agronomy

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Evaluation of Biochemical Methane Potential and Kinetics of Organic Waste Streams for Enhanced Biogas Production

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Abstract: Organic waste has the potential to produce methane gas as a substitute for petrol-based fuels, while reducing landfilling and possible environmental pollution. Generally, anaerobic digestion (AD) is used only in wastewater treatment plants as a tertiary stage of sewage sludge treatment, generating a fraction of the energy that such process plants require. In this study, four different wastes—food waste (FW), dairy industry waste (DIW), brewery waste (BW), and cardboard waste (CBW)—were tested for biogas production. The biochemical methane potential (BMP) of each sample was evaluated using an automatic methane potential system (AMPTS). Operating parameters such as pH, temperature, total solids, and volatile solids were measured. Experiments on the anaerobic digestion of the samples were monitored under mesophilic conditions (temperature 37 °C, retention time 30 days). Specific methane yields (SMYs), as well as the theoretical methane potential (BMPth), were used to calculate the biodegradability of the substrates, obtaining the highest biodegradability for BW at 95.1% and producing 462.3 ± 1.25 NmL CH_4/g volatile solids (VS), followed by FW at an inoculum-to-substrate ratio (ISR) of 2 at 84% generating 391.3 NmLCH_4/g VS. The BMP test of the dairy industry waste at an inoculum-to-substrate ratio of 1 was heavily inhibited by bacteria overloading of the easily degradable organic matter, obtaining a total methane production of 106.3 NmL CH_4/g VS and a biodegradability index of 24.8%. The kinetic modeling study demonstrated that the best-fitting model was the modified Gompertz model, presenting the highest coefficient of determination (R^2) values, the lowest root means square error (RMSE) values for five of the substrates, and the best specific biogas yield estimation with a percentage difference ranging from 0.3 to 3.6%.

Keywords: food waste; anaerobic digestion; biogas; biodegradability; specific methane yield; non-linear regression

Citation: Llanos-Lizcano, R.; Senila, L.; Modoi, O.C. Evaluation of Biochemical Methane Potential and Kinetics of Organic Waste Streams for Enhanced Biogas Production. *Agronomy* **2024**, *14*, 2546. https://doi.org/10.3390/agronomy14112546

Academic Editor: Maria Angeles Bustamante Muñoz

Received: 3 October 2024
Revised: 21 October 2024
Accepted: 29 October 2024
Published: 29 October 2024

1. Introduction

Global warming and the increase in the price of fossil fuels have led to the identification of new renewable sources for biofuel production, with biogas production being one of the most promising renewable biofuels [1].

Food waste (FW) is a significant component of biodegradable waste, comprising any products discarded during the retail or post-consumer stages that were meant for human use. Every year, as the population grows, more municipal solid waste (MSW) is produced; of this, 34–53% is biodegradable organic waste, primarily food waste, but the exact percentage varies by nation [2]. Food waste and food loss are not only produced by rich countries, current statistics underline that there are many similarities in food waste per capita between developed and developing countries, with direct effects on the global economy, but equally on the environment, climate, and resource depletion. The United Nations report (2021) estimated that people throw away 931 million tons of food annually, with food waste averaging 74 kg of food per household [3]. It is estimated that around one-third of the food produced in the world ends up as waste in one way or another. Because of the characteristics of these wastes (composition, moisture), anaerobic digestion (AD) is a sustainable solution for their management [4]. The fact that AD is a means of producing renewable energy makes it an appropriate technique for food waste recovery [5,6], while diminishing the potential environmental pollution caused by landfills as well. Food waste contains fibers, carbons, proteins, fat, and lipids and is biodegradable and reusable. Typically, the C/N ratio varies between 14 and 37 in food waste. Biogas contains various types of gases, including carbon dioxide (CO_2), methane (CH_4), and traces of water vapor (H_2O), hydrogen sulfide (H_2S), ammonia, hydrogen (H_2), and siloxanes. The composition of biogas depends on the type of biomass and the method of biogas production. In general, biogas contains 40–70% CH_4, 35–55% CO_2, 0.1–3% H_2S, and various trace gases [7]. This biogas can be used for electricity generation, heating, or as vehicle fuel, while the remaining digestate can be used as a fertilizer. Biogas production from food waste not only provides a sustainable solution for organic waste management but also contributes to energy security and climate change mitigation. The composition of the biomass influences the biogas content. The content of organic chemicals (proteins, carbohydrates, lipids, etc.) is favorable for microbial degradation [8].

Generally, food waste contains high concentrations of salt, sodium, potassium, calcium, and magnesium, which inhibit the decomposition of organic matter. In this case, the co-digestion of samples with low nitrogen and fatty acids is used. Co-digestion is a process that improves the anaerobic digestion by adding a nutrient-rich secondary substrate if the initial substrate is lacking [9].

The physical and chemical characteristics of food waste (moisture, total solids (TS), volatile solids (VS), nutrient content (C/N ratio)) and biodegradability (ratio between VS/TS) are crucial in anaerobic digestion for biogas production. In order to improve the microbial activity, the food waste combined with manure can improve a biogas yield. Also, the temperature, pH, carbon-to-nitrogen (C/N) ratio, organic loading rate, nutrient content, inhibitory compounds, moisture content, particle size, and inhibitory substances are important factors that influence the biogas yield [10]. Food waste contains almost 78% carbohydrates and significant amounts of hemicellulose, cellulose, and lignin. The dairy sector produces a large amount of waste, estimated at 4–11 million tons of dairy waste produced each year as solid waste and effluents. The recovery of these types of waste into biofuels using microbial processes (bioethanol, biohydrogen, biomethane) was evaluated using different bacteria. Anaerobic digestion of dairy wastes, including spoiled milk, cheese whey, dairy sludge, and dairy scum, were reported. A study reported the use of dairy waste mixed with manure (co-digestion) in order to improve the biogas yield [11]. Begum et al. (2021) [12] reported the anaerobic co-digestion of food waste and cardboard in the following mixing ratios: 100:0, 80:20, 60:40, and 50:50. The higher biogas yield of 471 mL/g VS added was obtained for an 80:20 mixing ratio.

A potential substrate for biogas may be obtained from a variety of organic wastes, including food waste, wastewater from milk-processing plants, breweries, and abattoirs, as well as black liquor from the pulp and paper industry. The high moisture content, volatile substances, and salt content of these types of waste makes them a primary source of greenhouse gas (GHG) emissions. The generation of 1 kg of food waste results in the emission of approximately 2.5 kg of CO_2 equivalents of greenhouse gases. The anerobic digestion of these types of wastes indicates a series of processes including hydrolysis, fermentation, acetogenesis, and methanogenesis. The generation of biogas represents an optimal strategy for the production of renewable energy, having the additional benefit of reducing GHG emissions [13].

In order to utilize a range of substrates for anaerobic digestion, it is essential to conduct a biochemical methane potential (BMP) test. This test permits quantifying the biodegradability of the organic waste under anaerobic conditions and the amount of methane produced, as well as knowing multiple factors that influence the AD process, such as possible inhibitors, solid retention time (SRT), and synergetic effects that may occur. Therefore, valuable insights related to the anaerobic digestion plant efficiency can be known. BMP has been used since 1979 [14], but the method has been continuously improved and standardized [15,16], and was subsequently adopted for specific applications in the investigation of the methane potential of different types of wastes and mixtures of waste and other organic products [17]. Nowadays, the BMP test can be performed following various experimental setups, such as the Hohenheim (syringe) biogas yield test (HBT), the Bergedorf fermentation test (BFT), the Eudiometer test (EUD), and the automatic methane potential test (AMP) [18], the latter being increasingly used due to its ability to report and save real-time values, and reduce human errors. An automatic methane potential equipment consists of three sections: a water bath, where the fermentation bottles are held at the desired temperature and where the AD reactions take place; to which a CO_2 absorber is attached, usually consisting of bottles filled with an NaOH solution and some indicator; and finally, a flow cell connected to a data-collecting device. Numerous factors, such as the inoculum-to-substrate ratio (ISR), the experimental setup, the inoculum storage, and the inoculum source, can influence the BMP test results [19–21]. The ISR plays a significant role in the BMP test due to the relationship between the microbial charge and the organic matter. A low ISR might overload the microbial community, impacting the specific methane yield curve and producing inaccurate BMP results due to fatty acids or ammonia accumulation [20]. On the other hand, a high ISR might delay methane production [20] and decrease the specific methane yield (SMY) [22,23]; nevertheless, each substrate has its own ISR range where the SMY is not affected nor is the substrate methane potential (SMP) curve. This range for most substrates is between an ISR of 1 and 4 [15,20,24].

The main purpose of this study is to evaluate the potential of biogas production from four different types of waste—food waste, dairy factory waste, brewery waste, and cardboard—using batch anaerobic fermentation. Additionally, the biodegradability index will be calculated for each waste type based on the amount of biogas produced. The use of kinetic models will help in understanding the dynamics of the anaerobic digestion process and could aid in optimizing biogas production for future applications.

2. Materials and Methods

2.1. Sample Description

All the substrates and inoculum were collected in Cluj-Napoca, Romania. For this study, we used waste samples from these sources in the area: (i) the main canteen of Babeș-Bolyai University (Cluj-Napoca, Romania); (ii) a dairy factory in the Cluj-Napoca area; (iii) a craft brewery in Cluj-Napoca; and (iv) egg cartons collected from several households in the area after residential use. The food waste (FW) samples were collected in the Hasdeu campus canteen of Babes-Bolyai University (Cluj-Napoca, Romania). The canteen serves food for students from over 13 different dorm buildings within the complex and the faculties located around the campus. Lacto serum, as dairy industry waste (DIW), was collected as a waste mix from different production lines, including cheese, butter, and pasteurized milk from the Napolact dairy plant in Cluj. There are several small craft beer producers in Cluj, but the brewery waste (BW) used in the study came from "Bere à la Cluj" (Cluj-Napoca, Romania). Spent grain was obtained after the lautering stage from the artisanal brewery that uses mainly barley as a raw material. Both FW and BW were crushed before use and impurities such as plastics, papers, or bones were hand-removed. All these substrates were kept cold at 4 °C until their characterization and subsequent use in the biochemical methane potential test. The inoculum (I) used in this study was obtained from an active anaerobic reactor from the Cluj-Napoca city wastewater treatment plant (Cluj-Napoca, Romania).

2.2. Analytical Methods

The TS from the samples and sludge were determined by drying the sample at 105 °C for 20 h in a universal oven (UFE 400, Memmert, Germany). The VS were determined by the ignition of the dried sample obtained above at 550 °C, for 2 h. The elemental analysis (C, H, O, N, S) was performed using a Flash EA 2000 CHNS/O analyzer (Thermo Fisher Scientific, Waltham, MA, USA) according to the ISO 16948 (2015) [25]. The protein content was estimated by multiplying the total nitrogen content from the elemental analysis by a conversion factor of 6.25, following the established protocols [26,27]. The pH of the slurry was measured using a calibrated pH meter (Mettler Toledo, Leicester, UK). The lipid content was measured using standard Soxhlet extraction with hexane as the solvent, utilizing a Soxhlet extractor (Behr-Labor Behrotest, R256S, Behr, Germany). The total carbohydrate content was determined using acid hydrolysis with H_2SO_4, followed by a spectrophotometric measurement. The contents of cellulose, hemicellulose, and lignin in brewery waste (BW) and cardboard waste (CBW) were determined according to a previously established method [28]. The lignin content was measured after treating the sample with 72% H_2SO_4, which isolates the lignin as the insoluble fraction. Cellulose and hemicellulose were analyzed using a sodium chlorite oxidation procedure. The sample was reacted with $NaClO_2$ in a 10% acetic acid solution at 75 °C for 1 h, followed by filtration (process repeated four times). The resulting holocellulose (combined cellulose and hemicellulose) was dried at 105 °C. The cellulose was then identified as the portion of holocellulose that was insoluble in a 17.5% NaOH solution, with hemicellulose calculated as the difference between holocellulose and cellulose. Klason lignin was measured as the insoluble fraction of the brewery waste hydrolyzed with 72% H_2SO_4 solution.

The C/N ratio was calculated by using Equation (1).

$$\text{C/N ratio} = \frac{\text{weight of carbon in the sample}/12}{\text{weight of nitrogen in the sample}/14} \tag{1}$$

2.3. Biochemical Methane Potential

The biochemical methane potential (BMP) tests were carried out using automatic methane potential (AMPTS II, Bioprocess Control, Lund, Sweden) equipment. The amount of substrate and an active inoculum (calculated from the TS and VS analysis) were added to 640 mL reactor bottles. For each experiment, the substrate inoculum ratios in a glass reactor were 1:1 and 2:1. After adding the substrates and inoculum, the bottles were purged with nitrogen (N_2) to create anaerobic conditions and then sealed with rubber septa. The bottles were placed in an incubator maintained at 37 °C for 30 days, representing mesophilic conditions. Temperature control was ensured using a water bath equipped with a thermostat. The contents of the bottles were continuously stirred to ensure uniform mixing of the substrates and inoculum. Three bottles were used as control samples containing only the inoculum to quantify the inoculum's influence on methane production.

2.4. Anaerobic Digestion

In this study, the theoretical biochemical methane potential (BMP_{th}) of each substrate was calculated based on the elemental composition (carbon, hydrogen, oxygen, and nitrogen) using the stoichiometric Buswell equation [29] (Equation (2)). The theoretical methane gas Equation (3) assumes the complete conversion of the organic matter. The general form of the Buswell equation for a substrate with the formula $C_nH_aO_b$ is:

$$C_nH_aO_b + \left(n - \frac{a}{4} - \frac{b}{2}\right)H_2O \rightarrow \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4}\right)CO_2 + \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)CH_4 \tag{2}$$

$$BMP_{th} = \frac{22,400\left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4}\right)}{12.017n + 1.007a + 15.999b} \tag{3}$$

where: n, *a*, and b are the molar fractions of C, H, and O, respectively.

The quantities of each substrate necessary to respect the ISRs 1 and 2 based on the volatile solids (VS) content. The quantities of each substrate required to achieve these ISR values were calculated using a specific equation (Equation (4)). The difference between the operating volume and the substrate mass was inferred to be the inoculum mass (Equation (5)), assuming that the total density of the system is infinitesimally affected by the quantities of the aggregate substrate matter.

$$M_s = \frac{M_T * X_{VSi}}{\left(\frac{VS_i}{VS_s}\right) * X_{VSs} + X_{VSi}} \quad (4)$$

$$M_I = 400 - M_S \quad (5)$$

where (VS_i/VS_s) is the inoculum-to-substrate ratio at a volatile solid basis; X_{VSi} and X_{VSs} are the volatile solid mass fractions of the inoculum and substrates; M_S is the quantity in grams of substrate required; M_T is the total amount of inoculum and substrate of the system; and M_I is the inoculum mass. The AMPTS II system automatically measures and records the volume of methane produced over time, allowing for the precise monitoring of biogas production from each waste type. The methane production from the control bottles (containing only inoculum) will be subtracted from the total methane production in the test bottles to determine the net methane yield from the substrates. The AMPTS II operation loads used for the BMP test are displayed in Table 1. Columns 3 and 4 provide the volatile solid mass fractions' arithmetic mean values that were utilized to compute M_I and M_s following Equations (4) and (5). Columns 2 and 5 display the mass quantities of the inoculum and substrate, expressed in grams. Table 1 also displays the ISRs that were used for each test.

Table 1. Digesters' operation loads for the BMP tests.

Substrate	M_I (g)	X_{VSi} (Mass Fraction)	X_{VSs} (Mass Fraction)	M_s (g)	I/S Ratio (VS_I/VS_S)
FW	387.9	0.00602	0.2	6.1	2.0
FW	393.9	0.00602	0.2	12.3	1.0
DIW	379.4	0.00602	0.1	20.6	2.0
DIW	360.8	0.00602	0.1	41.3	1.0
BW	393.5	0.00602	0.2	6.5	2.0
BW	387.2	0.00602	0.2	13.0	1.0
CBW	398.4	0.00602	0.8	1.6	2.0
CBW	396.8	0.00602	0.8	3.2	1.0

2.5. Biodegradability

The anaerobic biodegradability of a substrate represents a further critical parameter for the assessment of process performance and stability. It is calculated based on the stoichiometry of the process, taking into account the elemental composition of the substrate [30].

$$BD(\%) = \left(\frac{BMP_{exp}}{BMP_{th}}\right) * 100 \quad (6)$$

The extent of anaerobic biodegradability was calculated as the percentage of the theoretical methane yield (BMP_{th}) that was achieved by the BMP test according to Equation (6) [30,31].

2.6. Kinetics Parameters

The biogas production curve of complex organic materials tends to be smooth. These curves can be modeled by different kinetic models, among which the first-order model, the modified Gompertz model [32,33], and the Monod-type model [34] (Equations (7)–(9)) stand out due to their high correlation with the practical data obtained using the BMP test.

$$Y_t = Y_{max} * (1 - \exp(-\mu t)) \quad (7)$$

$$Y_t = Y_{max} * \exp\left(-\exp\left(\frac{R_m * e}{M_{max}} * (\lambda - t) + 1\right)\right) \quad (8)$$

$$Y_t = Y_{max} * \left(\frac{k * t}{1 + k * t}\right) \quad (9)$$

To find out the kinetic parameters of each of the models, a non-linear regression was applied using the EXCEL Solver function using the biogas yield (NmL CH_4/g VS) = Y_t) as the input.

Where Y_t = total biogas yield; Y_{max} = specific biogas yield (NmL CH_4/g VS); R_m = maximum specific biogas production rate (NmL CH_4/d/g VS); λ = lag phase (d); μ = hydrolysis constant (d − 1); e = 2.7183; and K = Monod half-saturation constant. The root means square error (RMSE), the coefficient of determination (R^2), the mean absolute percentage error (MAPE), and the percentage difference between the specific biogas yield and the specific methane yield were calculated to evaluate the model fitting.

3. Results and Discussion

3.1. Characterization of Organic Waste and Inoculum

The physicochemical characteristics of the different organic wastes and inoculum are presented in Table 2. The lowest total solids content was observed in dairy industry waste, with a value of 6.11% (*w*/*w*), while the highest value was recorded for cardboard waste, with a value of 90.79% (*w*/*w*). The inoculum VS was 6.14 g VS/L, a value that is below the recommended range of 10 to 30 g VS/L [21]. However, there was no discernible adverse effect, as evidenced by the underestimation of the specific methane potential results. The volatile solids content was more than 90% for all the organic residues, except for cardboard waste, which exhibited a value of 84.26%. The values obtained for these components, along with those for lipids, protein, ash, and carbohydrates, were found to be in accordance with the data presented by numerous researchers, given the considerable variability of these substrates based on seasonal changes, geographical location, dietary habits, sources, and manufacturing processes [35–37]. The C/N ratios of FW, DIW, BW, and CBW were 20.84, 17.64, 22.92, and 17.76, respectively, and were similar to the ones reported for FW as 17.28 by Oduor et al. (2022) [38], reported for BW as 16.4 by Mainardis et al. (2019) [39], and reported for DIW as 17.5 by Peña-Jurado et al. (2019) [40]. On the other hand, the CBW carbon-to-nitrogen ratio was 17.76, which was considerably lower than the ones reported by several authors ranging from 128.4 to 595 [41–43]. The carbon-to-nitrogen ratio is a fundamental parameter for the optimal functioning of anaerobic digestion (AD), as evidenced by various studies. Some studies, such as Capson-Tojo et al. (2017), Wang B et al. (2014), and Yenigün O and Demirel B (2013) have demonstrated that a low ratio of C/N can lead to the inhibition of the process due to the accumulation of volatile fatty acids or ammonia nitrogen [44–46]. On the other hand, at a high C/N ratio, nitrogen availability is suboptimal for microorganism reproduction, leading to low biogas productivity [47]; however, there is not a well-defined range for all substrates [48].

The C/N ratio was adjusted to 16, 20, and 25 for the anaerobic co-digestion (AcoD) of swine manure and three agricultural residues (corn stalks, wheat straw, and oat straw). The highest biogas yield was obtained at a C/N ratio of 20. Similarly, Wang et al. (2014) [45] investigated the anaerobic co-digestion of dairy manure, chicken manure, and rice straw. They observed ammonia inhibition at C/N ratios of 15 and 20 in mesophilic and thermophilic conditions, respectively. Additionally, they achieved maximum methane potentials with C/N ratios of 25 and 30 at 35 °C and 55 °C, respectively. In contrast, Mendieta et al. (2020) [49] reported a methane yield of 276 NmL CH_4/g VS, 77% organic matter removal, and a high process stability of sugarcane scum and agricultural crop residues: AcoD with a C/N ratio of 65.5. Similarly, Choi et al. (2020) [50] observed no significant difference in the maximum methane production of starch, cellulose, and xylan AD at C/N ratios of 10, 25, and 40, respectively.

Table 2. Composition of food waste, dairy industry waste, brewery waste, cardboard waste, and inoculum.

Characteristics	FW	DIW	BW	CBW	I
pH	5.1 ± 0.01	5.7 ± 0.01	nd.	nd.	7.2 ± 0.01
Total solids (%)	20.7 ± 0.18	6.11 ± 0.3	19.05 ± 0.24	90.79 ± 0.75	0.99 ± 0.01
Volatile solids (% TS)	93.3 ± 0.5	90.5 ± 0.4	95.5 ± 0.3	84.3 ± 0.5	60.74 ± 0.9
Lipids (% VS)	23 ± 0.8	6 ± 0.2	6.7 ± 0.2	1.0 ± 0.1	nd.
Ash (% TS)	6.7 ± 0.3	9.5 ± 0.5	4.5 ± 0.2	15.7 ± 1.0	39.3 ± 1.2
Proteins (% VS)	17.6 ± 0.9	19.50 ± 1.1	14.18 ± 1.1	nd.	nd.
Carbohydrates (% VS)	52.7 ± 1.2	70.3 ± 2.5	69.3 ± 4.2	nd.	nd.
C (% VS)	50.2 ± 1.3	47.2 ± 2.1	44.6 ± 1.5	42.8 ± 2.1	nd.
N (% VS)	2.81 ± 0.1	3.12 ± 0.2	2.27 ± 0.2	2.81 ± 0.1	nd.
H (% VS)	5.5 ± 0.2	6.44 ± 0.5	5.98 ± 0.3	6.11 ± 0.4	nd.
O (% VS)	41.5 ± 1.4	43.2 ± 1.2	47.2 ± 1.5	48.3 ± 1.3	nd.
Cellulose (%)	nd.	nd.	24.3 ± 0.9	58.2 ± 3.2	nd.
Hemicellulose (%)	nd.	nd.	33.1 ± 2.1	20.3 ± 1.8	nd.
Lignin (%)	nd.	nd.	20.1 ± 1.8	5.1 ± 0.4	nd.

nd.—not determined.

The potential for biogas production from the studied samples depends on their chemical composition, specifically the proportions of carbohydrates, proteins, lipids, and lignin. The DIW sample exhibits a higher carbohydrate content (70.3% VS) and a moderate level of protein (19.5% VS) in comparison with the other samples. The BW sample exhibits the highest total solids content (90.8%) and a high volatile solids content (95.5% dw), indicating a high content of degradable organic matter. Its composition is balanced, with cellulose (24.3%), hemicellulose (33.1%), and lignin (20.1%) representing the predominant components. CBW has the highest cellulose content (58.2%) and a high ash content (15.7% VS), indicating significant inorganic content. This suggests that the material is less digestible and, consequently, that the biogas yield will be low. A high lipid content can increase biogas production. FW has the highest lipid content (23.0%).

The chemical composition of the substrates indicated that BW is the most promising substrate for biogas production, followed by FW, DIW, and CBW.

3.2. Biochemical Methane Potential Test and Biodegradability

The theoretical methane potential (BMP_{th}) for each of the substrates used was calculated using Equation (3) and was based on an elemental analysis. The volume of methane can be obtained by converting the moles of methane into the volume using the ideal gas law at standard conditions. The highest BMPth calculated was 490.90 mL CH_4/g VS for FW, followed by BW at 483.43 mL CH_4/g VS, DIW at 428.24 mL CH_4/g VS, and CBW at 413.02 mL CH_4/g VS. FW shows the highest theoretical methane yield, making it a highly promising substrate for biogas production due to its rich organic content, which is readily biodegradable under anaerobic conditions. The highest BMP_{th} was attributed to the high content of degradable carbohydrates (52.7%) and lipids (23%). The absence of lignin from the substrate improved the biodegradability. The high BMP_{th} predicted for BW was due to a high content of degradable cellulose (24.3%) and hemicelluloses (33.1%). CBW had the lowest BMP_{th} due to the presence of lignocellulosic material, which presents a greater degree of difficulty in breaking down anaerobically. The BMP_{th} value is not always reported, or calculated using Buswell's equation. Other sets of formulas are also used, which take into account the amount of N and S, modifying the results. However, it is also possible to calculate the BMPth following other organic matter properties, such as the protein, lipid, and carbohydrate content or the chemical oxygen demand (COD), making this value comparison irrelevant in most cases. Such an example of this can be seen by Yasim and Buyong (2023) [51], where the theoretical methane potential was measured using an elemental analysis (C, H, O, N) and COD values. The lowest percentage difference between the theoretical methane potential values was 1.75% for vegetable waste, and the highest was 199.33% for textile waste. The biochemical methane potential (BMP) test was conducted for a period of 34 days at a mesophilic temperature of 37 °C until the BMP volumetric production exhibited a less than 1% increase in the dairy methane production. In general, samples with an inoculum-to-substrate ratio of 2 exhibited a brief lag phase in their BMP curves, indicating effective microbial adaptation. The specific methane production curves for all the substrates with ISRs 1 and 2 are illustrated in Figure 1. These curves demonstrated satisfactory behavior for all the substrates and inoculum-to-substrate ratios for methane production, with a brief lag phase for every ISR 1, except for the heavily inhibited DIW at ISR 1. The specific methane yield of food waste obtained in the current study ranged from 409.79 ± 4.22 NmL CH_4/g VS to 377.71 ± 1.66 NmL CH_4/g VS at ISRs 1 and 2, respectively. These values are within the range of 357.85 to 586 NmL CH_4/g VS reported by several authors [38,52–55]. Nevertheless, even if the methane production was less than the 586 mL reported by Alibardi and Cossu (2015) [52], the biodegradability remained high, between 76 and 83. The low variability of these results indicates that there was no evident inhibitory impact on the experiment's development at any ISR. A summary of the cumulative production of each substrate at the various integrated substrate ratios (ISRs) and their biodegradability is presented in Table 3. The highest specific methane yield and biodegradability were observed for brewery waste, with values of 462.07 ± 2.05 NmL CH_4/g VS and 95.35 ± 0.42%, respectively, for both ISRs. The findings indicate that mechanical treatments in conjunction with freezing pre-treatment were able to increase the surface area and porosity, facilitate the release of degradable matter, and enhance the availability of enzymes within the lignocellulosic matrix, as previously reported by Barakat et al. (2016) [56] and Rooni et al. (2017) [57].

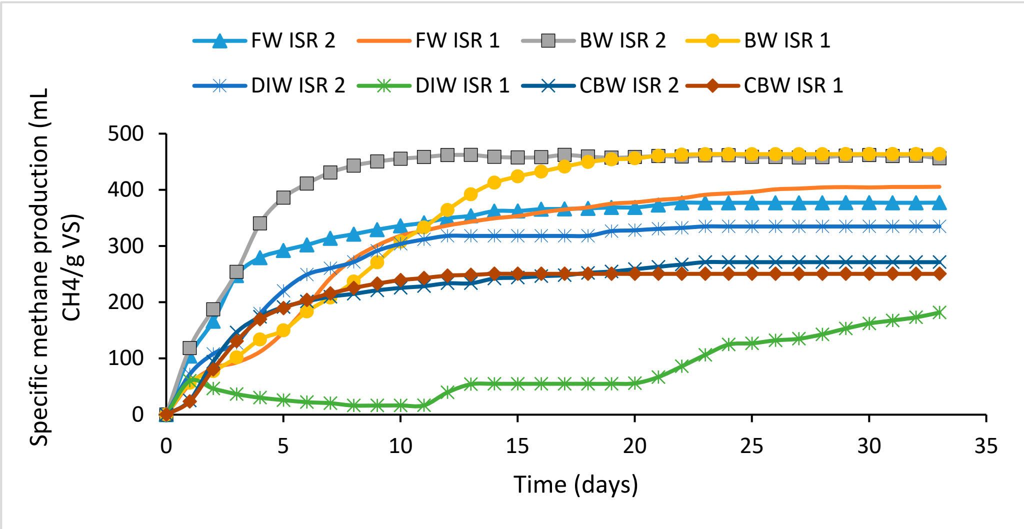

Figure 1. The amount of biogas produced from all wastes, for ISRs 1 and 2.

Table 3. Theoretical methane potential, specific methane yield, and biodegradability of the organic waste samples.

Organic Waste Type	BMP_{th} mL CH_4/g VS	SMY ISR 2 Nml CH_4/g VS	SMY ISR 1 Nml CH_4/g VS	Biodegradability ISR 2	Biodegradability ISR 1
FW	490.11	377.41 ± 1.66	409.79 ± 4.22	77.07% ± 0.34	83.75% ± 0.86
DIW	428.40	335.02 ± 3.61	105.01 ± 4.04	78.19% ± 0.84	24.51% ± 0.94
BW	484.63	460.62 ± 3.11	463.53 ± 5.20	95.05% ± 0.64	95.65% ± 1.07
CBW	413.02	271.09 ± 4.65	250.25 ± 3.24	65.64% ± 1.13	60.59% ± 0.79

Legend: BMP_{th} = Theoretical methane potential; SMY = Specific methane yield; ISR = Inoculum-to-substrate ratio.

Furthermore, these values illustrate the efficacy of the process' inoculum in adapting to this specific type of organic waste. These results exceed those reported by Vitanza et al. (2016) [58], who observed a biodegradability of 81.1% and a methane production of 429.0 NmL CH_4/g VS. Furthermore, a methane production of 350 NmL CH_4/g VS was reported by Bougrier et al. (2018) [59] for the brewer's spent grain. Furthermore, DIW with a BMP_{Th} of 428.4 mL CH_4/g VS demonstrated an adequate biodegradability of 78.20% with a production of 335.01 NmL CH_4/g VS at ISR 2. This value, however, is lower than the one reported by Adghim et al. (2020) [60], who obtained a methane production of 412.2 mL CH_4/g VS and a biodegradability of 99.75%. The lowest result in the current study was attained with a value of 105.01 mL CH_4/g VS, indicating a strong inhibition of methane formation when the inoculum-to-substrate ratio was 1. This is attributed to a rapid accumulation of volatile fatty acids in the digester, as well as total ammonia nitrogen and free ammonia nitrogen, which cause a reduction in pH and subsequently impact the methanogenesis stage [14,20,22].

The biodegradability of the substrates employed is dependent on their chemical composition, with relevance to the content of carbohydrates, proteins, lipids, and lignocellulosic material. FW and BW demonstrate a high biodegradability, whereas CBW evidences the lowest biodegradability, due to its high lignocellulosic content. The biodegradability of FW was 83.75% for ISR 1 and 77.07% for ISR 2. The substrate contains organic substances that are readily biodegradable and do not contain lignin, which is favorable for biogas production. The lower biodegradability (24.51%) observed at IST 1 is below the levels reported by other studies [12], which may be attributed to the formation of inhibitors from VS and ammonia (due to the high protein content). The same studies indicate that the co-digestion of CBW with food or preliminary pretreatment could enhance biodegradability and elevate digestibility to a range of 37–53%. In contrast, at ISR 2, an increase in biodegradability is observed due to the higher quantity of samples. In the case of BW, the biodegradability at ISRs 1 and 2 is almost identical. This explains the highest carbohydrate content, which is hydrolyzed in the first stage into monosaccharides, and then into volatile fatty acids, and finally into biogas [43].

Finally, cardboard waste generated a specific methane production of 250.25$\pm$ 3.24 and 271.09 $\pm$ 4.65 NmL CH_4/g VS, equivalent to a biodegradability of between 60 and 65% for SRIs of 1 and 2, respectively. Our findings are in accordance with those reported by Zhao et al. (2021) [43]: BMPth of 412 mL CH4/g VS and a specific methane yield of 246 mL CH_4/g VS. Without including the results of the dairy industry waste for an ISR of 1, which were extensively affected by the inhibition produced by the accumulation of volatile fatty acids, these are the lowest biodegradability values of the present study, which may be due to the high lignin content in these residues or the use of a toxic additive in the production process [44].

The results demonstrated that the highest biogas yields were produced from brewery waste, which has the potential to have significant implications in industrial applications. These findings may provide a solution for the recovery of such wastes by enhancing biogas production, which could have a significant impact on the reduction of greenhouse gas emissions. By converting BW into biogas, breweries can reduce their energy cost through the co-generation of heating and electricity and could have sustainable waste management. The yield of biogas can be enhanced by co-digestion with other substrate (sewage sludge, manure), the improvement of nutrient balance, the dilution of inhibitors, and the utilization of micro- and macro-nutrients [61].

3.3. Kinetics of the Digestion Process

The kinetics of anaerobic digestion are of great importance in the assessment of the biodegradability processes of organic matter, the prediction of methane production, and the simulation and design of full-scale digesters. These kinetic processes describe the rates at which microbial reactions occur during anaerobic digestion. In the past, researchers and engineers have typically employed mono-digestion models to capture these kinetic processes. As in the first-order kinetic model, the degradation rate is assumed to be directly proportional to the concentration of the substrate (organic matter) [62,63]. Furthermore, the

Monod-type model incorporates the concept of substrate saturation, taking into account both the substrate concentration and the maximum specific growth rate of microorganisms. Lastly, the modified Gompertz model accounts for the lag phase observed in microbial growth, thus providing insights into the initial adaptation of microorganisms during anaerobic digestion. Filer et al. (2019) [34] provides an extensive discussion on the practical implications and benefits of these models in the context of anaerobic digestion processes. Table 4 shows the kinetics parameters obtained after non-linear regression of the cumulative biogas production of each substrate for the Monod-type model, the first-order model, and the modified Gompertz model, at ISRs 1 and 2. Furthermore, RMSE, R^2, MAPE, and percentage difference values were calculated for the model suitability evaluation. Similar to Casallas-Ojeda et al. (2020) [64], the modified Gompertz model was the best-estimated model, obtaining the lower RMSE and the highest R^2 values in five of the eight tests. Oduor et al. (2022) [38] reported R^2 and RMSE values between 0.987 and 0.996, and 5.409 and 18.19 for the modified Gompertz model kinetic evaluation of food waste, water hyacinth (WH), and their co-digestion at different ratios. Capson-Tojo et al. (2017) [44] obtained R^2 values > 0.994 for food waste, cardboard, and their mixtures after a modified Gompertz kinetics evaluation, proving good prediction capabilities of this model for anaerobic mono- and co-digestion of FW and BW. The first-order model demonstrated the greatest degree of fit for FW and DIW with ISR 2, with R^2 values of 0.987 and 0.993, respectively. Finally, the Monod-type model was only able to achieve an optimal fit for the FW at ISR 2, with an R^2 value of 0.989. The lag phase was observed to be minimal for all the substrates except for dairy industry waste, where an inoculum-to-substrate ratio of 1 was employed. However, in the case of two samples, the lag phase was either absent or negligible in comparison to the curves with an ISR of 1. This suggests that a brief adaptation period may be sufficient [30]. The root mean square error and R^2 values did not accurately reflect the discrepancy between the actual results and the values obtained for each model following non-linear regressions for the dairy industry waste tests at an inoculum-to-substrate ratio of 1. Consequently, the mean absolute percentage error (MAPE) analysis was conducted, as this is a widely used metric for evaluating the forecasting precision of a model. MAPE is calculated by iterating through each data point, calculating the absolute percentage error, and averaging these values. For the dairy industry waste with an ISR of 1, the MAPE values for the first-order, modified Gompertz, and Monod-type models were determined to be 42.85%, 25.52%, and 43.40%, respectively. The results demonstrate that none of the models were capable of accurately predicting the high volatile acids' accumulation inhibition observed in this sample. Conversely, the mean absolute percentage error (MAPE) demonstrated excellent accuracy for the remaining models and samples, with values ranging from 1.041% in brewery waste at ISR 2 to 10.567% in cardboard waste at ISR 2.

Table 4. Report the corresponding kinetics constants calculated for the first-order, modified Gompertz, and Monod-type models that were obtained after non-linear regression of the specific methane production (SMP) curves.

Model		Unit	FW ISR 1	FW ISR 2	DIW ISR 2	DIW ISR 1	BW ISR 1	BW ISR 2	CBW ISR 1	CBW ISR 2
First-order	Y_{max}	NmL CH_4/g VS	419.0	372.3	335.8	10710.4	493.6	462.6	252.8	267.1
	μ	Day^{-1}	0.12	0.29	0.21	0.000	0.10	0.32	0.26	0.21
	RMSE	NmL CH_4/g VS	14.5	9.2	6.5	22.0	24.1	9.9	7.1	9.6
	R^2		0.985	0.987	0.993	0.890	0.973	0.991	0.989	0.977
	MAPE	%	5.11	2.34	7.86	2.08	42.86	1.99	5.55	5.83
	% Difference	%	7.10	1.27	6.48	0.34	2210.55	0.28	0.88	1.55

Table 4. *Cont.*

Model		**Unit**	**FW ISR 1**	**FW ISR 2**	**DIW ISR 2**	**DIW ISR 1**	**BW ISR 1**	**BW ISR 2**	**CBW ISR 1**	**CBW ISR 2**
Modified Gompertz	Y_{max}	NmL CH_4/g VS	401.7	367.6	330.9	348.7	470.7	459.5	249.6	261.5
	R_m	NmL CH_4/g VS*day	34.1	73.4	119.9	6.6	35.9	91.6	45.1	38.7
	λ	Day	0.186	0.000	0.000	7.681	0.723	0.003	0.318	0.000
	RMSE	NmL CH_4/g VS	11.13	16.0	7.93	16.16	10.75	6.72	4.47	14.35
	R^2		0.990	0.958	0.990	0.940	0.994	0.996	0.995	0.948
	MAPE	%	4.04	4.42	4.16	1.04	25.52	2.84	2.55	7.30
	% Difference	%	2.69	2.51	1.55	0.32	52.31	1.15	0.39	3.62
Monod type	Y_{max}	NmL CH_4/g VS	517.2	407.4	380.7	7028.6	632.2	502.4	281.0	302.6
	K		0.125	0.460	0.280	0.001	0.098	0.508	0.366	0.288
	RMSE	NmL CH_4/g VS	20.787	8.149	14.099	22.312	32.312	24.084	14.433	8.686
	R^2		0.968	0.989	0.970	0.888	0.948	0.943	0.945	0.982
	MAPE	%	7.79	2.35	10.14	5.80	43.40	4.89	10.56	6.35
	% Difference	%	32.19	8.04	36.40	8.97	1416.29	13.72	12.15	11.54

Furthermore, the discrepancies between the estimated and actual methane production were quantified by calculating the percentage difference between the cumulative methane production values and the non-linear regression values for each model. The modified Gompertz model provided the closest estimates to the specific methane yields obtained in this study with a percentage difference ranging from 0.36 to 3.62%, followed by the first-order model with a percentage difference ranging from 0.27 to 7.10%. Meanwhile, the Monod-type model overestimated all the methane production yields by 8.97 to 36.40% compared with the SMY collected values. This excludes the analysis of dairy waste with an inoculum-to-substrate ratio of 1 due to its high overestimation values.

The predicted maximum yield of the first-order model is in good agreement with the experimental data for all the substrates at ISR 2, indicating that this model is suitable for predicting the methane yield under stable conditions (i.e., in the absence of inhibitors). The R^2 values indicate a satisfactory fit, with the exception of DIW at ISR 1 (R^2 = 0.890), where inhibition was observed. The model is not applicable in cases where the substrate composition is complex. Conversely, the modified Gompertz model yielded the most precise estimation of Y_{max} for all the substrates, with a maximum discrepancy of 5%. In comparison, the Monod-type model demonstrated a comparatively lower degree of accuracy in predicting the methane yield. The accurate fit of the modified Gompertz model indicates that it can be used for processes that are undergoing optimization. The model incorporates a lag phase (λ), which represents the time before the methane production commences. This explains the prolonged period of 7.68 days for DIW at ISR 1, which was due to slow degradation and a high organic load. In contrast, the lag phase for FW is very short, indicating a rapid degradation process. The Monod-type model is more complex and incorporates substrate concentration and microbial activity, but it is unable to predict biogas production in practical applications that utilize inhibitors and a diverse range of substrates.

It has been demonstrated that each of the models can predict the biogas production; however, the accuracy of the predictions is dependent on a number of factors, including the composition of the substrate, the operational conditions, and the potential inhibitors formed during fermentation.

4. Conclusions

This study investigated the potential of biogas production from four different waste types: FW, DIW, BW, and CBW, using two different inoculum-to-substrate ratios. The biodegradability of each substrate was evaluated, and three kinetic models were developed to predict the optimal biogas yield. The physicochemical analysis of these wastes indicated a high organic matter content, supporting their suitability for anaerobic digestion. The BMP tests demonstrated a good anaerobic performance, with specific methane production (SMP) curves showing adequate biodegradability at ISR 2, and a small lag phase at ISR

1, likely due to hydrolysis limitations or minor bacterial inhibition. Notably, DIW at ISR 1 exhibited significant inhibition, producing only 106.25 NmL CH_4/g VS and achieving the lowest biodegradability (24.8%). In contrast, BW showed the highest biodegradability (95.35 $\pm$ 0.42%) and methane yield (462.07 $\pm$ 2.05 NmL CH_4/g VS). Three kinetic models—first-order, Monod-type, and modified Gompertz—were applied to the data, with the modified Gompertz model providing the most accurate methane yield predictions, with a percentage difference between 0.36% and 3.6%. The first-order model, while slightly overestimating the yields in some cases, was the second-best fit, with percentage differences from 0.27% to 7.10%. These results suggest that the modified Gompertz model is most suitable for predicting and optimizing methane production in future biogas systems.

Further research in the field of biogas production could enhance the biogas yield by studying the inhibitory compound, the types of microorganisms, and the application of machine learning in combination with kinetic models to predict biogas production with greater accuracy. Additionally, the realization of a life cycle assessment of biogas production from different types of waste could prove beneficial.

Author Contributions: Conceptualization, L.S. and R.L.-L.; methodology, O.C.M.; formal analysis, R.L.-L.; investigation, O.C.M.; resources, L.S.; writing—original draft preparation, R.L.-L.; writing—review and editing, L.S.; visualization, L.S.; supervision, O.C.M.; funding acquisition, L.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was carried out through the Core Program within the National Research Development and Innovation Plan 2022–2027, with the support of MCID, project no. PN 23 05.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Acknowledgments: Special thanks to our colleague, the researcher Camelia Botezan, who helped us with the necessary corrections for the accuracy of the English writing of the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

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