and after ensiling is shown in Figure 1. The concentration of MCC was higher from the fermentation of ensiled substrate than from the fermentation of the unensiled food waste, irrespective of the source of inoculum. One

reason is because of the higher concentration of lactic acid and ethanol in the silage. In CE processes, lactic acid and ethanol are used as electron donors for the elongation of short chain fatty acids, and their availability often leads to a higher increase in the concentration of MCC (Reddy *et al.* 2018). Another reason for the higher concentration of MCC from the ensiled silage could be because of the pretreatment effect that ensiling had on the substrate. The organic acids produced during ensiling hydrolysed the cellulose and hemicellulose components of lignocellulosic biomass to simple sugars (Nagle *et al.* 2020), which were then converted to more electron donors.

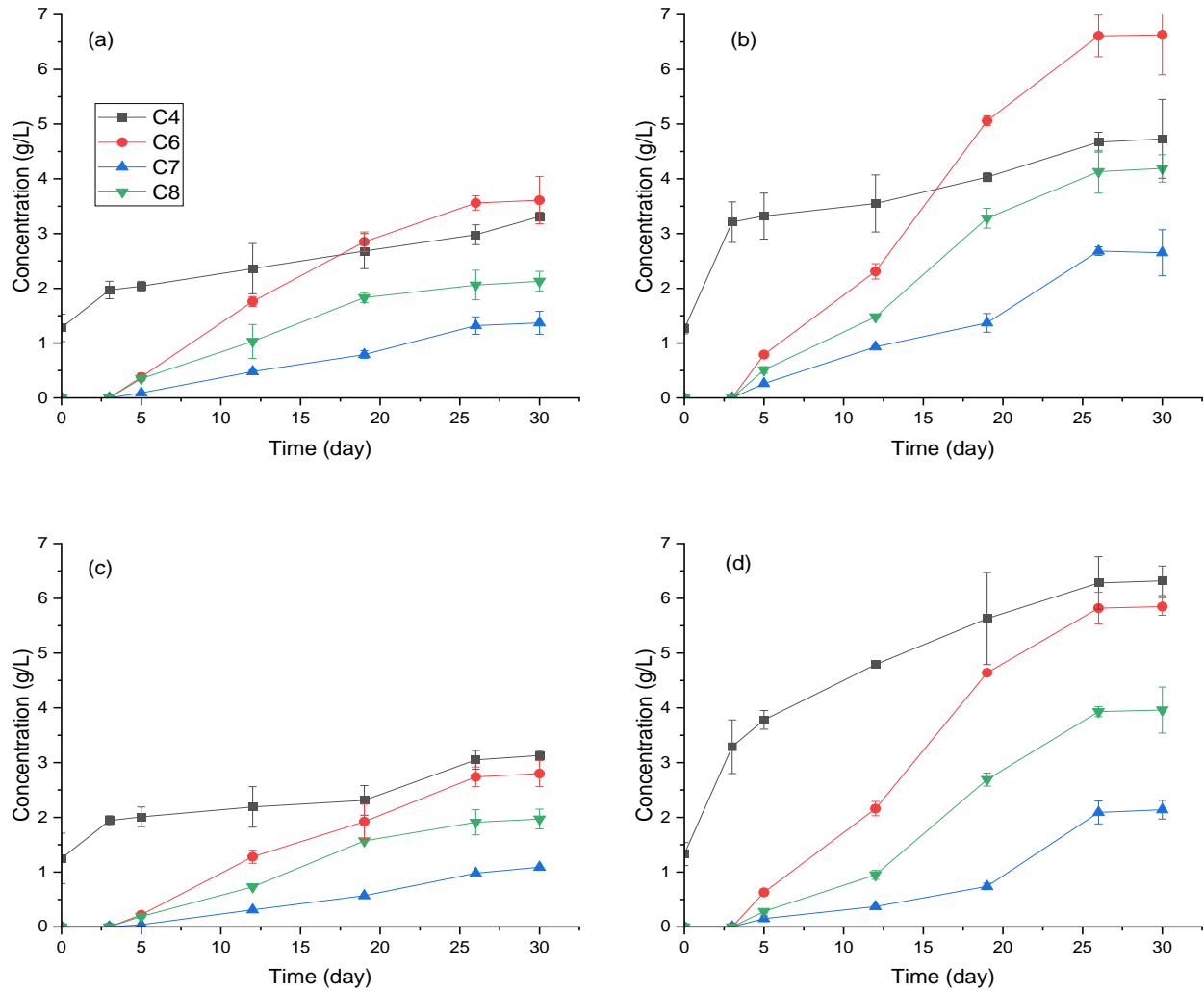


Figure 1. Fermentation profile of (a) unensiled substrate with leachate, (b) ensiled substrate with leachate, (c) unensiled substrate with rumen fluid and (d) ensiled substrate with rumen fluid (C4, butyric acid; C6, caproic acid; C7, heptanoic acid; C8, caprylic acid). Error bars indicate standard deviation of replicates.

3.2.2 Effect of Inoculum Source

The effect of inoculum source on the fermentation products is also shown in Figure 1. Apart from acetic acid (not shown), caproic acid dominated the fermentation product when leachate was used as inoculum whether the substrate was ensiled or not. The high concentration of

caproic acid is an indication that (i) the condition of experiment was favourable for MCC production and (ii) the microbial community in leachate are adapted for chain elongation especially if the leachate is young (Saadoun *et al.* 2021) as was the case in the present study. An important observation when rumen fluid was used as inoculum was that lactic acid and ethanol were not completely used up, and that butyric acid dominated the fermentation profile in the reactors containing ensiled and unensiled substrates. Usually, CE is a type of series reaction where acetic acid is elongated to butyric acid, butyric acid to caproic acid, and so on. Since lactic acid and ethanol were not completely used up, it indicates that the lower production of MCC was not as a result of a deficiency in electron donors but probably an indication that the microbial community in the inoculum are less adapted to CE when compared to leachate under the given conditions. For instance, in the fermentation of glycerol, Dams *et al.* (2018) reported a higher concentration of caproic acid than butyric acid while Weimer *et al.* (2015) reported a dominance of butyric acid in the fermentation of switchgrass with rumen fluid as inoculum in both studies. It is therefore possible that the source of substrate and operating conditions can influence the activity of microbial community and the dynamics of MCC production.

3.2.3 pH Fluctuation

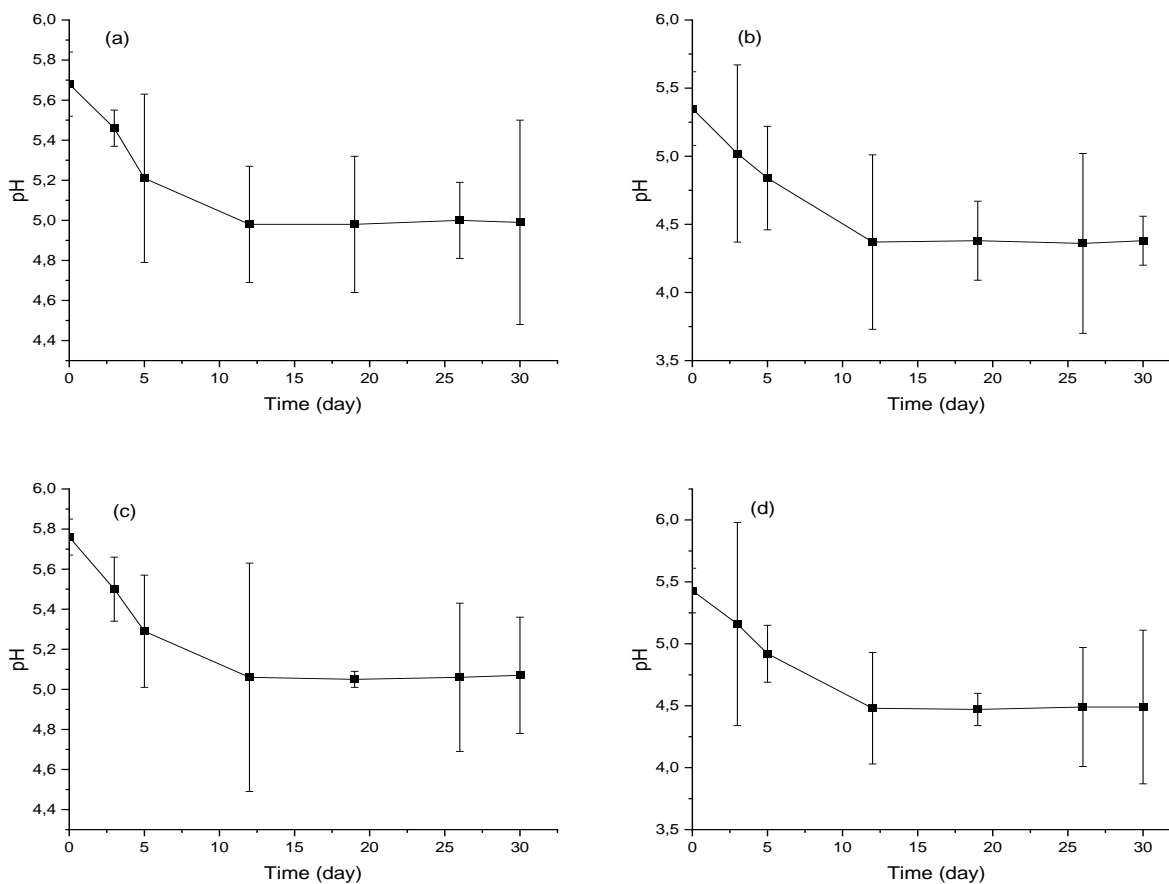


Figure 2. Variation in pH during the fermentation of (a) unensiled substrate with leachate, (b) ensiled substrate with leachate, (c) unensiled substrate with rumen fluid and (d) ensiled substrate with rumen fluid (Error bars indicate standard deviation of replicates).

Overall, there was a decrease in the pH of all systems until day 12, after which it stabilized (Figure 2). However, the pH in the systems containing unensiled substrate increased slightly on day 0. It is possible that since the unensiled substrates contained limited chain elongators, the first few hours were used for microbial hydrolysis which may have resulted in an initial increase in pH (Hirakura *et al.* 2006). A decrease in pH during anaerobic fermentation has been attributed to the formation of organic acids (Weimer *et al.* 2015), as a result of which the systems with the highest concentration of organic acids had the lowest pH at the end of fermentation time.

3.3 Product Yield and Productivity

Table 3. Mean values (\pm standard deviation) of Yield and productivity of MCC

Substrate	Yield (g/KgVS)			Productivity (g/L/day)		
	C6	C7	C8	C6	C7	C8
UENL	265.44 \pm 18.23	100.74 \pm 6.17	156.62 \pm 11.38	0.12 \pm 0.05	0.04 \pm 0.00	0.07 \pm 0.00
ENL	487.50 \pm 9.28	194.85 \pm 13.48	308.09 \pm 23.07	0.22 \pm 0.03	0.09 \pm 0.00	0.14 \pm 0.00
UENR	205.88 \pm 17.21	80.15 \pm 4.29	144.85 \pm 3.27	0.09 \pm 0.00	0.04 \pm 0.00	0.07 \pm 0.00
ENR	430.15 \pm 24.29	157.35 \pm 6.31	291.18 \pm 5.73	0.20 \pm 0.01	0.07 \pm 0.00	0.13 \pm 0.00

UENL, unensiled substrate with leachate; ENL, ensiled substrate with leachate; UENR, unensiled substrate with rumen fluid; ENR, ensiled substrate with rumen fluid; C6, caproic acid; C7, heptanoic acid; C8, caprylic acid.

The yield and productivity of MCC from the fermentation of the substrates is shown in Table 3. Clearly, ensiling and inoculum source significantly ($p < 0.05$) affected the yield of the measured MCC. There was a higher yield of even-numbered MCC like caproic acid (C6) and caprylic acid (C8) compared to odd-numbered MCC like heptanoic acid (C7). Indeed, CE is a complex process. Besides process parameters like initial pH, temperature and inoculum source, the composition of a substrate can significantly influence CE pathways. For instance, if the ratio of lactic acid to acetic acid content is higher than 3.0, the CE pathway for the formation of odd-numbered MCC may be favoured (Wu *et al.* 2019). Therefore, the higher yield of even-numbered MCC compared to that of odd-numbered MCC in the present study could be attributed to an availability of an appropriate lactic to acetic acid ratio (2.05) (Tang *et al.* 2022).

3.4 Biogas Production

Methane was not detected in the gas stream throughout the period of fermentation, an indication of the effect of heat-treating the inocula. Availability of active methanogenes would have led to the consumption of volatile acids for methane production (Dahiya and Mohan 2019), thereby resulting to a reduced yield of MCC. The major gas produced during the fermentation process was carbon (iv) oxide, as also reported by several authors (Dahiya and Mohan 2019; Saadoun *et al.* 2021; Tang *et al.* 2022). Hydrogen was a major co-product of the fermentation process, being present in significant quantity, an indication that the process can also be adapted for hydrogen production. Other authors have also reported a co-production of hydrogen and carboxylates during the fermentation of anaerobic waste (Brodowski *et al.* 2020) and food waste (Regueira-Marcos *et al.* 2023).

3.5 Kinetics

The first-order model and the modified Gompertz model were used to fit the experimental values of MCC produced from the substrates. Each of these models gave a reasonably good fit to the experimental data. In order to compare the degree of fitness of the two models to the experimental data, statistical parameters including the coefficient of determination (R^2), root-mean-square error (RMSE) and the Akaike Information Criterion (AIC) were used. As shown in Table 4, the production of MCC (C6) was better described by the first-order model as seen from the higher R^2 values as well as lower RMSE and AIC values. The fitness of the first-order model to the experimental data of MCC is shown in Figure 3.

Table 4. Model and statistical parameters for evaluation of fitness to experimental C6 production.

Model	Parameters	Substrates			
		UENL	ENL	UENR	ENR
FOM	C_{max}	3.63	6.64	2.82	5.87
	k	0.16	0.34	0.25	0.07
	R^2	0.997	0.989	0.993	0.999
	RMSE	0.006	0.002	0.007	0.003
	AIC	-29.47	-37.29	-19.38	-35.64
MGM	C_{max}	3.69	6.68	2.87	5.91
	R_{max}	0.125	0.226	0.11	0.198
	λ	4.07	3.93	4.28	4.16
	R^2	0.991	0.972	0.985	0.992
	RMSE	0.017	0.006	0.018	0.007
	AIC	-21.17	-33.23	-11.56	-28.74

FOM, first-order model; MGM, modified Gompertz model; UENL, unensiled substrates fermented with leachate; ENL, ensiled substrate fermented with leachate; UENR, unensiled substrate fermented with rumen fluid; ENR, ensiled substrate fermented with rumen fluid (kinetic parameters and their units have their usual meanings as described in Equations 4 and 5).

Kinetic constants are an indication of how fast a product is formed or consumed (Fogler 2016). From the first-order model, these constants were seen to vary significantly with respect to ensiling and inoculum source. Although Fogler (2016) has reported that k depends largely on temperature, recent studies have shown that process parameters like pH, inoculum to substrate ratio, substrate type and inoculum source can significantly affect the values of k (Zhu et al. 2017; Khadka et al. 2022). In the present study, the higher values of k obtained from the ensiled substrates could be attributed to the availability of the required electron donors at the start of the experiment. Kinetic constants between 0.059 and 0.321 /day have been reported in the fermentation of wastewater using anaerobic sludge as inoculum (Morais et al. 2019). From the modified Gompertz model, maximum rate of caproic acid production was also significantly higher from the ensiled substrates, which is in agreement with the measured data. The lag phase of approximately 4 days for C6 production was similar in all substrates as was also observed during the experiment where no MCC was detected until on day 5. The lag phase for the production of

MCC can vary significantly depending on the pH (Regueira-Marcos *et al.* 2023) and inoculum used. For instance, if a fermentation broth from a reactor producing MCC is used as inoculum, the lag phase can be negligible (Jerome Undiandeye, 2023unpublished PhD thesis, University of Rostock) since such inocula are already adapted to MCC production. Using sludge as inoculum, Morais *et al.* (2019) reported a lag phase of about 7 days in the fermentation of swine wastewater.

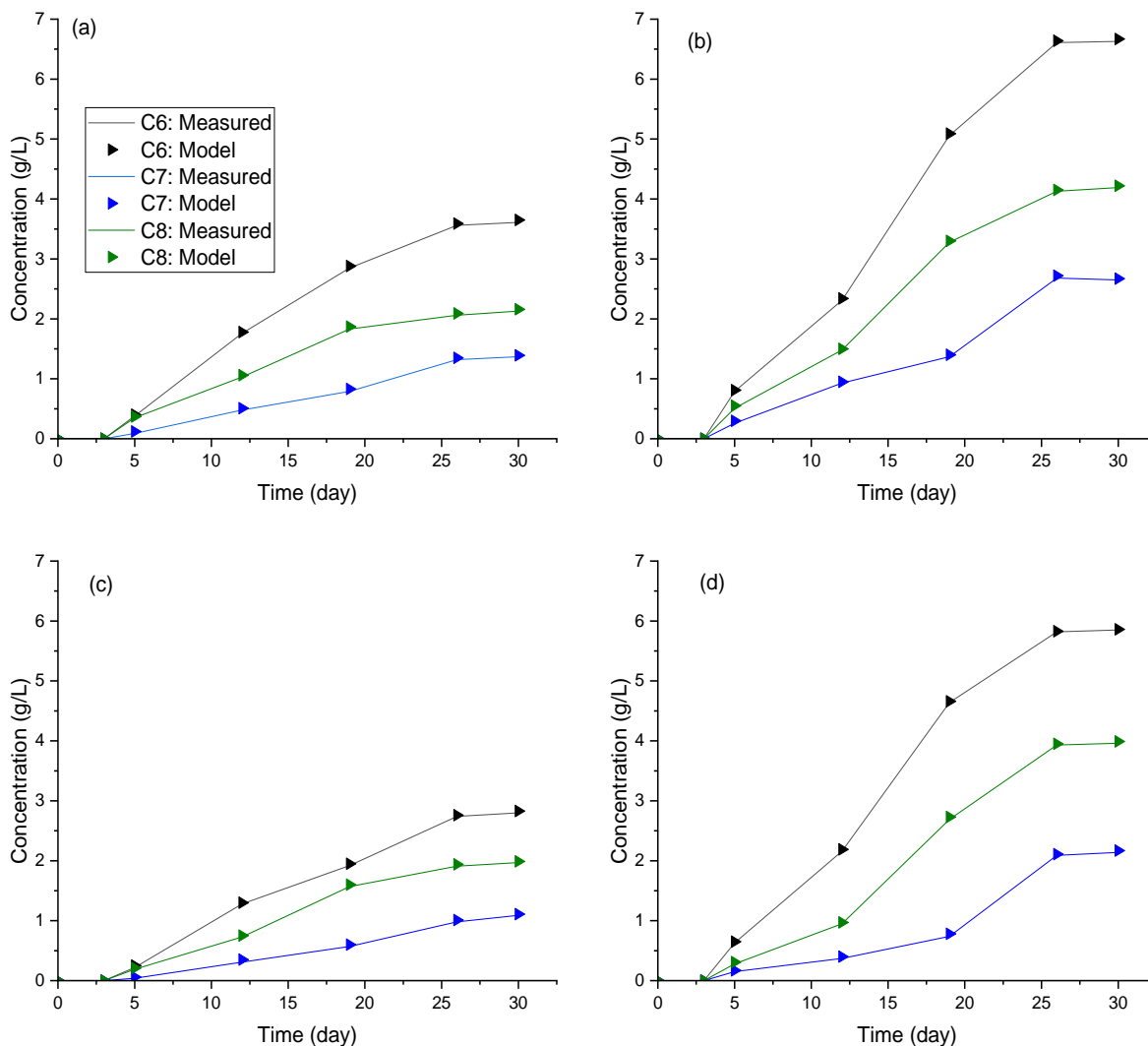


Figure 3. Fitness of the first-order model to the the measured data of MCC produced from the fermentation of (a) unensiled substrate with leachate, (b) ensiled substrate with leachate, (c) unensiled substrate with rumen fluid and (d) ensiled substrate with rumen fluid.

4. Conclusion

The use of food waste as a substrate for medium chain carboxylates (MCC) production is one way of achieving the goal of circular economy. The yield of MCC from food waste can be enhanced by ensiling, which is a cost effective, easy and sustainable method of pretreatment of lignocellulosic biomass. Ensiling degraded cellulose and hemicellulose contents of food waste as well as converted the water soluble carbohydrate content of food wastes into lactic acid and ethanol that were used for the chain elongation process, thereby enhancing the yield of MCC.

Compared to rumen fluid, leachate is a better inoculum for the production of MCC from food waste. As far as the modeling of the production of MCC is concern, the first-order model is a better model for the understanding and prediction of reactor performance compared to the modified Gompertz model. The parameters obtained from the model can, therefore, be used for the process simulation and optimization of biological reactors used in the fermentation of food wastes for MCC production.

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