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Evaluation of the Methane Potential and Kinetics of Supermarket Food Waste

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Abstract

AQ1 The methane potential of supermarket food waste (SMW) has scarcely been determined, especially at 55 °C. In this paper, the different types of SMW generated in a chain of supermarkets have been characterized over a period of 1 year. Batch anaerobic digestion tests employing six different mixtures of SMW were conducted under thermophilic conditions. Start-up was very rapid, with lag-phase values <1 day, reaching peak methane production rates before day 5. The observed methane yields ranged between 453 and 678 L/kg VS. The highest value was obtained with the mixture including waste generated from all the different sections of the supermarket (fish, fruit and vegetables, butchery, bakery, and charcuterie), followed by the mixture not including fruit and vegetable waste, with no statistical significant differences between these values. The lowest value was obtained when bakery waste was not included in the mixture. The results are consistent with the observed degradation in volatile solids, ranging from 78 to 91%. The modified Gompertz kinetic model provided a better fit than the first-order kinetic model, with R^2 values higher than 0.994 and deviations between experimental and theoretical values ranging from 1.5 to 6.1%. The technical digestion time (t_{80}–t_{90}) was calculated to range between 11.5 and 14 days, with the exception of the substrate containing all five types of waste generated in the supermarket, which ranged between 14.5 and 17 days. Scanning electron microscopy (SEM) images showed the further deterioration and size reduction of particles in the substrate producing the highest methane yield.

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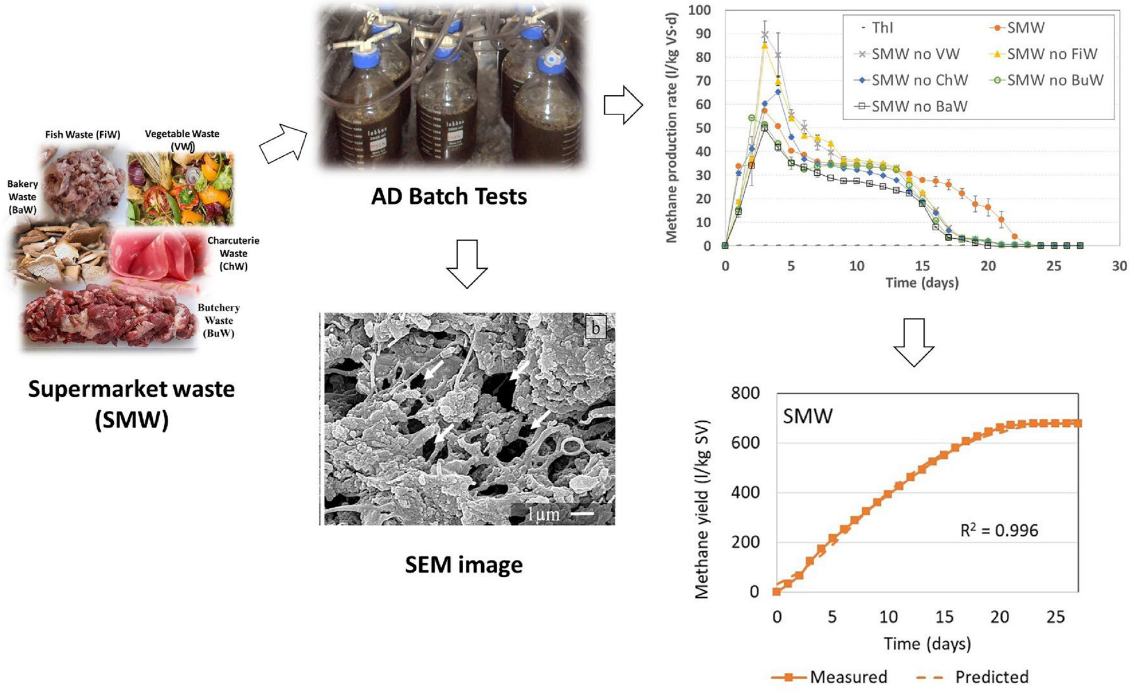
Graphic Abstract



Keywords Supermarket food waste · Anaerobic digestion · Biochemical methane potential (BMP) · Kinetics · SEM

Statement of Novelty

There are several studies on the digestion of food waste, but these generally refer to fruit and vegetable waste, fish waste, the organic fraction of municipal solid waste, mixed waste from markets, catering or bars and canteens. Studies on supermarket waste, especially under thermophilic conditions, are very scarce, however. This paper studies the batch thermophilic co-digestion of mixtures of the waste generated in the different supermarket sections, taking into consideration the ratios of generation. An extensive characterization was performed (over a period of 1 year, with samples taken from various supermarkets). This paper evaluates methane potentials depending on the components of the co-digested mixtures. An additional finding is the validation of two kinetic models, the first-order kinetic model and the modified Gompertz model, to predict experimental results and determine the corresponding kinetic parameters.

Introduction

According to FAO [1], approximately one third of the food produced worldwide goes to waste, corresponding to 1.3 Gtonnes of food waste every year. To put this figure into context, FAO also estimates that this food waste gives rise to greenhouse gases corresponding to 3.3 Gtonnes of carbon dioxide equivalents (CO_2eq) every year.

In the European Union, about 90 Mtonnes of food goes to waste every year [2, 3], equivalent to 175 kg per capita per year. Even though the amount of waste generated in the retail supply chain is less than in some other stages (agricultural production and harvesting, processing and domestic consumption), the amounts involved are still enormous, approximately 4.4 Mtonnes per year in the EU-27 [2]. Annual food wastages in the UK retail sector are estimated at 250 ktonnes [4]. Göbel et al. [5] estimated waste production in this industry sector in Germany of around 3%. In Sweden, Eriksson et al. [6] estimated waste production of around 3.8% in the same sector. According to Gustavsson et al. [7], the retail sector is responsible for approximately 5% of food losses in developed countries.

The number of supermarkets increased in Spain from 17,148 in 2008 to 19,554 in 2015 [8]. Rapid development in this sector is likely to result in increased waste generation.

According to a study by the European Commission [2], more than 7.7 Mtonnes end up in landfill each year in Spain, 5% of which corresponds to retail outlets (about 385,000 tonnes).

At the end of their shelf life, there are many techniques to avoid foodstuffs being disposed of in sanitary landfills. For example, of the estimated 250 ktonnes of annual food wastage in the UK retail sector [4]: ~ 2% of this amount is redistributed (donated) to people; ~ 10% is converted to animal feed; while ~ 30% is managed through recycling (anaerobic digestion (AD) and composting), recovery (incineration and landfill with energy recovery) and disposal.

Anaerobic digestion of vegetable and fruit waste, food waste, fish waste and the organic fraction of municipal solid waste has previously been evaluated in different studies [9–16]. As far as we know, however, information on the AD of supermarket waste is scarce in the literature. One such study was carried out by Alkanok et al. [17], who analysed the mesophilic AD of mixed market waste (fruit, vegetable and flower waste, dairy products waste, meat waste and sugar waste) in batch reactors at solids ratios of 5%, 8% and 10%. The highest methane yield, 440 L CH_4/kg volatile solids added, was obtained from AD of the waste with a total solids content of 10%, the methane content being 66.4%. Studies conducted under thermophilic conditions are even scarcer.

The evaluation of digestion kinetics helps to describe specific parameters for monitoring system performance and is a valuable tool in the design and operation of biological treatment plants. Several models can be implemented for anaerobic digestion, such as the first-order, Monod, Contois, Gompertz, Gompertz, Chen and Hashimoto, ADM1, Cone and Grau second-order models [18–22]. Segregated models involving a large number of equations and parameters are computationally more complex, which makes their implementation often cumbersome. Non-segregated models based on kinetic equations are simpler and widely used to model biodegradation and can take into account inhibition effects.

To develop practical models with a small number of fitting parameters, a rate-limiting step is usually assumed. Given that hydrolysis is the rate-limiting step in AD, especially when digesting complex materials, a simple and widely applied model is the first-order kinetic model [20–22], which enables calculating the methane potential and decay constant. Of particular interest is the modified Gompertz model [23–25], which accounts for different stages in the conversion of substrate to CH_4 and allows determining the duration of the lag phase and a maximum rate in the production of methane, as well as the methane potential or ultimate capacity of methane production.

Scanning electron microscopy (SEM) has also been previously used to investigate the degradative effect of AD on vegetable and other types of waste. Molinuevo-Salces et al. [26] used SEM characterization to investigate the effect of the co-digestion of vegetable wastes and swine manure on methane production. Li et al. [27] used SEM to investigate the structural changes in cattle manure fibres in anaerobically digested kitchen waste and cattle manure. SEM images from these studies showed a good correlation between degradation of the substrate components and biogas production. To the best of our knowledge, however, no information is available regarding SEM examination of the AD of supermarket food waste.

The objectives of this paper were to: (1) characterize the food waste produced in the different sections of supermarkets (fish, fruit and vegetables, butchery, bakery and charcuterie); (2) evaluate the methane potential of mixtures containing the different types of waste under thermophilic conditions (55 °C); and (3) evaluate the batch digestion process by fitting the experimental results to two kinetic models, namely the first-order kinetic model and the modified Gompertz model, determining the corresponding kinetic parameters.

Materials and Methods

Supermarket Food Waste and Inoculum

The supermarket food waste (SMW) was collected from Alimerka, a supermarket chain based in the north of Spain. The company has 173 supermarkets in the regions of Asturias, Galicia, and Castile and León and employs more than 6000 workers.

Five types of food waste are produced: waste from the fishmonger's section (FiW); fruit and vegetable waste (VW); meat scraps from the butcher's section (BuW), which includes chicken (small pieces of meat plus skin waste and bones, etc.), pork (meat, small bones and trotters), turkey (small pieces of meat plus skin waste and bones, etc.) and beef (meat, small bones, etc.); bakery waste (BaW), which includes bread, pies, cakes, etc.; and charcuterie waste (ChW). Currently, the waste generated by Alimerka is managed by a household waste manager and is disposed of in a municipal solid waste landfill, with the exception of the waste products from the butcher's and fishmonger's sections, which are classified as category three material [28] and are accordingly managed for treatment by another authorized manager. Other supermarket chains in Spain present similar characteristics to those of Alimerka.

To characterize the different types of waste, samples were taken at 10 of the company's supermarkets. The study was carried out over a period of 1 year in order to consider the variation in consumption depending on the season. At each supermarket, 12 samples were taken of the different types of waste that show greater variability (VW, BuW and FiW) and 6 samples of the other two types of waste (BaW and ChW). A minimum of 2 kg per sample of each waste was taken for the purposes of characterization. The waste produced in the different sections of the supermarket was ground in an industrial STR-2000 triturator, followed by a second grinding using a Philips 5000 HR355/00 blender, and stored at 4 °C before characterization, which was carried out within 2 days so as to avoid changes in composition.

The anaerobic sludge used as inoculum for the batch tests was obtained from a 20 L lab-scale thermophilic reactor digesting cattle manure and raw glycerin.

Biochemical Methane Potentials

After grinding the different types of supermarket waste, six mixtures were prepared always considering the proportion in which the different types of waste were generated: one mixture containing all the different types of waste (SMW), and five others, each containing four out of the five different types of waste [without fish waste (SMW no FiW), without fruit and vegetable waste (SMW no VW), without butchery waste (SMW no BuW), without bakery waste (SMW no BaW) and without charcuterie waste (SMW no ChW)].

BMP tests were conducted at 55 °C in batch reactors with a capacity of 2 L provided with a biogas outlet. The temperature was maintained by using a Selecta Dry-Big forced air convection drying furnace, with a temperature range from 40 to 250 °C. The feed-to-inoculum ratio was kept at 2.0 (based on the volatile solids content), the volatile solids content in the batch reactors being approximately 18 g/L. Given the characteristics of the inoculum, its high alkalinity to provide pH-buffering capacity and the presence of macro- and micro-nutrients, the addition of amendments was not considered necessary [29–31]. After the mixtures were shaken evenly by hand, the headspace of the reactors was flushed with nitrogen to obtain an anaerobic environment. All tests were carried out in triplicate, including the blank assay to evaluate the endogenous methane production of the inoculum, which was subsequently subtracted to obtain the net methane production for each substrate.

During the digestion period, the reactors were manually shaken every day prior to gas measurement to ensure close contact between microorganisms and substrate. Daily biogas production was measured by means of the water displacement method (the water was acidified to $pH < 2$ to prevent CO_2 dissolution) and the volume was corrected for standard temperature and pressure (STP). An Agilent 7890A gas chromatograph, equipped with a thermal conductivity detector (TCD) and a Porapak N packed column plus a molecular sieve, was used to determine the methane and carbon dioxide content of the biogas. The carrier gas was argon and the starting temperature was 35 °C (1.5 min), increasing up to 55 °C at a rate of 1.5 °C/min.

A statistical analysis was carried out on the results of the methane yield of the different mixtures of waste. SigmaPlot software and the one-way ANOVA were used to test the significance of the differences between pairs of samples, those with $p < 0.05$ being considered significant.

Analytical Methods

Parameters such as pH, total solids (TS) and volatile solids (VS) were determined according to the Standard Methods for the Examination of Water and Wastewater [32]. Nitrogen and phosphorus were determined by ion chromatography (861 Advanced Compact IC 2.861.0010), after their conversion into nitrates and phosphates, respectively, via digestion under pressure with H_2O_2 and HNO_3 in a microwave oven (Milestone Ethos 1 Advanced Microwave Digestion Labstation). Ammonium nitrogen (NH_4^+–N) was determined by titration with boric acid after distillation using a FOSS Tecator Kjeltec 2200 Auto Distillation System. Total alkalinity (TA) and volatile acidity (VA) were determined according to Degremont [33]. The carbon content was determined using an Elemental Vario EL analyser.

Kinetic Models

First-Order Kinetic Model

Hydrolysis is assumed to be a rate-limiting step in anaerobic digestion, especially when digesting solid waste, and the degradation of compounds may follow a first-order decay rate [20–22]. The production of methane is assumed to follow Eq. (1):

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

where $G(t)$ is the cumulative methane yield at time t (L/kg VS), G_0 is the methane potential of the substrate (L/kg VS), K is the first-order disintegration constant as well as the methane production rate constant (day^{-1}), which is determined by taking the reciprocal of the time from the start of the BMP test until $G(t)$ reaches 0.632 G_0, and t is the anaerobic digestion time (day).

A straight line is obtained by plotting ln [1-(G(t)/G_0)] versus time until G(t) reaches 0.632 G_0. The first-order disintegration constant can be calculated from the slope of the straight line by performing a linear regression.

Modified Gompertz Model

The modified Gompertz model has been widely used to predict methane yields and kinetic parameters and for designing batch biogas reactors [23–25].

$$G(t) = G_0 \cdot exp\left\{-exp\left[\frac{R_{max} \cdot e}{G_0}(\lambda - t) + 1\right]\right\} \quad (2)$$

where R_{max} is the maximum methane production rate (L/kg VS day), λ is the duration of the lag phase (day), t is the time over the digestion period, and e is equivalent to exp (1) or 2.7182. The Gompertz parameters, especially the lag phase and minimum time taken to produce biogas (λ), are important in determining the efficiency of anaerobic digestion.

A nonlinear least-square regression analysis was performed using Matlab software R2020a (9.8.0.1323502) to determine λ, Rmax and the predicted methane potential.

The statistical parameters coefficient of determination (R^2) and root mean square error (RMSE) were also obtained for both kinetic models using Matlab software.

$$RMSE = \left(\frac{1}{m} \sum_{j=1}^{m} \left(\frac{d_j}{Y_j} \right)^2 \right)^{1/2} \quad (3)$$

where m is the number of data pairs, j is jth values, Y is the measured methane yield (mL/g VS) and d is the deviation between the measured and the predicted methane yields.

Scanning Electron Microscopy

In order to analyse the microstructural changes that took place in the process, samples of the thermophilic inoculum and the supermarket food waste were taken for SEM examination before and after anaerobic treatment. Dry samples were mounted on double-sided tape placed on aluminium stubs. A thin layer of gold was sputtered onto the mounted sample using a Bal-Tec SCD 005 sputtering device (40 mA, 360 sg sputtering) in order to reduce electron-altering effects. Finally, the gold-coated samples were observed at an accelerating voltage of 20 kV. Microstructural observation of the waste before and after digestion was carried out using a JEOL JSM 5600 scanning electron microscope (JEOL Ltd., Tokyo, Japan).

Table 1 Generation of the different types of waste in the supermarket chain

Type of waste	Generation (%)
Fish waste (FiW)	34.1 ± 1.7
Fruit and vegetable waste (VW)	26.1 ± 2.1
Butchery waste (BuW)	23.5 ± 1.2
Bakery waste (BaW)	15.1 ± 0.9
Charcuterie waste (ChW)	1.2 ± 0.2

Results and Discussion

Physicochemical Characteristics of the Supermarket Food Waste

Table 1 shows the percentages by weight in which the different types of waste are generated in the supermarket chain. The results obtained over a period of 1 year at 10 supermarkets show little variability, the highest standard deviation (2.1%) being found for fruit and vegetable waste. This waste plus the fish waste and butchery waste represent 84% of the total waste generated.

The results of the characterization of the different type of supermarket waste are shown in Table 2. The solids content (TS) is highly variable, ranging from approximately 65% in the waste from the charcuterie section to 14% in the fruit and vegetable waste. In the characterization of the latter type of waste, Jiang et al. [34] reported TS values below 20%, and Esteban et al. [35], values of around 12%. The TS values found in this research for fish waste, FiW (27%), were similar to the value of 26% reported by Esteban et al. [35]. Volatile solids (VS) represent between 81 and 96% of TS. pH values are neutral or close to neutral, with the exception of fruit and vegetable waste (pH 4.6).

Nitrogen and, to a lesser extent, phosphorus are present in protein-rich foods; hence, the highest content in these elements was found in fish waste and butchery waste. Ammonium concentrations are very low, with values below 0.1 mg/kg in all types of waste (data not included). C/N ratios vary substantially depending on the components of foodstuffs, ranging between 14 for fish waste to 79 for bakery waste.

Table 2 Physicochemical characteristics of the fish waste (FiW), fruit and vegetable waste (VW), butchery waste (BuW), bakery waste (BaW), and charcuterie waste (ChW)

	FiW	VW	BuW	BaW	ChW
TS (g/kg)	274.12 ± 40.01	140.00 ± 28.02	453.01 ± 53.21	405.21 ± 48.13	647.32 ± 104.11
VS (g/kg)	222.10 ± 33.11	123.00 ± 28.23	422.15 ± 51.05	388.31 ± 45.15	596.12 ± 95.00
pH	7.2 ± 0.1	4.6 ± 0.2	6.0 ± 0.1	6.2 ± 0.1	6.5 ± 0.1
C (g/kg)	112 ± 1.68	66 ± 3.52	206 ± 12.35	199 ± 9.80	313 ± 10.45
N (g/kg)	8.01 ± 0.42	1.61 ± 0.63	9.42 ± 0.41	2.52 ± 0.23	7.82 ± 0.71
C/N	14 ± 0.30	41 ± 0.42	22 ± 0.32	79 ± 0.41	40 ± 0.38
P (mg/kg)	19.22 ± 10.61	2.73 ± 3.22	10.80 ± 9.31	6.00 ± 2.71	7.72 ± 1.42
VA (mg/kg)	2102 ± 41.6	1509 ± 32.1	2030 ± 62.0	1024 ± 58.5	2802 ± 33.0
TA (mg/kg)	4225 ± 43.5	1103 ± 28.0	3008 ± 42.3	1526 ± 65.2	3212 ± 43.1

Although C/N ratio values between 20 and 30 are the most recommendable for anaerobic digestion, operating outside this range of values is also possible [20, 36–40]. In the present study, these values fluctuate in the mixtures of the different types of waste, prepared according to the proportion in which they are generated.

Batch Aanaerobic Digestion Test Results

Six mixtures of supermarket food waste were studied: one containing the five different types of waste generated at the supermarket and the others each containing four different types of waste. As stated in Sect. "Biochemical Methane Potentials", each type of waste was added according to the proportion in which it is generated. Table 3 shows the characteristics of the different substrates employed in the batch tests.

The total solids content of the substrates ranges from 21% in the mixture without butchery waste to 34.5% when no fruit and vegetable waste is present in the mixture (due to the high water content of this waste). As to volatile solids, the values represent around 87–89% of total solids, with the exception of the mixture not containing fish waste (76%). C/N ratios fall within the suitable range for AD in three of the substrates, but are somewhat higher in the substrates not containing fish or butchery waste, with values of 43 and 36, respectively. These wastes present the highest nitrogen values, contributing to lowering the C/N ratio when they are present in the mixtures. Although the optimal values considered in the literature vary between 20 and 30, some researchers have reported good performance at other values. For example, Guarino et al. [41], when digesting buffalo manure under mesophilic conditions, obtained high biomethane productivity in a wider C/N range, between 9 and 50. Romano and Zhang [36] proposed that the C/N ratio should be maintained at 15 for co-digestion of sewage sludge and onion juice.

The inoculum added for the AD batch tests came from a lab-scale thermophilic anaerobic reactor co-digesting cattle manure with small amounts of residual glycerin from a biodiesel plant. The physicochemical characteristics of this inoculum are given in Table 4. The inoculum has very high alkalinity, providing a good pH buffering capacity to prevent acidification in the digestion process despite the high biodegradability of the substrates. Minimal changes can be observed after digestion, in line with the very low methane production observed in the blank tests, representing between 0.9 and 1.4% of the methane obtained when digesting the different mixtures of supermarket food waste.

Table 4 Physicochemical characteristics of the thermophilic inoculum (ThI) before and after digestion (blank tests)

Parameter	Before AD	After AD
TS (g/kg)	10.41 ± 0.51	10.32 ± 0.05
VS (g/kg)	8.07 ± 0.46	8.00 ± 0.02
pH	7.5 ± 0.1	7.4 ± 0.1
N (g/kg)	2.00 ± 0.04	1.98 ± 0.05
NH_4^+–N (mg/kg)	990 ± 10	975 ± 10
P (g/kg)	1.39 ± 0.05	1.35 ± 0.06
VA (mg/kg)	100 ± 10	56 ± 1.0
TA (mg/kg)	7103 ± 120	7060 ± 11

Figure 1 shows the daily and cumulative methane production of the different mixtures of supermarket food waste during the batch thermophilic digestion tests, as well as the methane produced by the inoculum in the blank tests. Methane production commenced in all 18 reactors on the first day. A fast start-up and a rapid production rate may be associated with the thermophilic process, as well as the high biodegradability of the components of foodstuffs. The highest methane production rate appeared before day 5 and production dropped significantly after 15 days, with the exception of the mixture containing the five types of waste, in which the rate decreased more slowly. The peak values of the daily methane production rates were calculated to be 57.2, 54.2, 85.1, 89.7, 65.3 and 49.9 L/kg VS day after 3, 2, 3, 3, 4 and 3 days of digestion for SMW, SMW no Bu, SMW no FiW, SMW no

Table 3 Physicochemical characteristics of the substrates used for AD batch tests

Parameter	SMW	SMW no BuW	SMW no FiW	SMW no VW	SMW no ChW	SMW no BaW
TS (g/kg)	273 ± 6.2	211 ± 3.2	296 ± 5.6	345 ± 4.8	296 ± 2.9	266 ± 3.5
VS (g/kg)	244 ± 4.5	183 ± 3.9	225 ± 4.6	303 ± 3.8	260 ± 3.7	231 ± 3.3
pH	7.5 ± 0.1	7.5 ± 0.1	7.1 ± 0.1	7.6 ± 0.1	7.6 ± 0.1	7.4 ± 0.1
C (g/kg)	188 ± 1.8	166 ± 2.2	195 ± 2.1	220 ± 1.9	188 ± 2.7	156 ± 3.2
N (g/kg)	5.71 ± 0.82	4.62 ± 0.55	4.56 ± 0.68	7.35 ± 0.84	5.69 ± 0.41	6.24 ± 0.76
C/N	33 ± 1.1	36 ± 1.4	43 ± 1.4	30 ± 1.2	33 ± 1.6	25 ± 1.8
P (mg/kg)	10.57 ± 0.7	10.5 ± 1.1	13.32 ± 1.0	13.71 ± 0.9	10.61 ± 1.1	11.34 ± 0.9
VA (mg/kg)	1768 ± 10.5	1691 ± 10.3	1602 ± 14.2	1871 ± 11.1	1756 ± 13.1	1893 ± 12.7
TA (mg/kg)	2655 ± 12.5	2551 ± 11.8	1873 ± 13.4	3277 ± 15.6	2649 ± 12.1	2845 ± 16.3

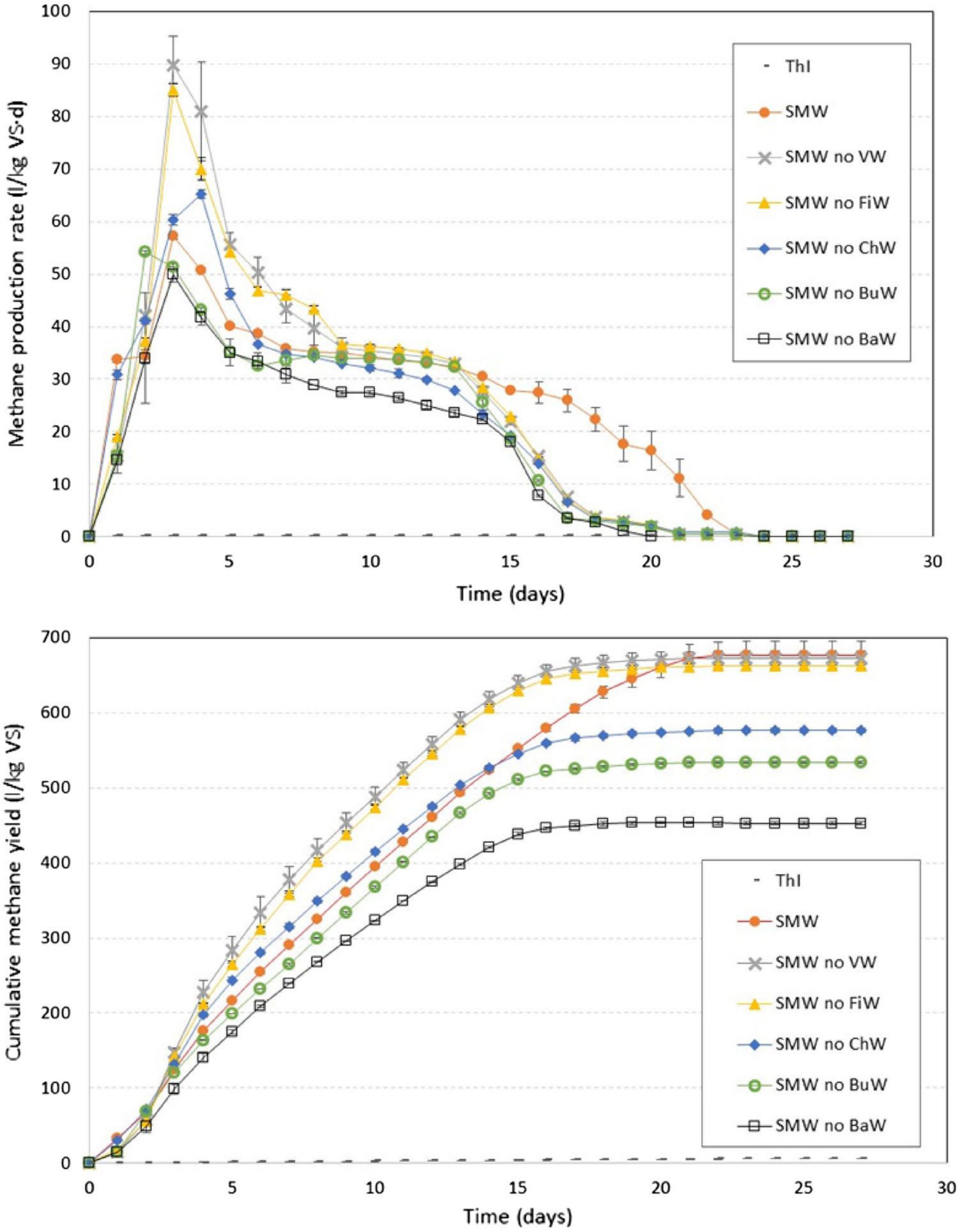


Fig. 1 Daily and cumulative methane production from different mixtures of supermarket food waste. The values are means ± standard deviations

VW, SMW no ChW and SMW no BaW, respectively. These values are in agreement with those obtained when applying the modified Gompertz model to the experimental results, as will be discussed in the next section.

Table 5 shows the results regarding methane yield, the time taken to achieve 80–90% of the ultimate methane production, the methane content of the biogas and the volatile solids degradation. The highest methane yields were obtained for the substrate containing all five types of waste and for the substrate not containing fruit and vegetables (678 and 673 L CH_4/kg VS, respectively), which is in line with the higher volatile solids degradation obtained in these two substrates (90.8% and 90.4%). Statistically, no significant difference was found between the methane yield of the mixture containing the five types of supermarket food waste and the mixture not containing fruit and vegetables (p-value 0.785). This result may bee to the higher water content of the fruit and vegetable waste and hence its lower contribution to the volatile solids in the mixture compared to the other types of waste. Moreover, fruit and vegetables are mainly composed of carbohydrates, which have a lower methane potential than proteins or lipids [42]. The substrate that generated the lowest methane yield (453 L CH_4/kg VS) was the one containing no bakery waste (SMW no BaW), representing a 33% decrease with respect to the maximum value obtained. The decreases in methane potential of the other substrates with respect to the maximum value ranged from 8.6% for the substrate containing no fish waste (SMW no FiW) to 21%

Table 5 Measured biochemical methane potential, methane content in the biogas, technical digestion time, and volatile solids removal for the different mixtures of SMW

	BMP (L CH_4/kgVS)	VS removal (%)	Aver. CH_4 (%)	Aver. CH_4 from day 3 (%)	Max. CH_4 (%)	t_{80} (days)	t_{90} (days)
SMW	678 ± 17.5	90.8 ± 1.2	56.7 ± 0.2	59.9 ± 0.2	60.9	14.5	17
SMW no BuW	534 ± 1.4	81.6 ± 1.1	54.5 ± 0.7	57.5 ± 0.5	59.2	12	14
SMW no FiW	620 ± 4.4	87.5 ± 0.9	56.8 ± 0.8	60.1 ± 0.5	62.4	11.5	13.5
SMW no VW	673 ± 9.2	90.4 ± 1.3	57.4 ± 0.8	60.3 ± 0.6	66.0	11.5	13.5
SMW no ChW	577 ± 3.1	84.3 ± 0.8	55.1 ± 0.9	57.9 ± 0.5	60.8	11.5	13.5
SMW no BaW	453 ± 1.7	77.8 ± 1.7	56.1 ± 0.5	60.3 ± 0.3	61.5	11.5	13.5

for the substrate containing no butchery waste (SMW no BuW). The differences in methane yields were found to be statistically significant, with p-values < 0.001 for MSW and MSW no BuW, MSW and MSW no ChW, MSW and MSW no BaW, and a p-value of 0.049 for SMW and SMW no FiW.

The degree of degradation of volatile solids shows a good correlation with methane potential, as can be appreciated in Eq. (3).

$$VS_{degradation\ degree}(\%) = 50.593 + 0.0591\ G_0 \tag{4}$$

$$(R^2 = 0.9944)$$

The results obtained by other authors in batch anaerobic digestion of different supermarket food waste, carried out under mesophilic conditions, gave rise to higher methane yields when co-digesting different substrates, although lower values were obtained. Alkanok et al. [17] reported 440 L/kg VS when digesting supermarket waste consisting of fruit, vegetable and flower waste, dairy products waste, meat waste and sugar waste. Bouallagui et al. [43] showed that the addition of fish waste as a co-substrate in anaerobic digestion of fruit and vegetable waste, also under mesophilic conditions, increased the biogas production yield by 8.1%.

As regards the methane content in the biogas, Table 5 shows the average values obtained throughout the entire digestion process from the start-up of the reactor; the average values excluding the first 2 days; and the maximum values obtained during the process. The methane content rose rapidly during the first 2 days in all the tests. Average values, excluding the first 2 days, range between 58 and 60%, with no significant differences being found between these values.

The time period to obtain 80–90% of the ultimate methane production, known as the technical digestion time (t_{80-90}), can be used as a recommendation for a suitable hydraulic residence time for continuous AD [44]. The technical digestion time was calculated to be between 11.5 and 14 days, with the exception of SMW, which contains all five types of waste generated in the supermarket, which was within 14.5–17 days. Despite needing a longer time, it would be more convenient to co-digest all the different types of waste produced due to the higher methane potential, as well as the reduction in logistics costs and environmental impact in waste management.

Kinetic Analysis Results

Figures 2 and 3 show the results of the non-linear fitting of values of the experimental methane yield for the six studied substrates applying the first-order kinetic model and the modified Gompertz model, respectively. Both models showed very good performance, obtaining higher determination coefficients (R^2) for the Gompertz model (0.994–0.996) compared to the first-order kinetic model (0.964–0.984).

Table 6 summarises the fitting results of the model parameters. The modified Gompertz model shows less difference between the predicted and measured values (1.5–6.1%). Besides the extremely high values of the R^2 coefficient for both models, the modified Gompertz model matches the experimental results more closely than the other model. The lag phase (λ) of the six substrates was lower than 1 day (0.57–0.97 days). Deepanraj et al. [45] found values within the 0.1–1.0 range when applying this model to anaerobic digestion of food waste from a hostel under mesophilic conditions. Much higher values (10 days) were obtained by Pramanik et al. [46] in their study on the mesophilic anaerobic digestion of food waste from a cafeteria, though under continuous operation. Results may differ greatly due to the dependence on various variables, such as substrate characteristics, volatile solids concentration, inoculum activity, digestion temperature and initial pH [20, 43]. Regarding the maximum biogas rate (R_{max}), values ranged between 40.6 and 61.6 L/kg VS day. The highest R_{max} was estimated for the substrate containing no fruit and vegetable waste, while the lowest value was estimated for the mixture containing no bakery waste, in line with the experimental results. For the first-order kinetic model, the disintegration constant (K) ranged between 0.084 and 0.113 day^{-1}. The RMSE value fell within the 0.212–0.645 range in the first-order kinetic model and within the 0.100–0.343 range in the modified

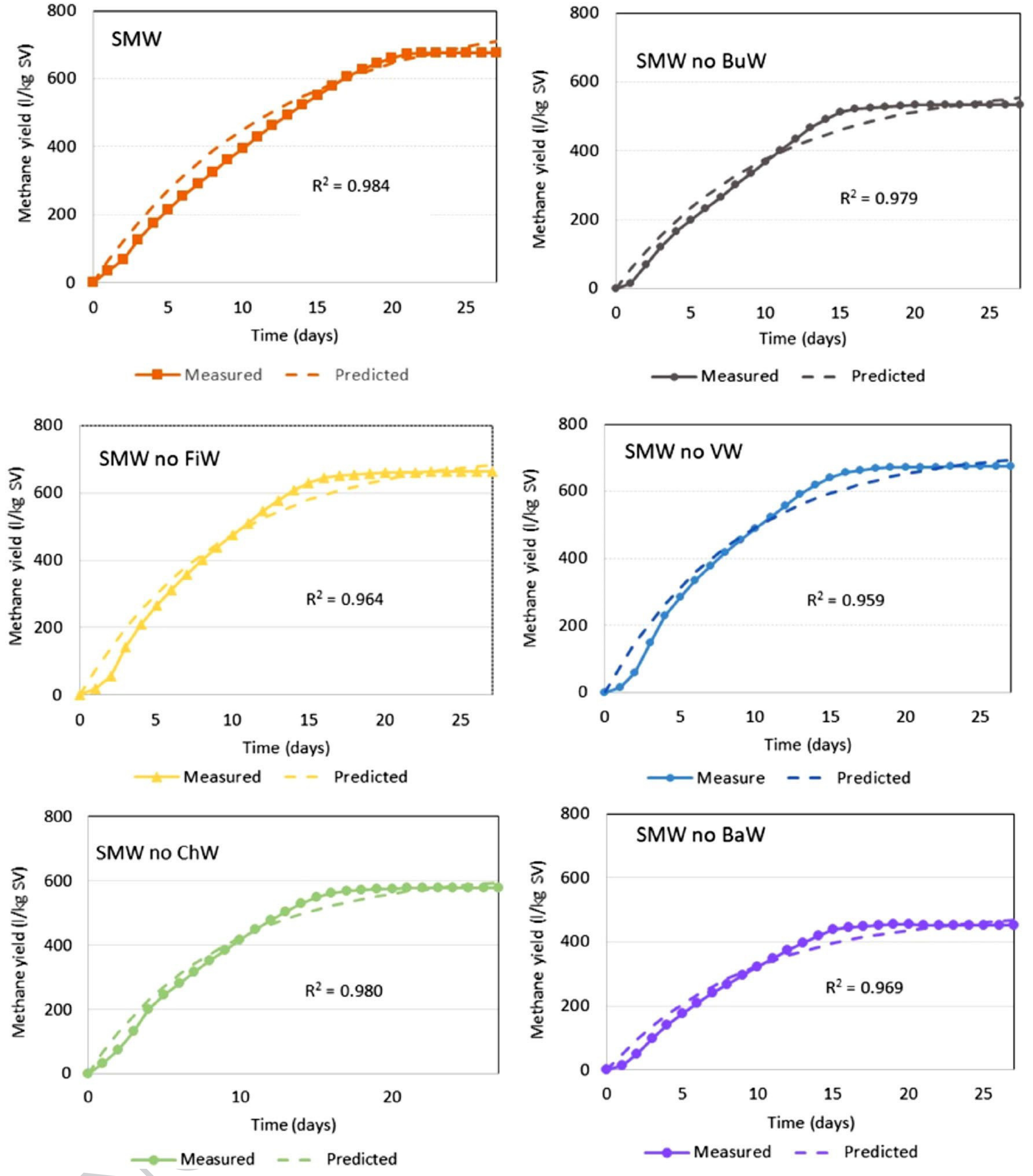


Fig. 2 Experimental and predicted values of the methane yield of mixtures of supermarket food waste using the first-order kinetic model

Gompertz model. Comparing the values of the statistical parameters, it can be appreciated that the modified Gompertz model provides a better fit to the experimental results, showing higher R^2 values and lower RMSE values.

SEM Characterization

SEM observation of the structure and surface characteristics of the thermophilic inoculum (ThI) and supermarket food waste (SMW) are shown in Fig. 4. Figure 4a shows the SEM image of ThI. It can be seen that ThI consists of very small aggregate components, most particles being less than 1 µm in size. Figure 4b shows a SEM image of the SMW. It is compact, regular and smooth in appearance, showing the presence of particles with an acicular morphology.

SEM characterization of the substrates was carried out on those producing the highest and lowest methane yield (Fig. 5a and c, respectively). The two substrates are similar in appearance. In both cases, two particle size ranges can be observed: fine particles ($< <$ 10 µm), and coarse particles (>

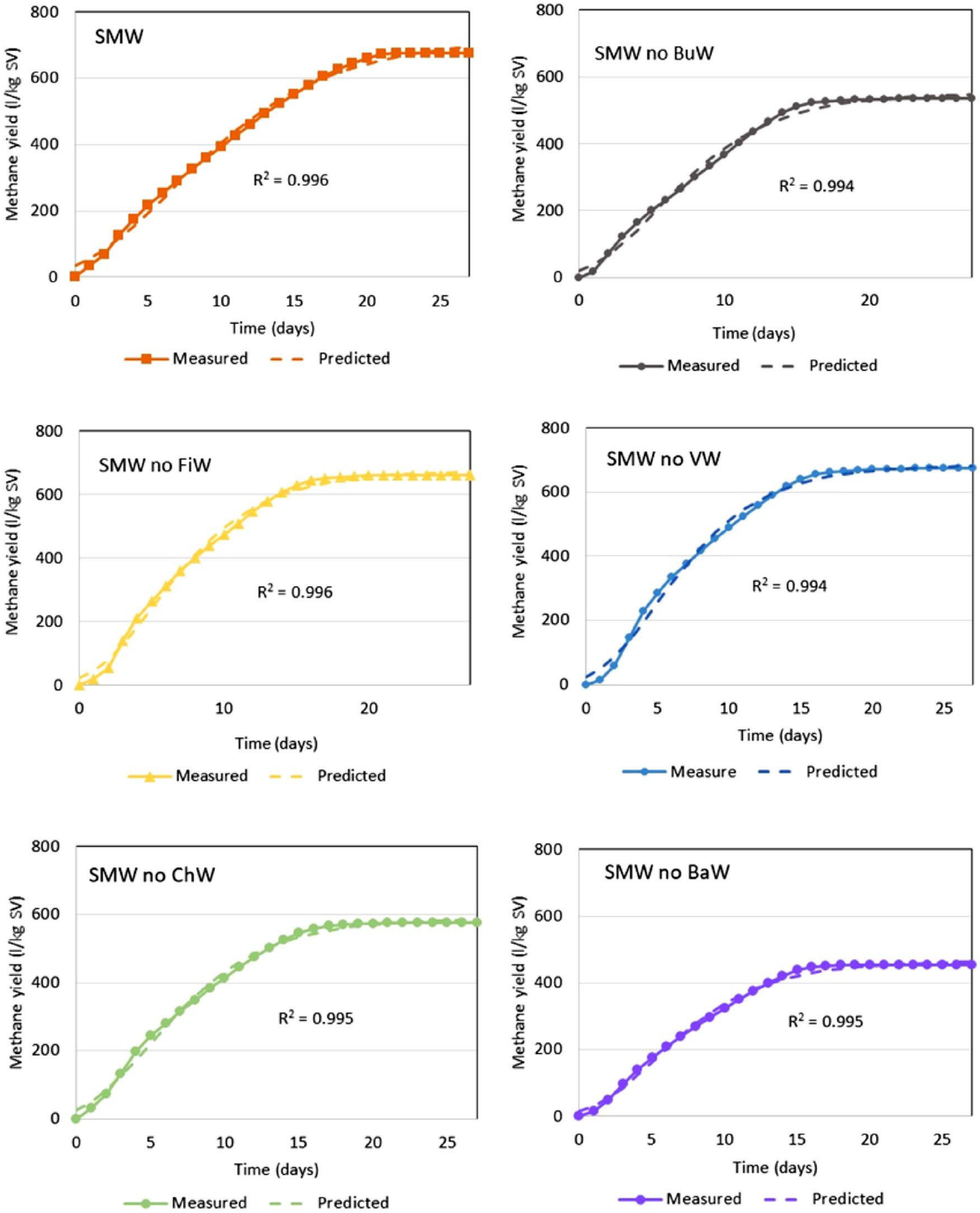


Fig. 3 Experimental and predicted values of the methane yield of mixtures of supermarket food waste using the modified Gompertz model

10 µm). The fine particles are more abundant in both samples and envelop the coarse particles. Li et al. [27] used SEM to observe the structural changes in an anaerobically digested mixture of kitchen waste and cattle manure. The structure of the digested mixture was rough and partially destroyed, in line with the results of this study. After AD, the SEM images show a broken, heterogeneous structure with different sized particles. The size of the fine particles decreased in both samples, the decrease being greater in the SMW sample (Fig. 5b and d). Worth mentioning with respect to these findings is the study by Zeng et al. [47] on the structural changes of corn after enzymatic hydrolysis. These authors conclude that particle size, which is related to the particle's accessible surface area, significantly influences

Table 6 Results of the kinetic study using two different models

Parameters	Units	SMW	SMW no BuW	SMW no FiW	SMW no VW	SMW no ChW	SMW no BaW
First-order kinetic model							
K	Days^{-1}	0.084	0.100	0.108	0.112	0.113	0.107
G_0	L CH_4/kg/VS	792.3	593.9	723.7	728.3	623.1	494.9
Difference*	%	16.9	11.1	9.2	8.2	8.0	9.2
R^2		0.984	0.979	0.964	0.959	0.980	0.969
RMSE		0.212	0.413	0.483	0.645	0.215	0.400
Modified Gompertz model							
R_{max}	L CH_4/kgVS day	43.8	45.3	59.7	61.6	50.0	40.6
λ	days	0.59	0.89	0.95	0.85	0.57	0.97
G_0	L CH_4/kgVS	718.8	550.8	675.0	683.6	588.6	464.7
Difference*	%	6.1	3.1	1.9	1.5	2.0	2.6
R^2		0.996	0.994	0.996	0.994	0.995	0.995
RMSE		0.113	0.230	0.222	0.343	0.100	0.191

*Difference between the predicted and the measured value

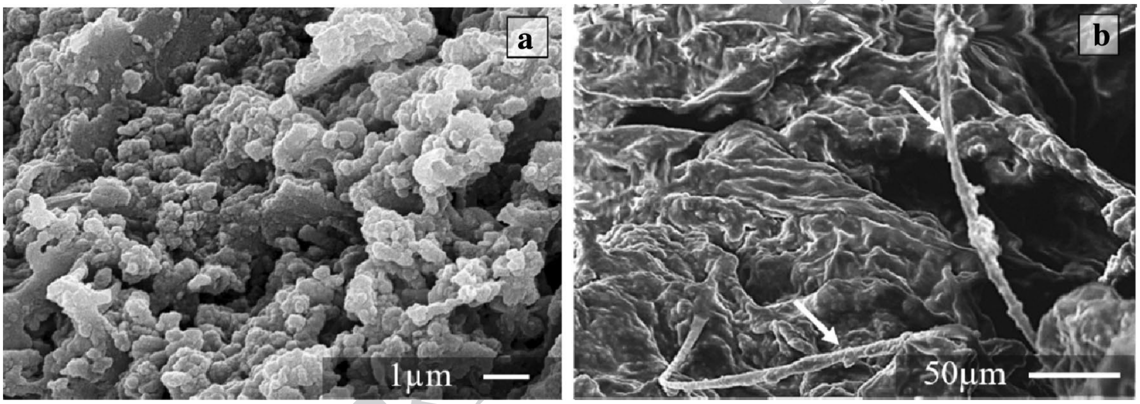


Fig. 4 SEM images of: **a** a thermophilic inoculum sample (ThI); and **b** a mixed waste sample (SMW). Arrows point to acicular particles

enzymatic hydrolysis. Small particles hydrolyse more easily than large ones due to their greater specific surface area.

In the present study, the solid substrates are composed of varying proportions of biopolymers such as lignin, hemicellulose and cellulose [48, 49], the last two being biodegradable components [50]. Molinuevo-Salces et al. [26] investigated the effect of adding vegetable waste as a co-substrate in the anaerobic digestion of swine manure. Their SEM observations demonstrated that lignin did not degrade, as its initial fragmentation requires molecular oxygen [51]. It is worth noting that the SMW without BaW sample in our study presents a higher proportion of cell walls than the SMW sample. The outer walls of the coarse particles in the SMW without BaW sample show no damage (Fig. 5d) and may thus correspond to a non-degradable lignin structure. However, a greater degree of cell wall rupture can be seen in the coarse particles in the SMW sample (Fig. 5b). Cavities and pores with sizes of around 1 μm can be observed. These pores are large enough to be accessible to enzyme molecules [47, 52]. SEM images from Li et al. [27] show the partially destroyed structure of cattle manure co-digested with kitchen waste and a number of small holes, similar to those shown in Fig. 5b. The authors concluded that these structural changes facilitated methane production. It would appear that surface damage occurred in these particles during AD, thereby increasing the exposure of their inner tissues to enzyme molecules. Broken tissues facilitate accessibility to carbohydrolytic enzymes and facilitate their degradation to CH_4 and CO_2 [53], thus contributing to enhanced methanogenesis [27].

The SEM images show that the changes in the structure of the fine and coarse particles that occurred during AD of both samples. Further size reduction in the fine fraction and further deterioration of the coarse fraction occurred in the SMW sample.

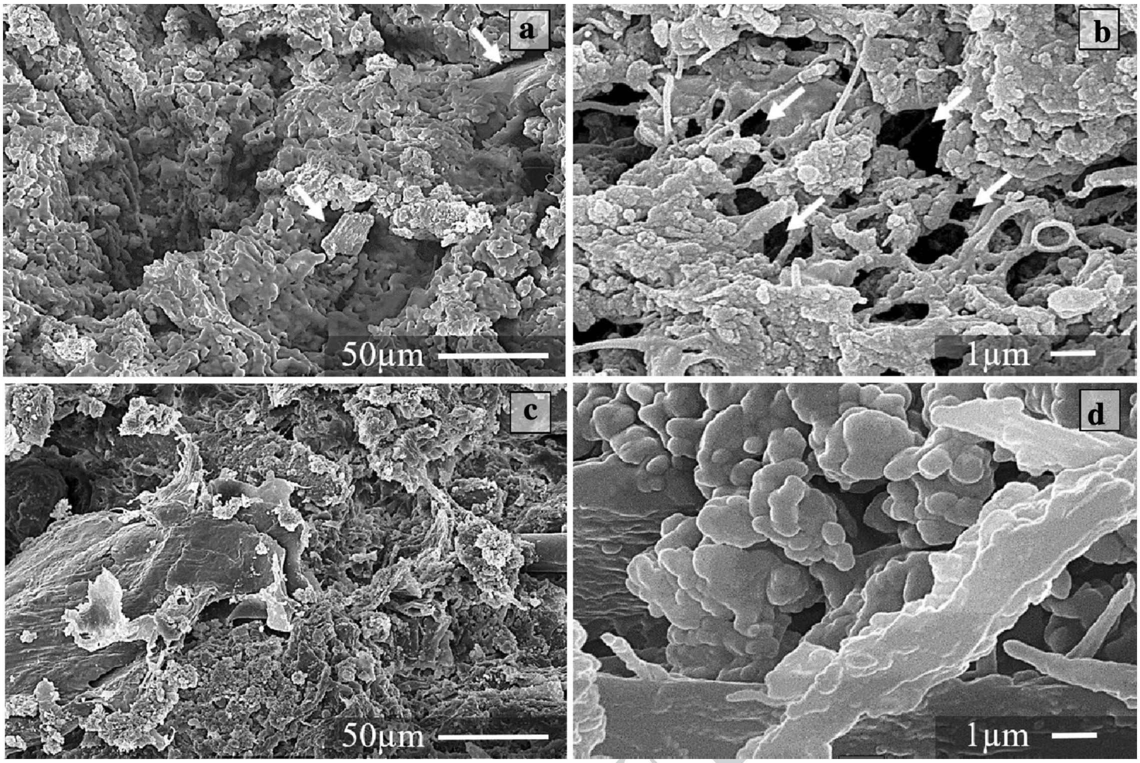


Fig. 5 SEM images of: **a** mixed supermarket food waste (SMW) plus thermophilic inoculum. Arrows point to coarse particles; **b** thermophilic anaerobic digestion of mixed supermarket food waste (SMW) plus thermophilic inoculum. Arrows point to cavities and pores in the coarse particles; **c** mixed supermarket food waste without bakery waste (SMW no BaW) plus thermophilic inoculum; and **d** thermophilic anaerobic digestion of mixed supermarket food waste without bakery waste (SMW no BaW) plus thermophilic inoculum

In short, the SEM observations seem to indicate that greater degradation occurred in the SMW sample during AD than in the SMW without BaW sample. The structural changes observed by SEM are in line with methane production. According to the above observations, there was a 33% decrease in methane yield in the SMW without BaW sample compared to the SMW sample. It would appear that the observed increase in the available surface of the particles facilitated their subsequent hydrolysis, the limiting step in anaerobic treatment processes [54].

Discussion of the Results

There is a need to increase the valorisation rates in the management of supermarket food waste. With the aim of applying anaerobic digestion to this type of waste, the extensive characterization campaign carried out over a period of one year at 10 supermarkets allowed the authors to obtain useful data on the generation and composition of the different types of waste generated. Although data on the composition of food waste are available in the literature, the majority of studies refer to household waste, restaurant waste, school canteen waste or fruit and vegetable waste from harvesting or generated during the distribution processes. Our findings indicate very little variability with respect to the generation of the different types of waste, the maximum deviation being 2.1% in fruit and vegetable waste. As expected, all food wastes show a very high content in volatile solids, from 81 to 96%, in line with their components. Some of the C/N ratios of the substrates containing either the five types of waste produced in the supermarkets or four out of the five fall within or are close to 20–30, values considered to be optimum for AD [20, 36–40], although the values for the substrates containing no butchery waste (36) or no fish waste (43) were higher due to the low C/N of these wastes as a result of their high protein content. However, these higher values did not appear to have any effect on the methane potential. In fact, the substrate with the lowest methane potential was the one without bakery waste, with a C/N ratio of 25, producing 453 L CH_4/kg VS, compared to the substrate without fish waste, producing 620 L CH_4/kg VS or the substrate without butchery waste, producing 534 L CH_4/kg VS. The lower methane production in the substrate without bakery waste seems to be related more to the fact that this waste, which represents 15% of the total waste generated, is mainly composed of carbohydrates, which may be more efficiently degraded than proteins and fats.

Although the methane potential values obtained in the batch tests cannot be extrapolated to the values that may be obtained in continuous operation processes, they provide useful data to address the anaerobic digestion process in reactors operating under a continuous or semi-continuous regime. The technical digestion time (t_{80-90}) obtained, between 12 and 17 days depending on the substrates, can be used as a guide for the hydraulic retention time for continuous AD [44]. The highest time was obtained when co-digesting the five types of waste generated, although this substrate led to a higher methane potential, which is more convenient in terms of logistics costs and environmental impact in waste management.

The two applied kinetic models fit the experimental data very well, although the modified Gompertz model provides a better fit than the first-order kinetic model.

The main limitation of this study is the low concentration of solids in the batch tests. However, the aim was to determine whether there were significant differences in methane production and digestion time when co-digesting all the generated wastes and in the proportions that were generated, or when one of the wastes was not included. The results have allowed us to conclude that all types of waste may be co-digested, giving the highest methane potential, very similar to that obtained with the substrate without fruit and vegetable waste. In this respect, a study has been undertaken under continuous regime, using two types of reactors, completely stirred tank reactors and induced bed reactors, operating under thermophilic conditions at solid concentrations of up to 10%.

Conclusions

Batch anaerobic digestion tests carried out on supermarket food waste at 55 °C showed very fast start-up, with low lag-phase values (< 1 day) and peak values of the daily methane production rate on days 2 to 4, depending on the substrate. Production dropped significantly after 15 days, with the exception of the substrate containing all five types of supermarket food waste, in which it decreased more slowly.

The highest methane yields were obtained for the substrate containing the five types of waste and for the substrate not containing fruit and vegetables (678 and 673 L CH_4/kg VS, respectively), with no statistical significant difference between these values. These results are consistent with the higher biodegradation of volatile solids achieved in both substrates (90.8% and 90.4%). The substrate with the lowest methane yield (453 L CH_4/kg VS) was the one containing no bakery waste, which showed a lower biodegradation of volatile solids (77.8%).

Structural changes observed by SEM are in line with methane yields. SEM images showed further deterioration and size reduction of particles in the substrate producing the highest methane yield (SMW).

The technical digestion time (t_{80}–t_{90}) was calculated to range between 11.5 and 14 days, with the exception of the substrate containing all five types of waste generated in the supermarket, which ranged between 14.5 and 17 days.

The modified Gompertz model fits the experimental results more closely than the first-order kinetic model, with differences between predicted and measured values ranging between 1.5 and 6.1% and R^2 values of between 0.994 and 0.996.

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