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Bioenergy, Electricity, Biogas Production, and Emission Reduction Using the Anaerobic Digestion of Organic Municipal Solid Waste in Campinas, One of the Largest Brazilian Cities

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Abstract: Anaerobic digestion (AD) is an attractive process for bioenergy production and is considered to be an alternative way to reduce landfills. AD improves municipal solid waste (MSW) management, representing a profitable application of the circular economy and could reduce environmental impact. The methane (CH_4) potential of four different organic fractions of MSW—paper (PFW), garden (GFW), food (FFW), and a mixture of these three (OFMSW)—via AD was used to investigate the energy potential and the economic and environmental impact of Campinas. Theoretical and experimental biochemical methane potential (BMP) and substrate biodegradability were determined using the Buswell and Müller equation and the VDI 4630 method. The Gompertz model was used to predict the kinetics of the biochemical processes. The highest experimental BMP (410.7 $NmLCH_4$ gVS^{-1}) and biodegradability (86.6%) were reached with OFMSW. OFMSW can avail an energetic potential of approximately 119 GWh year^{-1}, with a biomethane production equivalent to diesel at 49.9×10^3 m^3 year^{-1}, hence, potentially curtailing the CO_2 emissions of heavy-duty vehicles by almost 133 kt year^{-1}. The electricity demand for approximately 11% of the households in Campinas could be met by the biogas produced by OFMSW, thus increasing local energy security. The replacement of fossil diesel with biomethane to fuel garbage trucks in Campinas could reduce 25% of the diesel demand.

Keywords: municipal solid waste; anaerobic digestion; biochemical methane potential; bioenergy; CO_2 emission

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Citation: Pacheco, L.A.; Tamayo-Peña, J.; Moraes, B.d.S.; Franco, T.T. Bioenergy, Electricity, Biogas Production, and Emission Reduction Using the Anaerobic Digestion of Organic Municipal Solid Waste in Campinas, One of the Largest Brazilian Cities. *Processes* **2022**, *10*, 2662. https://doi.org/10.3390/pr10122662

Academic Editor: Pietro Bartocci

Received: 1 November 2022
Accepted: 8 December 2022
Published: 10 December 2022

1. Introduction

Technological advances and population growth have led to a high amount of daily solid waste generation in the world, with 2.6 billion tons of waste expected to be produced in 2030 [1,2]. At the same time, in most cases, the management of this waste is not environmentally sound, leading to, for example, soil and water contamination, as well as a release of odors and polluting gases, mainly methane (CH_4) and carbon dioxide (CO_2). All these factors pose risks to the environment and human health [1,3].

In Brazil, 79 million tons of municipal solid waste (MSW) was produced in 2019; this is an increase of 18% over a period of almost a decade [4]. The fraction of MSW disposed of in sanitary landfills is 97.4% [5]. However, the National Policy on Solid Waste, Brazilian federal law no. 12.305 [6] promotes the treatment and recycling of MSW to reduce environmental impacts and promote the development of clean energy. Recently, the Brazilian government established a new incentive program called RenovaBio for biofuel production in the country. Besides stimulating the production of biofuels, the program is also a policy to mitigate the effects of gases harmful to the environment [7].

Campinas, one of the largest cities in Brazil, has a gross domestic product (GDP) per capita of approximately 10,000 dollars and an estimated population of 1.2 million people, which is similar to Toulouse city in France, with more than 1 million people [8,9]. Campinas produces approximately 1300 tons of MSW daily [10] and has problems closing landfills and building new ones, leading to increased operating costs of transporting this MSW to other cities [11].

MSW is often generated by garbage from households and urban cleaning [4,6]. Solid waste is a heterogeneous material and can vary for different regions according to their activities in those regions; however, the average composition of MSW in the country, including both recyclable and nonrecyclable materials, is approximately 50% organic matter [12–14]. Different technological approaches for managing MSW exist, including thermochemical and biochemical [5]. Nevertheless, the most employed approach by large Brazilian cities is the biochemical route, which comprises landfills and anaerobic digestion (AD) [2]. Both methods produce biogas composed mostly of CH_4, CO_2, and other gases, such as hydrogen sulfide (H_2S) and ammonia (NH_3). Biogas has a high content of CH_4, which has a higher global warming potential when compared to CO_2. An alternative way of treating MSW gas emissions in landfills could be to use the emissions as a source of carbon-neutral bioenergy to mitigate the effects of greenhouse gas emissions (GHG) and to reduce fossil fuel dependence and climate change [15–18].

The AD process happens in the absence of oxygen and involves the biodegradation of organic biomass through a microbial consortium. The process involves four phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [15,19,20]. Methane production and substrate biodegradability can be determined using biochemical methane potential (BMP) tests [21–23]. Another economical and rapid alternative to estimate the production of methane employs mathematical (multiphasic) models [24,25].

Biogas and biomethane, which are a platform for the energetic cogeneration of, for example, electricity and biofuel, have been increasingly investigated to broaden their applications [26–28]. Because the world today has a high demand for energy production, it is necessary to develop economic, viable, and environmentally friendly technologies for safe MSW disposal [11,17,29]. Due to the current European scenario that points to the necessity of diversifying the energy supply, the AD of MSW gives evidence of being a flexible alternative not only for managing residue accumulations but also reducing gas dependence using clean energy [30].

Therefore, this study analyzed the alternative management and treatment of MSW in Campinas (São Paulo, Brazil) by using the biomethane generated in the AD process from different organic fractions of MSW (food fraction waste (FFW), garden fraction waste (GFW), paper fraction waste (PFW), and a mixture of these three fractions (OFMSW)). Theoretical and experimental methods, a kinetic model, and substrate biodegradability were developed to investigate the potential of methane production. In addition, this study quantified the potential for electricity and biofuel generation and estimated CO_2 emission reduction and economic impact.

2. Materials and Methods

2.1. Gravimetric Composition of Campinas MSW

Campinas is located in the state of São Paulo (SP), 100 km away from the largest Brazilian city, the capital São Paulo. Campinas is classified as the fourteenth largest city in Brazil [8]. The gravimetric composition of MSW in Campinas was obtained from street sweeping solid waste, and household solid waste data from the department of urban cleaning [31], and their respective amounts of MSW were provided by the Environmental Company of the state of São Paulo [32]. FFW, PFW, and GFW were selected for the study as biodegradable fractions of MSW.

2.2. Substrates and Inoculum

Four substrates (FFW, GFW, PFW, and OFMSW) were assessed in the BMP tests, and microcrystalline cellulose (MC) (CAS n° 9004-34-6, MICROCEL®) was used as a blank control to evaluate the inoculum potential degradation. The BMP of the inoculum was used as a negative control.

The FFW sample was assumed to contain the same proportion of consumed and discarded foods as the regional diet composition of the southeast Brazilian region. A household budget survey [33] listed the most consumed foods in the region by food group. Thus, the gravimetric composition of this fraction was obtained (beans—42%; rice—34%; beef—12%; potatoes—5%; oranges—4%; tomatoes—2%; cabbages—1%) and simulated according to these proportions. The FFW had been previously conditioned: rice, beans, and meat were precooked, while oranges, potatoes, tomatoes, and cabbages were peeled, sliced, and used in their raw form.

Simulated PFW contained 50% of paper and paperboard. GFW composition consisted of heterogeneous material, which would be difficult to simulate on a laboratory scale. Therefore, only leaves and grass were used for this study fraction.

OFMSW was obtained by mixing the FFW, GFW, and PFW samples in the organic gravimetric composition proportion described in Section 2.1. The sample fractions were prepared separately 24 h before testing started. For the physical pretreatment of the biomasses, all samples were ground in a blender (model L-25 Ultra) for 5 to 10 min.

The inoculum was obtained from an anaerobic reactor for the treatment of vinasse at the Iracema sugar mill in Iracemápolis, São Paulo State, Brazil. The inoculum was stored in a refrigerator at 4 °C in order to minimize physicochemical reactions and conserve the microbial community.

2.3. Theoretical Biochemical Methane Potential (TBMP), Biochemical Methane Potential (BMP) Test, and Anaerobic Biodegradability

The organic molecular composition of each fraction had been previously obtained using the Tchobanoglous model [25] to evaluate the TBMP. Then, using Equation (1), developed by Buswell and Mueller [34], the elementary composition of the fractions was calculated. From these data, the TBMP was determined using Equation (2) [35–38].

$$\begin{aligned} C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_2O \\ \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 \\ + \left(\frac{4a-b+2c+3d}{8}\right)CO_2 + dNH_3 \end{aligned} \tag{1}$$

$$\mathrm{TBMP}\left(\mathrm{NmLCH_4\ gVS^{-1}}\right) = \frac{22.4\cdot\left(\frac{a}{2}+\frac{b}{8}-\frac{c}{4}-\frac{3d}{8}\right)}{12a+b+16c+14d} \tag{2}$$

BMP experimental tests were conducted according to the VDI 4630 method [39]. The tests were carried out in SCHOTT DURAN® glass bottles with a capacity of 1 L and a working volume of approximately 500 mL. To avoid overestimating gas production from the mixture of the substrate and inoculum, the inoculum was acclimatized to the working temperature (37 °C) for 7 days before starting the experiments. The proportion of substrate and inoculum was maintained in all experiments at a ratio of 1:3 on a volatile solids (VS) basis. Then, to ensure the reaction environment remained under anaerobic conditions, nitrogen gas was fluxed in two steps: initially, the gas was added directly to the mixture for a 5 min period. At the end of this period, the flasks were immediately sealed with a rubber septum (SCHOTT GL 45), and then gas flowed for another 5 min through the septum for complete oxygen removal. The flasks were statically incubated in a shaker (Nova Ética model 430, Brazil) at 37 °C for 60 days or until the difference in daily gas volume production reached ≤1%. The volume of gas produced throughout the experiment was analyzed by water column displacement. All experiments were performed in triplicate. The real BMP of each substrate was determined using Equation (3) [22,37].

$$\mathrm{BMP} = \frac{V_{sample} - V_{inoculum}\cdot\left(\frac{VS_{i,sample}}{VS_{inoculum}}\right)}{VS_{substrate}} \tag{3}$$

where BMP ($NmLCH_4$ gVS^{-1}) is the experimental BMP under dry and standard temperature and pressure (STP) conditions, V_{sample} (mL) is the methane volume accumulated in the sample flask, $V_{inoculum}$ (mL) is the methane volume accumulated in the inoculum flask, $VS_{i,sample}$ (g) is the mass of inoculum added in the flask with the substrate, $VS_{inoculum}$ (g) is the mass of inoculum added to the inoculum flask and $VS_{substrate}$ (g) is the mass of substrate added to the flask.

Anaerobic biodegradability was expressed as the ratio between BMP and TBMP results, as shown in Equation (4) [20,40].

$$\text{Anaerobic degradability} = \frac{\text{BMP}\left(\text{NmLCH}_4\ \text{VS}^{-1}\right)}{\text{TBMP}\left(\text{NmLCH}_4\ \text{VS}^{-1}\right)} \cdot 100\% \quad (4)$$

2.4. Kinetic Model: Modified Gompertz

The modified Gompertz model was used to evaluate the kinetic parameters of the methane produced using biological activity: Equation (5) [20,35,41].

$$B(t) = B_0 \cdot \exp\left\{-\exp\left[\frac{\mu_m . e}{B_0}\right] \cdot (\lambda - t) + 1\right\} \quad (5)$$

where these parameters include B(t): accumulated specific methane production ($NmLCH_4$ gVS^{-1}); (B_0): accumulated maximum potential methane ($NmLCH_4$ gVS^{-1}); (μ_m): specific CH_4 production rate ($NmLCH_4$ gVS^{-1} day^{-1}); (λ): lag phase (day); (t): incubation time (day).

2.5. Analytical Methods

Analytical steps were carried out in triplicate. Solid content, total solids (TS), and VS were calculated using the Standard Methods for the Examination of Water and Wastewater—2540B method [42], while the pH was measured using a portable pH meter (Tec-3MP, TECNAL, Brazil). A gas chromatograph (Shimadzu, CG 2014, Kyoto, Japan) was coupled to a 60/80 Carboxen-1000 column (15′ × 18″) using helium as a carrier gas at a flow rate of 30 mL min^{-1} at 225 °C. A previously constructed calibration curve was used to analyze the CH_4 and CO_2 content from biogas production.

2.6. Case Study: Electric Potential Generation and Environmental and Economic Impact

The city of Campinas in São Paulo (Brazil) was chosen as a case study based on the experimental results of the gas content obtained in this work for each fraction. The economic, environmental, and energy potential impacts of the biomasses in this study were calculated using additional information from the literature, which is described in Table S1 (Supplementary Information).

Equations (6) and (7) were employed [29,43] to estimate the electric power ($P_{electric}$) and the potential for energy generation (E_{energy}) of each fraction of the MSW investigated in this research:

$$P_{electric}(MW) = \frac{LHV \cdot \eta \cdot Q_{CH_4}}{31536000} \quad (6)$$

$$E_{energy}\ (MWh) = P \cdot \Delta t \cdot A_{op} \quad (7)$$

where LHV is the low calorific value of methane (35.8 MJ m^{-3}), η is the energy conversion efficiency for combustion engines (30%), Q is the biomethane flow rate for each fraction of MSW (Nm^3 $year^{-1}$), Δt is the number of hours in a year (h), and A_{op} is the annual operating capacity of the power plant (0.8).

In Campinas, solid waste is transported by garbage trucks, which are heavy-duty vehicles powered by diesel engines, to the main regional landfill located in Paulínia City. The estimated emission (ECO_2 emission) of this transportation, the potential CO_2 emission reduction (RCO_2 emission), and the economic potential (EP) of replacing diesel fuel with biomethane are represented by Equations (8)–(10), respectively [43].

$$\text{ECO}_2\text{emission}\left(\text{tCO}_2\ \text{year}^{-1}\right) = \frac{\vartheta \cdot \text{E}_\text{f}}{\gamma_{\text{diesel}} \cdot 1000} \quad (8)$$

$$\text{RCO}_2\text{emission}\left(\text{tCO}_2\ \text{year}^{-1}\right) = \frac{\text{Q}_{\text{CH}_4} \cdot \gamma_{\text{CH}_4} \cdot \text{E}_\text{f}}{\gamma_{\text{diesel}} \cdot 1000} \quad (9)$$

$$\text{EP}\left(\text{R\$ year}^{-1}\right) = \left(\frac{\text{Q}_{\text{CH}_4} \cdot \gamma_{\text{CH}_4}}{\gamma_{\text{diesel}}} \cdot \text{Price}_{\text{diesel}}\right) - \left(\text{Q}_{\text{CH}_4} \cdot \text{Price}_{\text{CH}_4}\right) \quad (10)$$

where ϑ represents the distance (km) traveled by a garbage truck completely filled with each MSW organic fraction studied per year (km year^{-1}) between Campinas and Paulínia. The data used for the calculations in Equations (8)–(10) are also described in Table S1 (Supplementary Information).

2.7. Data Processing

The experimental results and data modeling were analyzed and fitted using MATLAB® (R2014b). The energetic potential, as well as the economic and environmental impact, were calculated using Excel (Microsoft Office 365).

3. Results and Discussion

3.1. Campinas MSW Gravimetric Composition

Knowledge of the gravimetric composition of waste is relevant in the classification of the types of waste residues generated in a region for their efficient disposal based on the four Rs policy (reduce, reuse, recycle, and recover) [2]. The gravimetric composition of MSW depends on demographic factors, climate conditions, city size, and local economic activities, among other aspects, which explain the heterogeneity of the residues [13,44]. This composition is normally classified as organics, recyclables, and other fractions. Figure 1 shows the gravimetric composition of the MSW of Campinas in 2016. The main fraction found constituted FFW (32.2%), GFW (20.0%), and PFW (15.5%). A minor content (0.6%) of the composition was found to be wood, leather, and rubble. The OFMSW in this study reached 67.7%, which was similar to Brazil's MSW production (64.5%) [14]. However, the composition of this study differed from that found in the literature, which is approximately 50.0–59.0% for Santo André (São Paulo) and Campinas in 2015 [11,12], revealing the heterogeneity of MSW. The substantial fraction of the organic load in Campinas MSW indicates the potential of MSW to be used as a renewable source of energy, for instance, biogas and biomethane production through AD [45]; thus, minimizing the waste accumulation in landfills and, consequently, its impacts on the environment through energy cogeneration. This production represents an opportunity for economic and social–environmental gains.

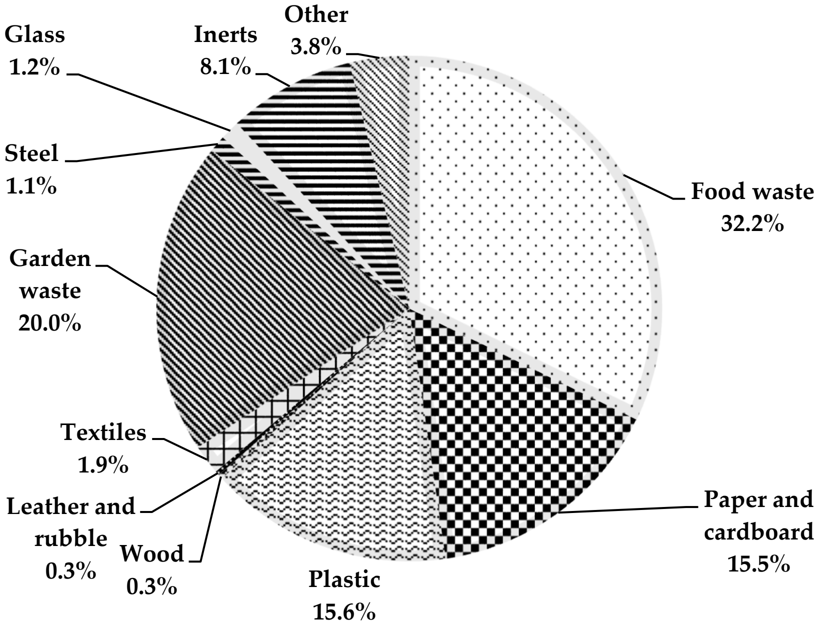

Figure 1. Campinas MSW composition.

3.2. Chemical Characterization

Characterizing the organic fraction of MSW is essential in determining the biodegradability of substrates because this fraction influences biomethane production [45]. In order to obtain an appropriate characterization for BMP, we evaluated the chemical parameters of MC, FFW, PFW, GFW, OFMSW, and the microbial consortia used (Table 1). At the end of the experimental tests, the researchers did not observe the inhibition of *Methanogenic archaea* during the AD process because of the absence of acidity in the process, as the average pH of the cultures was 7.8, while the optimal pH range for this microbial group is 6.5–8.2 [20,46]. The MC used in this work presented a similar value for VS as the TS ratio reported by Raposo et al. [47], who attained values of 100%. In the residue fraction, the lowest moisture content (4.8 $\pm$ 0.1%) and the highest TS (952.3 $\pm$ 1.4 g kg^{-1}) were found for PFW. PFW also had the highest proportional contents of VS, which was 846.0 $\pm$ 2.2 g kg^{-1}. The results for PFW—940 g kg^{-1} of TS and 731 g kg^{-1} of VS—were in agreement with those reported by Nielfa et al. [48]. Moreover, the highest moisture value related to the waste fractions was found for GFW (70.6 $\pm$ 0.9%) with a TS of 293.7 $\pm$ 9.4 g kg^{-1} and a VS of 266.2 $\pm$ 2.1 g kg^{-1}. These results were less than those reported by Nielfa et al. [48] for this same fraction, where TS was 508 g kg^{-1}, and VS was 449 g kg^{-1}, although this variation can be explained by the difference in the residue composition analyzed. OFMSW had a lower ratio of VS to TS (86.8%) because the composition of OFMSW represents different types of constituents, such as lipids, proteins, and carbohydrates. The inoculum results for the VS to TS ratio was 69.3%, which indicates a suitable source for the AD process as it is in the range considered optimal (42% to 68%) [47]. Table 1 shows that VS is not a constant parameter; it depends on the substrate used in the tests and is directly related to the methane results expressed as NmLCH_4 gVS^{-1}.

Table 1. Substrate and inoculum characteristics.

Substrate	pH	Moisture (%)	TS (g kg^{-1})	VS (g kg^{-1})	VS/TS (%)
MC	6.2	5.4 $\pm$ 0.1	945.6 $\pm$ 0.9	945.2 $\pm$ 1.1	100
PFW	7.1	4.8 $\pm$ 0.1	952.3 $\pm$ 1.4	846.5 $\pm$ 2.2	88.9
GFW	7.3	70.6 $\pm$ 0.9	293.7 $\pm$ 9.4	266.2 $\pm$ 2.1	90.6
FFW	6.0	67.5 $\pm$ 0.2	325.2 $\pm$ 2.0	312.5 $\pm$ 1.8	96.1
OFMSW	7.2	56.3 $\pm$ 5.3	434.8 $\pm$ 50.6	377.4 $\pm$ 8.8	86.8
Inoculum	7.9	92.6 $\pm$ 0.5	74.2 $\pm$ 4.8	51.4 $\pm$ 3.6	69.3

3.3. TBMP and BMP Results

The literature presents different models for predicting the biogas and biomethane content produced by a variety of substrates. However, the model used in this work was developed by Thobanoglous et al. [25] to determine the amount of these gases in MSW, in which the carbon, hydrogen, oxygen, and nitrogen content was considered to determine the molecular composition of each fraction to evaluate the TBMP.

The TBMP results revealed that the PFW fraction had the highest content of carbon, hydrogen, and oxygen, corroborating the study by Thobanoglous et al. [25], as this fraction has the lowest moisture content (4.8%). The empirical formulas of PFW, GFW, and OFMSW normalized by the nitrogen were $C_{169.2}H_{280}O_{128.3}N$, $C_{16.4}H_{24.7}O_{9.8}N$, and $C_{30.4}H_{48.7}O_{20.2}N$, respectively, and agreed with those reported in the literature for OFMSW ($C_{32}H_{55}O_{16}N$) [49]. High theoretical biogas (0.8 m^3 kg^{-1} of MSW) and biomethane (0.4 m^3 kg^{-1} of MSW) volumes were found for PFW. However, the average methane composition in all the substrates analyzed was 52.2%, and this result can be explained by the method used, which estimates the gas content in landfill at approximately 50% for both CH_4 and CO_2 [50].

FFW had the highest theoretical potential to produce methane (507 $mLCH_4$ gVS^{-1}) when compared to the other substrates analyzed (Table 2). Browne et al. [51] indicated the range of the theoretical methane potential in a food fraction was 530–696 $mLCH_4$ gVS^{-1}; this lower limit is similar to that found in this work, while studies using agricultural waste as a substrate in the AD process indicated values ranging from 544.1–641.9 $mLCH_4$ gVS^{-1} [52] to 437.6–476.9 $mLCH_4$ gVS^{-1} [53], corroborating the values that depend on the elemental composition of the residues and that can yield a variety of TBMP values.

Table 2. Substrate characteristics according to TBMP method.

Substrate	Molecule	Biogas (m^3 kg^{-1} of MSW)	CH_4 (m^3 kg^{-1} of MSW)	CH_4 Composition (%)	TBMP ($mLCH_4$ gVS^{-1})
PFW	$C_{169,2}H_{280}O_{128,3}N$	0.8	0.4	51.5	446
GFW	$C_{16,4}H_{24,7}O_{9,8}N$	0.4	0.2	51.6	484
FFW	$C_{21,5}H_{34,5}O_{12,7}N$	0.3	0.1	53.6	507
OFMSW	$C_{30,4}H_{48,7}O_{20,2}N$	0.3	0.2	52.2	474

The mixture (OFMSW) had a TBMP value of 474 $mLCH_4$ gVS^{-1}, which is similar to the values reported by Nielfa et al. [54], who found 494.3 $mLCH_4$ gVS^{-1} and concluded that methods based on stoichiometric composition provide useful estimates of methane production. According to Equation (2), the TBMP calculation is connected to a molecular formula. Therefore, the TBMP values depend on the substrate source, which can vary according to a region's gravimetric composition [44,55].

Biogas production in the AD experimental process involves mainly hydrolysis, acidogenesis, acetogenesis, and methanogenesis routes and different microbial consortia, which use organic substrates to degrade a material into small molecules and transform it into CH_4 and CO_2 gases. Depending on a microorganism's access to the substrates, the biogas accumulation curve can be normal or gradual and indicate the retardation or inhibition of degradation [19,20,39]. The BMP results for the organic substrates and inoculum are shown in Figure 2a–e. A daily biogas production lower than 1% of the cumulative CH_4 production by PFW, GFW, FFW, and OFMSW was achieved after 60 days and, in the inoculum, after 66 days. Another point is the ratio of the inoculum to the substrate, which, in this work, was established as 3:1. A previous study showed that the highest methane production was achieved at a 2:1 ratio, suggesting that at an association greater than this, where the ideal is between 2:1 and 4:1, the inhibition and overload factors are reduced, thus increasing and improving gas production performance [37].

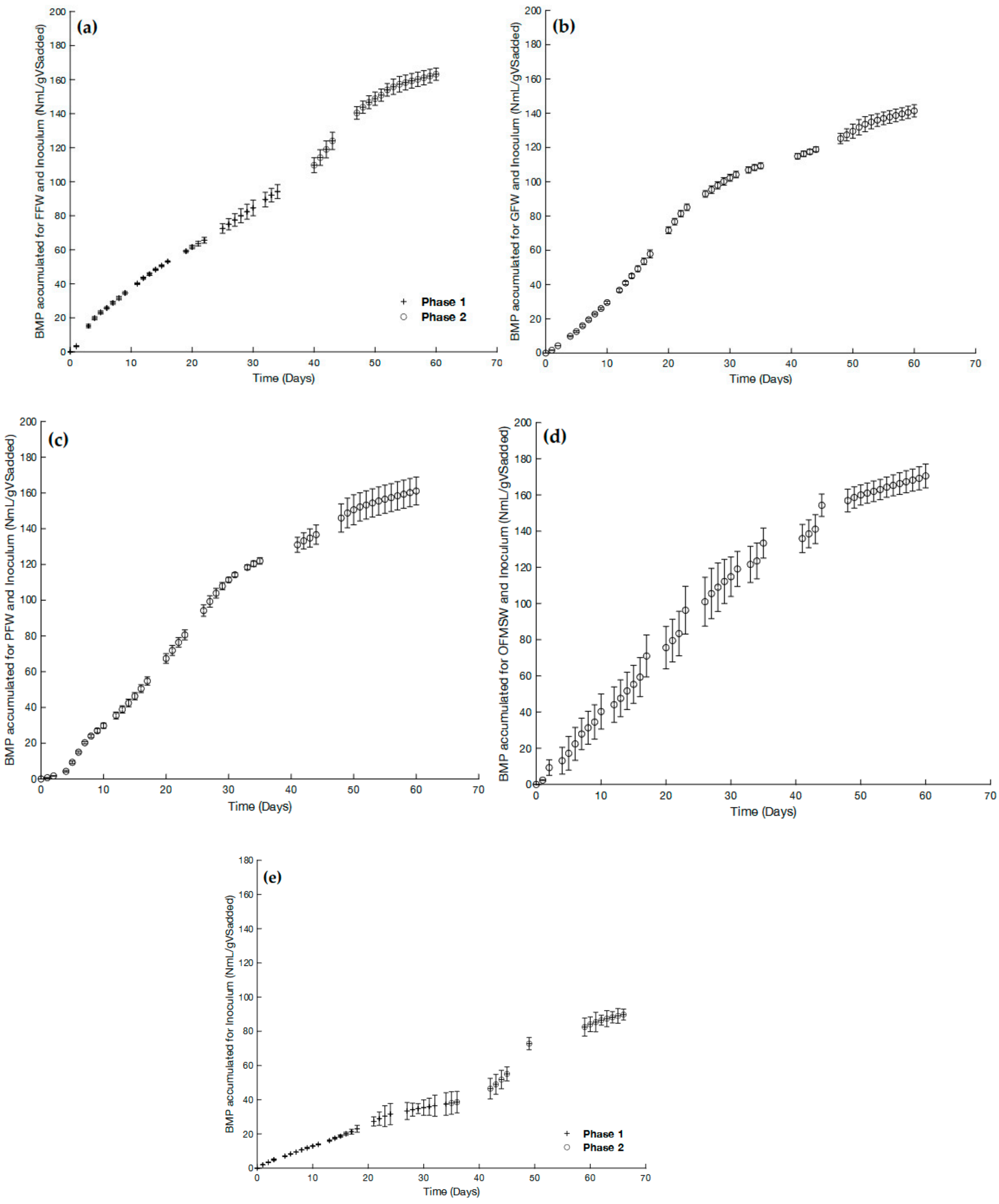

Figure 2. Experimental BMP results: (**a**) FFW + inoculum; (**b**) GFW + inoculum; (**c**) PFW + inoculum; (**d**) OFMSW + inoculum, and (**e**) inoculum.

According to Figure 2a,b,d, all the substrate degradation curves presented a lag phase during the first days; on average, the lag was 2 days for FFW, GFW, and OFMSW (Figure 2a,b,d), while as shown in Figure 2c for PFW, the lag phase was longer: 5 days. In the final BMP results presented in Figure 2, the highest BMP was achieved by OFMSW (170.5 ± 6.6 $NmLCH_4$ gVS^{-1}), followed by FFW (163.2 ± 3.6 $NmLCH_4$ gVS^{-1}) and PFW (161.1 ± 7.81 $NmLCH_4$ gVS^{-1}). The lowest value was for GFW, which had a production of 141.1 ± 3.6 $NmLCH_4$ gVS^{-1}. In comparative terms, the OFMSW produced approximately 21% more methane than GFW at the end of the experiments. The average methane composition in the biogas produced by all substrates was 58% during the whole experiment.

Figure 2e represents the performance of the inoculum through its gradual degradation and methane production in two phases. The first phase lasted for 34 days and was characterized by the substrate, and the second lasted until the end of the assay. In another study, a different use of the inoculum and substrate proportions (2–0.5) was reported, and the same behavior was found for the 1.0 and 0.8 ratios, suggesting that this characteristic kinetic profile is due to the acclimatization phase, where the microbial consortium undergoes an adaptation to the reaction stress so that it can have stability and facilitate the organic material transformation into biogas and biomethane [37].

Equation (3) determined the BMP result for each substrate, where the methane production by the inoculum was discounted to calculate the real BMP. OFMSW produced the highest BMP (410.7 $\pm$ 24.9 $NmLCH_4$ gVS^{-1}), followed by FFW (381.9 $\pm$ 14.5 $NmLCH_4$ gVS^{-1}) and PFW (373.3 $\pm$ 31.2 $NmLCH_4$ gVS^{-1}). GFW produced the lowest BMP: 294.5 $\pm$ 15.6 $NmLCH_4$ gVS^{-1}. As observed, OFMSW produced 39.5% more methane than GFW, which had the lowest value observed in all experiments. The BMP results suggest that the biomethane produced in the experimental test was generated mostly from the investigated MSW substrates, and the results can be explained by the ratios of VS/TS. As shown in Figure S1—Supplementary Information, the inoculum achieved only 90 $NmLCH_4$ gVS^{-1} and the lowest VS/TS (69.3%). Furthermore, the substrates attained values superior to 290 $NmLCH_4$ gVS^{-1}.

The experimental result obtained for PFW (373.3 $\pm$ 31.2 $NmLCH_4$ gVS^{-1}) was similar to that obtained for the industrially treated paper pulp (323 $\pm$ 4.96 $NmLCH_4$ gVS^{-1}) [55]. GFW (294.5 $\pm$ 15.6 $NmLCH_4$ gVS^{-1}), which had the lowest value achieved in the experiments, produced a similar result to that of the 283–383 $NmLCH_4$ gVS^{-1} reported in another study [56].

The biomethane production by FFW was similar to that of the inoculum; that is, it exhibited two phases of gas production and followed a gradual path. The result in this work was 381.9 $\pm$ 14.5 $NmLCH_4$ gVS^{-1}, which approximates the AD process for banana waste (373.3 $NmLCH_4$ gVS^{-1}) [57]. Zhang et al. [58] found an inoculum-to-substrate ratio that varied between 445 $\pm$ 2 $NmLCH_4$ gVS^{-1} and 456 $\pm$ 7 $NmLCH_4$ gVS^{-1}. Another study evaluating the codigestion of FFW with dairy manure obtained 477–499 $NmLCH_4$ gVS^{-1} and concluded that codigestion has advantages, such as achieving a high methane yield because of different microbial consortia. Moreover, the relationship between carbon and nitrogen can improve the nutrient content in the process [59].

The BMP of OFMSW found in this study was similar to that reported by Carchesio et al. [60] (445.6 $NmLCH_4$ gVS^{-1}) for a mechanically separated organic fraction from MSW. Similar, albeit higher values, for OFMSW were reported in the literature recently, where an evaluation of different timespans (days) and the AD process gave BMP yields of 495 $NmLCH_4$ gVS^{-1}, 594 $NmLCH_4$ gVS^{-1}, and 644 $NmLCH_4$ gVS^{-1} [61]. On the other hand, low values were also determined for this fraction, reaching 344 $\pm$ 10 and 364 $\pm$ 4 $NmLCH_4$ gVS^{-1} for an inoculum-to-substrate ratio of 2:1 [58] (145 $\pm$ 12 $NmLCH_4$ gVS^{-1}) [48], and in the range of 320–529 $NmLCH_4$ gVS^{-1} [45]. The results presented in the literature showed that OFMSW is a mixture of different residues, and its composition varies according to the region studied. This fact impacts biomethane production at the end of the assay.

Both OFMSW and FFW are potentially relevant feedstocks for biofuel and bioelectricity production based on the biomethane capacity production of both fractions. There is potential to improve these values using the AD process and codigestion. Our findings also indicate that OFMSW, the best substrate, could be a potential feedstock to produce methane through AD, thus avoiding the separation of the residues fractions in landfills and presenting an alternative means to reduce the costs of methane production.

3.4. Substrate Biodegradability

A substrate's biodegradability determines the relation between the experimental (BMP) and the theoretical (TBMP) results based on Equation (4). Figure 3 shows the biodegradability, which was tested to compare the TBMP and BMP results. The low degradability of FFW (74.8%) and GFW (61.3%) is related to the possible recalcitrance of both substrates, which slows the hydrolysis efficiency of the AD process and limits biomethane production from lignocellulosic materials [62]. This same characteristic (of this low degradability) was observed for banana waste (76.2%) [57].

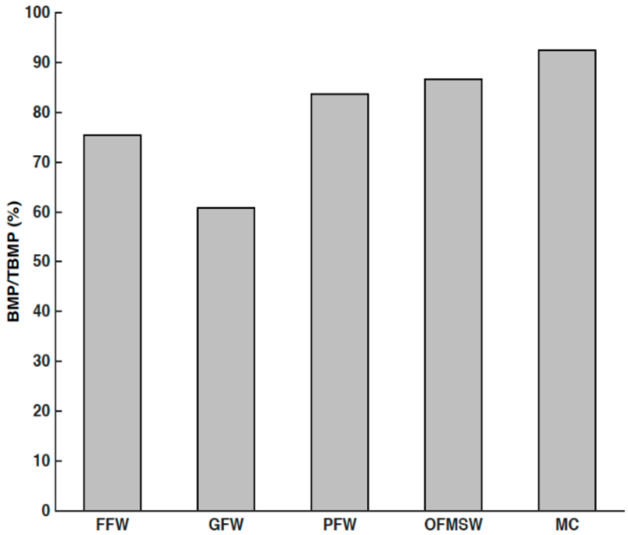

Figure 3. Substrate degradability.

However, efficient biodegradability was found for OFMSW (87.4%) and PFW (84.0%), which had a high methane production (degradation above 85% is considered a high rate) [37]. Different biodegradability was reported in the literature for OFMSW, where a high rate of approximately 93% [48] and a low rate of almost 41% [54] was found. This factor is linked to substrate composition, degradation capacity, and a suitable consortium of inoculum microbiota. Another highlight is that the MC biodegradability test found 92.5%, suggesting a high quality and efficiency in the inoculum consortia. The methane production measured in the experiment differed from the theoretical value, and one reason for this is that part of the substrate was used for microbial metabolic activities. Another explanation is that the Buswell and Muller equation considered the total use of the substrate for CH_4 production, and thus TBMP was overestimated [36,63].

3.5. BMP Using the Modified Gompertz Model

Substrate kinetic degradation allows for an understanding of the behavior of how the materials are degraded. The most widely used test for BMP is the modified Gompertz equation. Therefore, the researchers validated the kinetic degradation and methane production of each substrate through this model at a 95% confidence interval, and the curves fit the experimental results (Figure S2—Supplementary Information).

According to Table 3, the range of BMP calculated using the Gompertz model was between 95.0 and 184.8 $NmLCH_4$ gVS^{-1}, and the mixture of the inoculum and FFW showed a gradual degradation (analyzed in a two-phase CH_4 production). The first phase was from 0 to 32 days, and the second phase was from 33 to 60 days before achieving maximum productivity. Another characteristic of the model is that, in the lag phase (λ), the FFW and inoculum did not present an initial λ in the first and second phases: -1.4 ± 1.3 and 0.7 ± 0.7 days, respectively, (simultaneously with the methane production). As reported by Pantini et al. [64], the absence of λ suggests that the experiments occurred under optimal conditions in the AD process. In terms of the specific CH_4 rate (μ_m), PFW had the highest value (4.4 ± 0.2 $NmLCH_4$ gVS^{-1} day^{-1}), followed by FFW (4.3 ± 0.3 $NmLCH_4$ gVS^{-1} day^{-1}) in the second phase, and the lowest result was found in the first phase of the inoculum (1.4 ± 0.1 $NmLCH_4$ gVS^{-1} day^{-1}).

Table 3. Parameter results from kinetic modified Gompertz model.

Substrate	B_0 ($NmLCH_4$ gVS^{-1})	μ_m ($NmLCH_4$ $gVS^{-1}day^{-1}$)	λ (day)	R^2
PFW	166. 9 ± 3.1	4.4 ± 0.2	4.4 ± 0.6	0.9975
GFW	140.0 ± 3.0	4.1 ± 0.2	2.9 ± 0.9	0.9947
FFW Phase 1 (0–32 days)	99.6 ± 11.2	3.1 ± 0.3	−1.34 ± 1.3	0.9855
FFW Phase 2 (33–60 days)	85.1 ± 3.3	4.3 ± 0.3	33.7 ± 0.7	0.9965
OFMSW	181.1 ± 4.3	4.2 ± 0.2	1.9 ± 0.7	0.9969
Inoculum Phase 1 (0–34 days)	44.5 ± 2.6	1.4 ± 0.1	1.1 ± 0.6	0.9962
Inoculum Phase 2 (35–66 days)	50.5 ± 2.1	3.8 ± 0.8	40.1 ± 1.0	0.9946

The Gompertz model was used to predict the AD experimental results of OFMSW and was evaluated by Pangallo et al. [61]. In this study, methane production was analyzed at different time intervals (2, 6, and 10 days). The results showed that the highest methane concentration was found in the 6-day experiment (0.625 $NmLCH_4$ gVS^{-1}), with a production rate of 0.090 $NmLCH_4$ gVS^{-1} day^{-1}. It was observed that in the 2- and 6-day tests, the λ phase was absent, while in the 10-day assay, the λ phase was 0.574 days. It was, therefore, concluded that this model had a good fit related to the experimental measurements. Likewise, the kinetic model studied had adequate experimental results for a good fit based on the R^2 value (0.985–0.997). The Gompertz model predicted the final BMP of all substrates with the inoculum as the experimental and model values were similar.

3.6. The Energetic Potential, CO_2 Emissions, and Economic Impact of the Biomethane Production from Organic Waste

There is currently worldwide interest in developing new processes and technologies using renewable resources based on the circular economy. In the literature, biomethane has been identified as a relevant product for the bioeconomy, besides being important in initiating the transition to clean energy and increasing the energetic independence of a region [30]. There are different uses for biogas and biomethane applications; for example, their use in electricity generation and biofuel production as an alternative to diesel oil, consequently leading to a reduction in economic and environmental impact [26].

Valorized biomethane and biogas were obtained from raw material residues through the AD process on a laboratory scale from different fractions of MSW. A case study for Campinas City was carried out. For data entry, this research used the experimental results obtained from the BMP tests. Energy and fuel production were quantified, while an evaluation of economic and environmental impacts was performed.

Table 4 shows the energy potential of each organic fraction studied, depending on the amounts of MSW generated in Campinas and based on data in Table S1 (Supplementary Information). OFMSW showed the highest potential for gas production at 49.9×10^6 Nm^3 CH_4 $year^{-1}$, while GFW had the lowest potential at 7.4×10^6 Nm^3 CH_4 $year^{-1}$. These results corroborate the BMP assay. According to a report in SIMA [65], the energy consumption in 2018 in Campinas was 3285 GWh (for households, it was 1099 GWh), and the biomethane potentially produced by OFMSW in Campinas was equivalent to 118.9 GWh per year (Equations (6) and (7)). Therefore, compared to the energy consumed by households (Table S1—Supplementary Information), OFMSW could supply almost 11% of the energy demand in the city, representing around 37,700 households per year. In economic terms, considering the electricity price in the city (BRL 0.62 kWh^{-1} or USD 0.12 kWh^{-1}), the total price of energy consumption for households was USD 129.4×10^6 $year^{-1}$. OFMSW can generate USD 14×10^6 per year, which represents 10.8% of the cost of energy price demand for households in the city.

Table 4. Energy potential generated by BMP from each fraction of OFMSW in Campinas by AD process.

	MSW Fraction			
Description	FFW	PFW	GFW	OFMSW
BMP (10^6 N m^3 CH_4·year^{-1})	18.1	23.3	7.5	49.9
Electric Power (MW·year^{-1})	6	8	3	17
Energy Potential (GWh·year^{-1})	43.3	55.5	17.8	118.9
Potential households supplied by energy demand per biomass per year	13,716	17,591	5631	37,686
Potential Energy total price (USD 10^6 year^{-1}) *	5.1	6.5	2.1	14

* USD 1 = BRL 5.27.

In a study carried out in 2019 by Dalmo et al., different technological routes (thermochemical and biochemical) and two hybrid combinations were evaluated to determine the electrical energy potential of MSW from landfills in 32 cities belonging to the São Paulo state [5]. In municipalities with more than 1 million inhabitants, electrical generation was estimated as follows: landfill gas (43,121 MWh year^{-1}), AD (66,168 MWh year^{-1}), gasification (279,623 MWh year^{-1}), and incineration (283,126 MWh year^{-1}). A hybrid method (incineration + AD) achieved 296,689 MWh year^{-1}, and the highest value found was for the combination of gasification and AD (303,789 MWh year^{-1}) [5]. Comparing the present case study (Table 4) with the study carried out by Dalmo et al. [5], PFW and FFW yielded values close to those reported for the biochemical routes (landfill gas and AD), while OFMSW was 2.8 and 1.8 times higher than what was reported for landfill gas and the AD process, respectively.

As shown in Figure 1, OFMSW represents 67.7% of the MSW in Campinas, followed by FFW (32.2%), GFW (20.0%), and PFW (15.5%). Table 5 presents the potential for biofuel production for heavy-duty vehicles and the environmental and economic impact, respectively, of biomethane when replacing diesel for each of these fractions, according to Equations (8)–(10) and the data from Table S1 (Supplementary Information).

Table 5. Economic and environmental impacts using biomethane from OFMSW as a renewable fuel, replacing diesel for heavy-duty vehicles in Campinas.

	MSW Fraction			
Description	FFW	PFW	GFW	OFMSW
Equivalence of BMP to diesel production (10^3 m^3diesel year $^{-1}$)	18.1	23.2	7.4	49.9
Biomethane heavy-duty vehicle (10^6 km year $^{-1}$)	40.7	52.2	16.7	111.9
CO_2 avoided emission per year using CH_4 instead of diesel (kt CO_2 year $^{-1}$)	49.4	63.4	20.3	133.1
Economic impact of replacing diesel with CH_4 (USD 10^6 year^{-1}) *	9.2	11.8	3.8	25.2

* US$1 = BRL 5.27.

Diesel oil consumption in Campinas reached 1.99×10^5 m^3 in 2018, while the CO_2 emissions were 2.1 Mt, which represents the third highest emission in the São Paulo state [65]. The OFMSW of this study has the highest potential to produce biomethane to allow for the replacement of diesel (49.9×10^3 m^3 diesel year^{-1}), while GFW has the lowest potential (7.4×10^3 m^3 diesel year^{-1}). When considering OFMSW, if all the BMP potential was used in the AD process, the garbage trucks could cover approximately 112×10^6 km year^{-1}, reducing the emissions of CO_2 by 133.1 kt year^{-1}. Thus, this OFMSW could supply 25% of the diesel demand in the city and prevent 6.3% of CO_2 emissions by replacing diesel. Moreover, the economic impact caused by this substitution could generate savings in the range of USD 9.2×10^6 and 25.2×10^6 year^{-1}.

In a study for a solid-state batch methanization system using 1.3% of OFMSW as a substrate for Rio de Janeiro (Brazil), the economic and environmental potentials generated from the plant conditions were evaluated [43]. The results showed that the biomethane generation system could replace 528 m^3 of diesel per year, reducing costs by almost USD

300,000 per year and preventing 1.4 kt of CO_2 emissions per year. The methanization system has the potential to provide economic and environmental benefits even though the results achieved represent only a small fraction of OFMSW. Therefore, if the full OFMSW potential (as described by Ornelas-Ferreira et al.) [43] was used, the final values obtained would approximate those observed for OFMSW in the present study (Table 5), thus providing economic and environmental advantages to Campinas City due to the replacement of diesel by methane production. In terms of nationally determined contributions, Brazil has committed to reducing national emissions by 43% by 2030 [7].

4. Conclusions

Biomethane is a relevant gas due to its potential to reduce climate change and allow for the replacement of nonrenewable energy sources. Currently, OFMSW represents 67.7% of the total mass of MSW in Campinas and can be easily converted into biomethane due to its high BMP potential (410.7 $\pm$ 24.9 NmLCH$_4$ gVS^{-1}) and biodegradability (87.4%). For all organic substrates, the modified Gompertz model was used to predict the kinetic parameters of the AD process and showed a satisfactory fit to the experimental results.

Concerning the case study of Campinas related to energy, the potential electric generation could supply the energy demand of almost 11% of the households in the city, and replacing fossil diesel with biomethane to fuel the garbage trucks in Campinas would reduce diesel demand in the city by 25%. The economic gains from replacing diesel with methane could reach USD 25.2 $\times$ 10^6 per year, and it could eliminate nearly 6.3% of the city's GHG emissions.

These results emphasize that the AD process of OFMSW could produce biomethane as a green energy source and reduce residues in landfills, shifting them towards the circular economy. Improving the energy security of the region and generating electricity that could be distributed by local grids could increase their safety and avoid GHG emissions. However, to achieve the total potential of the AD process, it is necessary to consider the adequate management of residues and local policies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10122662/s1, Table S1. Parameters used to estimate electricity generation potential and environmental and economic impacts. Figure S1. Relationship between VS/TS ratio and methane production. Figure S2. Modified Gompertz model results for the BMP experiment: (a) FFW + inoculum; (b) GFW + inoculum; (c) PFW + inoculum; (d) OFMSW + inoculum and (e) Inoculum. References [8,10,43,66–70] are cited in the supplementary materials.

Author Contributions: Conceptualization, L.A.P. and T.T.F.; experimental results, L.A.P.; development of experimental and theoretical methodologies, L.A.P. and B.d.S.M.; investigation, L.A.P.; formal analysis, L.A.P. and B.d.S.M.; data curation, writing—original draft, L.A.P., J.T.-P., B.d.S.M., T.T.F.; writing—reviewing and editing, L.A.P., J.T.-P., B.d.S.M., T.T.F.; editing and data visualization, L.A.P. and J.T.-P.; B.d.S.M.; T.T.F.; resources provider, supervision, project administration, funding acquisition, T.T.F. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Brazilian Coordination for the Improvement of Higher Education Personnel (CAPES) [grant N°. 33003017034P8], by São Paulo Research Foundation (FAPESP) [grant N°. 2015/50612-8] and by CNPq (grant N°. 140930/2017-5).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the São Martinho Mill for its cooperation in providing the inoculum to carry out this study and M. Eng. Bruno Rangel Pacheco for the MATLAB technical support.

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

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