

Article

Thermochemical Pretreatment for Improving the Psychrophilic Anaerobic Digestion of Coffee Husks

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Abstract: Psychrophilic anaerobic digestion emerges as an appealing integrated solution for the management of agricultural waste, particularly for farmers in regions where the average temperature does not exceed 26 °C, as seen in coffee cultivation. Therefore, this study seeks to assess the biomethane potential of thermochemical-treated coffee husk through psychrophilic anaerobic digestion (C3-20 °C-w/pretreatment). To examine its viability, outcomes were compared with reactors operating at both mesophilic (C1-35 °C) and psychrophilic (C2-20 °C) conditions, albeit without the use of pretreated coffee husk. The C3-20 °C-w/pretreatment test demonstrated a 36.89% increase (150.47 NmL CH₄/g VS; 161.04 NmL CH₄/g COD), while the C1-35 °C test exhibited a 24.03% increase (124.99 NmL CH₄/g VS; 133.77 NmL CH₄/g COD), both in comparison to the C2-20 °C test (94.96 NmL CH₄/g VS; 101.63 NmL CH₄/g COD). Notably, the C3-20 °C-w/pretreatment trial yielded superior outcomes, accompanied by an associated energy output of 3199.25 GWh/year, sufficient to meet the annual energy demands of 494 residences. This marks an increase of 83 and 182 million residences compared to the mesophilic and psychrophilic AD of CH without pretreatment, respectively.

Keywords: methane yield; energy output; psychrophilic anaerobic digestion; agricultural residue; coffee husk



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1. Introduction

Agricultural residues, commonly known as agro-wastes, are the byproducts (i.e., crop remnants, fruits, roots, husks, residual stalks, and various types of vegetables) resulting from a wide range of agricultural procedures and activities. Their primary composition consists of carbohydrate polymers such as starch, lignocellulose, cellulose, and hemicellulose, as well as proteins, lipids, fibers, and other organic constituents. The substantial organic content in these residues, when not disposed of properly, can have adverse environmental implications (e.g., greenhouse gas (GHG) emissions and effects of global warming). Therefore, utilizing these residues as a feedstock for clean energy production represents an environmentally friendly approach to residue management [1–4]. In this perspective, the use of residuals from coffee chain production, which is one of the most popular beverages in the world, is of utmost importance due to the large quantity produced [5]. According to [6], in the fiscal year 2019/2020, global coffee production and consumption reached 169.34 million bags (60 kg each) and 168.39 million bags, respectively, resulting

in a surplus of 950,000 bags. The overall trend in coffee consumption has demonstrated a continuous increase. To illustrate, the annual global coffee production witnessed increases of 83.35%, 50%, and 20% in the fiscal years 2018/2019 as compared to the respective production in 1990/1991, 2000/2001, and 2010/2011 [6]. By country, Brazil is the world's largest coffee producer, followed by Vietnam, Colombia, and Indonesia. In 2020, Brazil produced more than 60 million bags (63,400) of processed coffee, constituting 37% of global production (169,634). This substantial output also led to the generation of a significant amount of waste (coffee husks), which could be a source for the sustainable generation of bioenergy and biofuels [1–4,7].

Brazilian coffee production covers an extensive area accommodating both Arabic and Conilon coffee species. In Brazil, Arabic coffee thrives in cooler regions, typically at altitudes above 500 m, where the annual average temperature falls between 18 °C and 22 °C. In contrast, Conilon coffee is more suitable for areas where the average temperature ranges from 22 °C to 26 °C [8]. In Brazilian plantations, coffee cherries are typically dried to remove the exocarp, mesocarp, and endocarp, generating approximately 1 kg of husk for every 1 kg of coffee bean produced [9–12]. This residual is commonly employed as an organic fertilizer, distributing it across their plantation soils. Nonetheless, despite its favorable chemical composition, particularly in terms of nitrogen (N) and potassium (K) content when compared to other organic fertilizers, the husk poses challenges due to its bulkiness [11,13,14]. This makes storage, handling, and soil integration problematic, resulting in only a portion of the husks being utilized as fertilizer. Additionally, its unwieldy texture renders coffee husks unsuitable as a caffeine source for pharmaceutical and beverage companies but hold great potential for applications in anaerobic digestion (AD) due to the high energy density stored per unit mass (13–21 MJ/kg) [9,11,15–19].

AD mineralizes organic compounds to methane (CH₄) and carbon dioxide (CO₂) and stands as the most ancient technology for harnessing energy from the biological breakdown of organics [20]. At present, the primary role of AD biodigesters is to capture CH₄ emissions arising from the decomposition of organic matter, such as that from agricultural activities. In doing so, the release of greenhouse gases into the environment is mitigated [21]. The AD process involves four key stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Among these, hydrolysis is the limiting factor due to the rigid cell walls in vegetal organics, resulting in extended digestion times and reduced biogas production [21]. Many studies on lignocellulosic biomass-fed AD operate at 35–55 °C, where reactions generally proceed more efficiently [22]. Yet, maintaining these temperature ranges involves considerable energy costs, reducing the viability of anaerobic digestion for cost-effective smallholder digesters, which are generally operated at ambient temperatures (10 °C–25 °C) and influenced by seasonal variations [23–26]. Psychrophilic AD has the potential to replace mesophilic or thermophilic AD, providing a promising solution for year-round sustainable biogas production, applying not only to tropical and sub-tropical regions with temperatures up to 25 °C but also to temperate regions where temperatures can drop as low as 10 °C [23–26].

Research on psychrophilic AD is limited, and there is a noteworthy need for increased focus on strategies to accelerate the rate-limiting steps at this operational condition [23,24]. This could include the study of waste pretreatment, specifically the ones developed to enhance the digestion of lignocellulosic substrates. Thus, given the above and considering that coffee is more suitable for areas where the average temperature ranges from 18 °C to 26 °C, this research aims to compare the AD of coffee husk for CH₄ production at mesophilic (35 °C) and at psychrophilic (20 °C) operational conditions, as well as, at psychrophilic (20 °C) temperature but using biomass thermochemically pretreated as a biomimetic strategy for the fermentation of lignocellulosic biomass. The results might provide a solution to agricultural waste management at ambient temperature for farmers.

2. Materials and Methods

2.1. Coffee Husk and Inoculum

The coffee husk (CH) used in this study came from the 2022/2023 crop harvest of agricultural land in the municipality of São Sebastião do Paraíso, Minas Gerais, Brazil. Prior to anaerobic digestion, biomass was ground to obtain pieces of 10 cm. The anaerobic sludge (AS) used as inoculum came from a pilot-scale anaerobic reactor treating slaughterhouse wastewater in Pereiras, São Paulo, Brazil. Before undergoing the AD process, the main physicochemical parameters of both the CH and AS were assessed. The total and volatile solid (TS and VS) contents were measured according to the USEPA method 1684, while, the measurement of pH was analyzed by procedures described in the APHA method 4500B. The elemental composition (C, H, O, N, and S) analysis was performed with a CHNS elemental analyzer (LECO, CHNS-932). Table 1 summarizes the main characteristics of CH and AS.

Table 1. Characteristics of coffee husk and the inoculum.

Parameters	Coffee Husk	Anaerobic Sludge
Total solids (% TS)	87.36 ± 0.002	6.05 ± 0.003
Total volatile solids (% VS) *	92.32 ± 0.683	85.12 ± 0.149
pH	-	7.3 ± 0.058
C (%) **	44.99 ± 3.423	-
H (%) **	5.75 ± 0.738	-
O (%) **	47.31 ± 5.950	-
N (%) **	1.76 ± 0.971	-
S (%) **	0.16 ± 0.100	-
C/N	25.56	-

* Based on total solids. ** Based on volatile solids.

2.2. Experimental Setup

2.2.1. Adaptation and Degassing Stage

Biomethane potential (BMP) assays were carried out to determine the CH₄ production of CH residues at mesophilic (C1-35 °C) and psychrophilic (C2-20 °C) operational conditions, as well as at psychrophilic (20 °C) conditions but using biomass that was thermochemically pretreated (C3-20 °C-w/pretreatment). BMP tests were carried out according to the guidelines in the VDI 4630 norm [27] and the recommendations in Holliger et al. [28] and Hafner et al. [29] to increase the probability of obtaining validated and reproducible results. Prior to the BMP assays, an adaptation stage was established to develop and intensify the lignocellulose (cellulose and hemicellulose) degrading activity in the culture [30]. The adaptation stage shows the acclimation of the AS with CH, and it was performed in a glass bottle (2000 mL) with a working volume of 1200 mL. The operation solution was prepared by mixing CH with AS at a substrate/inoculum ratio of 0.1, as stated in the VDI 4630 standard [27]. Prior to the operation, the glass bottle was flushed with nitrogen gas (N₂), sealed, and incubated at 35 ± 1 °C. Feeding was carried out once, and the stage was stopped when daily methane production ceased to deplete the residual biodegradable organic material present in it (methane production per day became less than 0.5% of the cumulative methane) [27,31–34].

2.2.2. BMP Tests

After six weeks of acclimation, glass bottles (500 mL) were fixed with an inoculum-to-substrate ratio of 0.5 based on a volatile solid (%VS) [4]. Each test was performed using three biological replicates. Then, each glass bottle was connected to a glass graduated eudiometer and filled with a NaCl 6M phenolphthalein colored barrier solution. In the C1-35 °C test, the temperature was maintained at 35 °C, whereas in the C2-20 °C and C3-20 °C-w/pretreatment tests, the temperature was regulated at 20 °C. In the C3-20 °C-

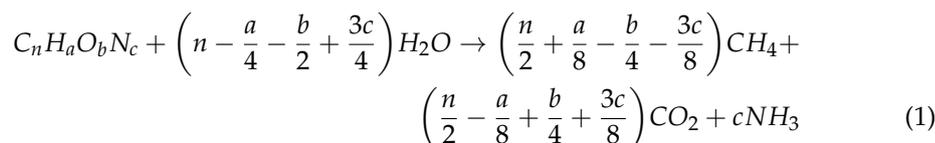
w/pretreatment test, coffee husk was exposed to a thermochemical pretreatment (120 °C, 0.5% HCl (v/v), 30 min of exposition time) prior to the BMP assay [35,36].

2.2.3. Monitoring Biogas Production

The BMP performance of each test was evaluated in terms of CH₄ production rate, cumulative CH₄ production (NmL), and CH₄ yield (NmL CH₄/g VS). CH₄ production was recorded twice a week. Samples from the eudiometer headspace were taken to determine the amount of CH₄ in biogas by gas chromatography (Shimadzu mark GC-2030 model) equipped with a thermal conductivity detector. For the gas volume normalization under standard temperature (T₀ = 273.15 K) and pressure (P₀ = 1 atmosphere) (STP), the actual room temperature (T_r) and atmospheric pressure (P_r) were recorded at the same time as when the gas volume (V) was measured [37]. All methane yields were expressed as NmL of CH₄ at STP conditions per gram of organic substrate added (g VS).

2.2.4. Theoretical Chemical Oxygen Demand, Theoretical Biomethane Potential, and Biodegradability

Theoretical methane potential is utilized to estimate the methane generation from a particular substrate characterized by its specific chemical composition. According to Cangussu et al. [38] coffee husk has a high content of crude protein (7–17%). For biomass that contains proteins, a modified Buswell's formula is generally used. The expression representing the stoichiometric formula and the methane yield is represented in Equations (1) and (2) [39–41].



$$BMP_{Th} (NmL CH_4/g VS) = \frac{22400 \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)}{12n + a + 16b + 14c} \quad (2)$$

where $n = \frac{\%C(\% \text{ by weight})}{12}$, $a = \frac{\%H(\% \text{ by weigh})}{1}$, $b = \frac{\%O(\% \text{ by weigh})}{16}$ and $c = \frac{\%N(\% \text{ by weigh})}{14}$; BMP_{Th} is the theoretical biomethane potential. The stoichiometrically calculated chemical oxygen demand (COD_{Th}) was determined using the theoretical Equation (3) [42].

$$COD_{Th} (gCOD_4/gVS) = \frac{(2n + 0.5a - 1.5c - b) \times 16}{12n + a + 16b + 14c} \quad (3)$$

The adjusted Dulong formula (Equations (4) and (5)) was utilized to predict the energy potential and the maximum (CH₄) yield [43]. This prediction relies on the energy value of the input material, which is also determined from its elemental composition [33,43]. The energy potential in kWh/Mt units was then determined by using the conversion factor of 3.6 MJ/kWh, and the conversion factor of the stoichiometrically calculated oxygen demand.

$$E^0 \left(\frac{MJ}{kgVS} \right) = 337C + 1419 \left(H - \frac{1}{8}O \right) + 93S + 23.26N \quad (4)$$

$$BMP_{E^0} \left(\frac{NmLCH_4}{gVS} \right) = \frac{E^0(\text{based on \%VS})}{37.78} \quad (5)$$

where E_0 is the energy value of the substrate (MJ/kg) and methane energy content = 37.78 MJ/m³ at STP.

Biodegradability was calculated as shown in Equation (6).

$$BD_{CH_4} = \frac{BMP_{Exp}}{BMP_{Th}} \times 100 \quad (6)$$

where BMP_{exp} (NmLCH₄/gVS) is the accumulated CH₄ yield; BMP_{Th} is the theoretical CH₄ yield at STP; and BD_{CH_4} is the anaerobic biodegradability (%).

The methane yield experimental data obtained in the BMP tests was used to determine the energy output using Equation (7):

$$E_{CH_4Exp} \left(\frac{KJ}{gVS} \right) = BMP_{Exp} \times \mathcal{E} \times \Lambda_m \quad (7)$$

where E_{CH_4Exp} is the energy output in (kJ/g VS removed), BMP_{Exp} is the cumulative CH₄ yield (NmL CH₄/g VS), \mathcal{E} is the lower heating value of CH₄ (35.800 kJ/m³ CH₄), and Λ_m is the energy conversion factor of methane (0.9).

2.2.5. First-Order Kinetic Model

A first-order kinetic model was employed to fit the cumulative methane production data. It assumes that the substrate quantity to be hydrolyzed strongly influences the overall hydrolysis rate and the bio-conversion efficiency, constituting a critical point where pretreatments of lignocellulosic biomass play a fundamental role. Therefore, a successful hydrolysis conversion of the biodegradable components within CH aligns with an effective biomethanation process [44]. In addition, this model can simulate the biomethane accumulation based on an exponential rise to the maximum [45–47]. The production of methane was assumed to follow Equation (8) and was simulated via a non-linear regression analysis using the ‘Solver’ function in Microsoft Excel Software, 2007. Then, the model predicted the CH₄ yields, which were plotted with their respective experimental CH₄ yields.

$$BMP_{Pred(t)} = BMP_{Exp} [1 - e^{-kt}] \quad (8)$$

where $BMP_{Pred(t)}$ is the cumulative predicted CH₄ production (NmL/g VS); BMP_{Exp} is the maximum CH₄ production (NmL/g VS); e is $Exp(1) = 2.718282$; k is the first-order kinetic constant (day⁻¹); and t is the digestion time (days). The kinetics of biogas production were evaluated using the following parameters: BMP_{Pred} , BMP_{Exp} , k , Adjusted R², and root mean square error (RMSE).

3. Results and Discussion

3.1. Changes in Biogas and Methane Productivity

The biogas production and CH₄ production were analyzed periodically to evaluate the effects of temperature and the effect of thermochemical pretreatment on the BMP performance. The results were recorded for 47 days and ended when the BMP tests produced less than 0.5% of daily production. As it may be observed in Figure 1a, the maximum gas production occurs between 4 and 12 days, after which the rate of gas production declines. Among all conditions, C2-20 °C produced the lowest biogas production, reaching a maximum value of 235.25 NmL on day 7, while C1-35 °C and C3-20 °C-w/pretreatment tests reached 439.29 NmL and 368.61 NmL on day 4 and day 7, respectively. In these days, a similar performance was observed with the CH₄ productivity, where the C3-20 °C-w/pretreatment test presented a maximum value with a 73% increase (139.15 NmL CH₄) when compared with C2-20 °C (101.69 NmL CH₄), while C1-35 °C just achieved a 54% increase (186.87 NmL CH₄). The cumulative biogas and cumulative CH₄ production are shown in Figure 1b. The results revealed that the use of thermochemically pretreated CH positively influenced the increase in biogas production (C3-20 °C-w/pretreatment). This reached 3539.90 NmL, approximately 20.64% higher than that produced by the untreated samples and operated at psychrophilic conditions (C2-20 °C), while the cumulative biogas production by the untreated samples and operated at mesophilic conditions (C1-35 °C) was approximately 11.20% higher (3163.38 NmL). Likewise, their respective cumulative methane productivity was higher by 12.8% (1376.36 NmL) and 15.3% (1417.38 NmL). It can be noted that the AD process was constrained by the lower temperature (C2-20 °C). This low performance could be attributed to the fact that

the anaerobic digestion of lignocellulosic biomass encounters limitations in psychrophilic (cold) conditions primarily because of the decreased activity and efficiency of enzymes and microorganisms, which are significantly enhanced in mesophilic and thermophilic anaerobic digestion processes [48]. However, mesophilic operation does not outperform that of psychrophilic operation with pretreated CH; this exceptional outcome can be ascribed to the availability of cellulose, hemicellulose, and fermentable substances that become readily accessible to microorganisms when a feedstock is pretreated [49–51]. According to [35], this breakdown includes the deacetylation of hemicelluloses, which could lead to an elevation in acetic acid concentration within the reactive mixture, promoting the hydrolysis and deriving in higher biogas production consequently [35,49–51].

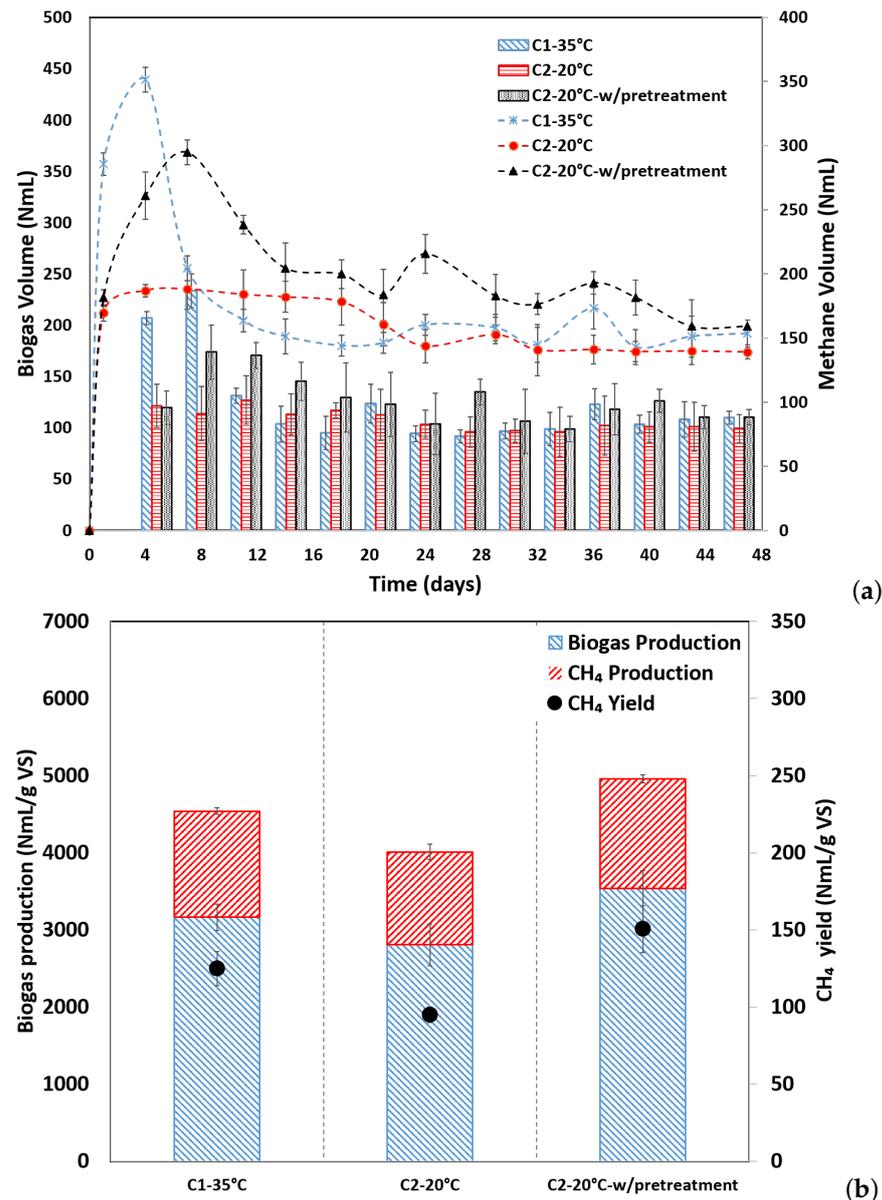


Figure 1. (a) Biogas volume rate (dashed line) and methane volume rate (vertical bars). (b) Cumulative biogas (blue bars), methane (red bars) productivity, and methane yield (black dots).

3.2. Stoichiometry, Theoretical COD, Theoretical Biomethane Potential, and Biodegradability

The chemical formula of the CH was found to be $C_{0.55}H_{0.85}O_{0.43}N_{0.02}$ regarding the elements C, H, O, and N from the stoichiometric equation (Equation (2)) (Table 2). H_2S was not considered since it was absent in the biogas mixture. As shown in Table 3, BMP_{Th} , as calculated from the elemental composition, exceeded the BMP_{Exp} . Buswell's equation predicted

a BMP_{TH} of 405.52 NmL CH₄/g VS (434 NmL CH₄/g COD), while the corresponding BMP_{E^0} with modified Dulong's equation was 402.26 NmL CH₄/g VS (430.50 NmL CH₄/g COD). However, experimental BMP_{EXP} among all conditions ranged from 94.96 to 150 NmL/g VS (Figure 1b). As discussed in [32], the BMP_{TH} approaches tend to overstate the CH₄ production in comparison to the experimental methods due to the Buswell formula's inability to distinguish between biodegradable and non-biodegradable matter, with a portion of biodegradable material being allocated for cell growth, metabolites, and the protoplasm synthesis of microbes [52]. According to previous authors, CH has large variability values for cellulose (14.7–46.1%), hemicellulose (10.2–29.7%), and lignin (10.1–34.2%) [38]. As lignin is a component of the cell wall and is known for its high resistance, it may have exerted a significant influence on both the yield and efficiency of the process [53,54].

Table 2. Coefficients of the elements.

Component	Weight Fraction (%)	Contribution Mass (g)	Molecular Weight (g/mol)	Coefficients (mol)
Carbon	44.99	6.59	12	0.55
Hydrogen	5.79	0.848	1	0.85
Oxygen	47.31	6.938	16	0.43
Nitrogen	1.76	0.258	14	0.02
Sulfur	0.16	0.023	32	0.001
	100%	14.667		

Table 3. Summary of key energy production parameters.

Parameter	Theoretical Energy Content	C1-35 °C	C2-20 °C	C3-20 °C-w/Pretreatment
Substrate formula		$C_{0.55}H_{0.85}O_{0.43}N_{0.02}$		
BMP_{EXP} (NmL CH ₄ /g VS)		124.99 ± 11	94.96 ± 5	150.47 ± 15
COD_{TH} (g COD/g VS)	0.93			
$BMP_{EXP-COD_{TH}}$ (NmL CH ₄ /g VS)		133.77	101.63	161.04
BMP_{TH} (NmL CH ₄ /g VS)	405.52			
BMP_{TH} (NmL CH ₄ /g COD)	434.00			
BMP_{E^0} (NmL CH ₄ /g VS)	402.26			
BMP_{E^0} (NmL CH ₄ /g COD)	430.50			
E^0 (MJ/kg VS) *	15.04			
E^0 (MJ/kg COD) *	16.09			
BD (%)		30.82	23.42	37.11

* Calculated using the conversion factor of 3.6 MJ/kWh and COD_{TH} .

The C3-20 °C-w/pretreatment test resulted in an increase of 36.89% (150.47 NmL CH₄/g VS; 161.04 NmL CH₄/g COD), whereas the C1-35 °C test showed a 24.03% increase (124.99 NmL CH₄/g VS; 133.77 NmL CH₄/g COD), both compared to the C2-20 °C test (94.96 NmL CH₄/g VS; 101.63 NmL CH₄/g COD). Notably, the C3-20 °C-w/pretreatment test yielded superior results. This could be ascribed to the high biodegradability (37.11%) of CH when it was thermochemically pretreated. The biodegradability decreased under untreated conditions at mesophilic AD (30.82%), followed by psychrophilic AD (23.42%) conditions. The order of biodegradation could be understood as being inversely related to the lignin content and directly related to the quantity of cellulose and hemicelluloses, which may contribute to an increase in the concentration of readily degradable organics [53,55]. Comparable findings were achieved in earlier studies concentrating on various pretreatment approaches to enhance the biodegradability and bioavailability of CH to microorganisms during mesophilic AD. For instance, as reported in [56], the CH₄ yield was significantly lower in the absence of any pretreatment (i.e., 100 NmL CH₄/g VS). However, when subjected to thermal hydrolysis pretreatment, there was an improvement in the ultimate CH₄ yield, with increases of 37% and 23% observed at 120 and 180 °C,

respectively. Furthermore, significantly improved outcomes were observed through the co-digestion and co-pretreatment of coffee husks and microalgal biomass, demonstrating enhancements ranging from 61% to 96%. In [55], all steam explosion pretreatment conditions applied were worthwhile when compared to non-pretreated CH. Here, the best condition was 120 °C for 60 min, in which a 2.37 severity showed the highest methane yield (144.96 NmL CH₄/g COD).

3.3. First-Order Kinetic Model

The model fitness statistics are detailed in Table 4. Plots of the experimental data and simulation of the first-order model are depicted in Figure 2. The methane yield and hydrolysis constant covered a range of values from 149.07 NmL to 221.90 NmL and from 0.019 days⁻¹ to 0.033 days⁻¹, respectively. All results fit very well with the measured data with Adj. R² > 0.97 for all BMPs. The coefficient of determination (R²) between the cumulative methane production curve and first-order kinetic curves was highest for the C2-20 °C test, i.e., 0.996. For the C3-20 °C-w/pretreatment test, the value obtained was similar (0.994), while for the C1-35 °C test, R₂ was comparatively low (0.970). The first-order kinetic constant *k* was highest when coffee husks were fermented at 35 °C (0.033 days⁻¹), showing rapid degradation of the substrate (in 30 days). The reason for the higher degradation rate is probably the influence of mesophilic conditions that provide a kinetic advantage for the degradation rate. The C3-20 °C-w/pretreatment test (0.023 days⁻¹) had a slightly lower *k* value than the C1-35 °C test. This could be because pretreatment could increase the generation of toxic and recalcitrant compounds that may have been inhibitory to the methanogenic population.

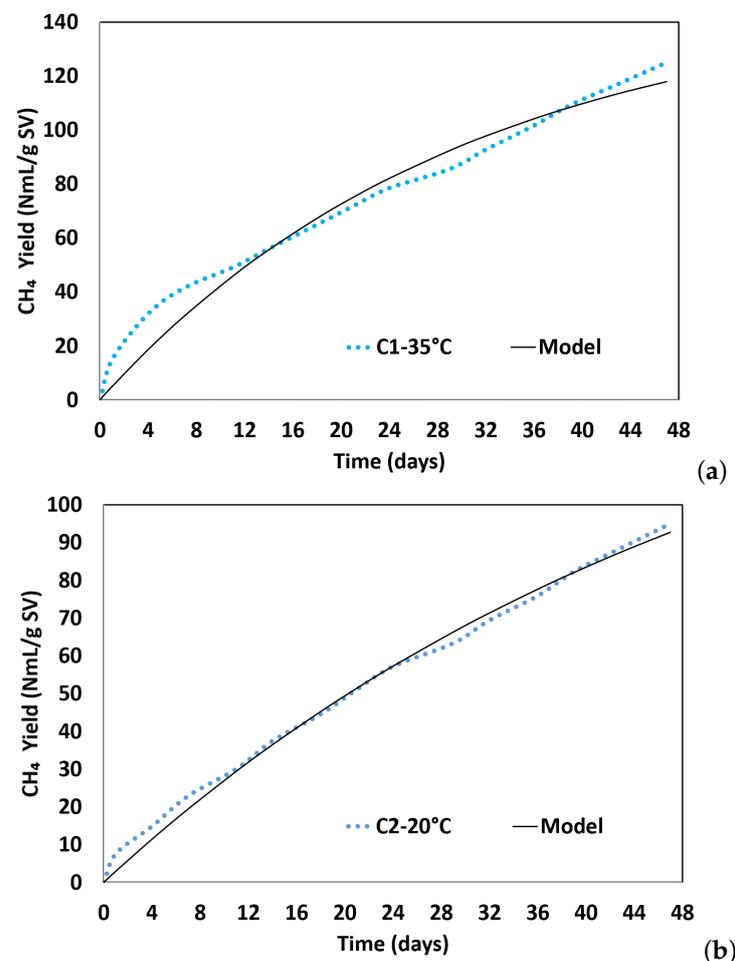


Figure 2. Cont.

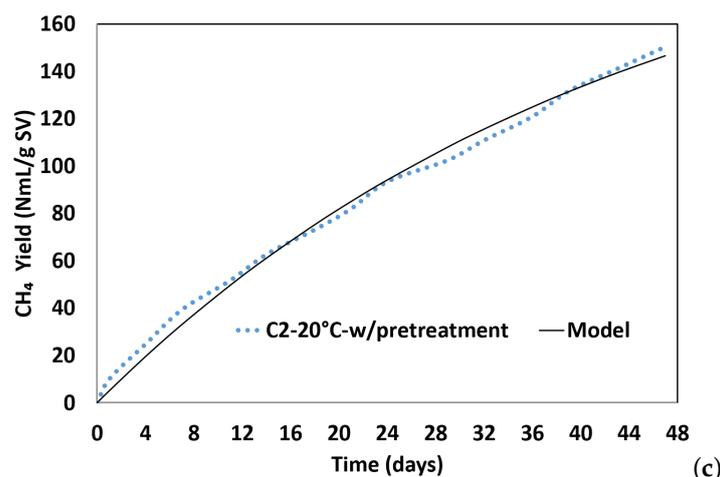


Figure 2. Experimental versus predicted values of ultimate CH_4 yield of the coffee husk (a) at mesophilic conditions, (b) at psychrophilic conditions, and (c) at psychrophilic conditions with thermochemical pretreatment. Black line corresponds to the predicted CH_4 yield, and the blue dots correspond to the experimental CH_4 yield.

Table 4. First-order kinetic parameters of average cumulative methane production curves.

BMP Tests	BMP_{Exp} (NmL gVS ⁻¹)	BMP_{Pred} (NmL gVS ⁻¹)	k (per Day)	Time (Days)	Adj. R ²	RMSE
C1-35 °C	124.99	149.07	0.033	30	0.970	6.19
C2-20 °C	94.96	159.42	0.019	54	0.996	2.17
C3-20 °C-w/pretreatment	150.47	221.90	0.023	43	0.994	3.68

3.4. Energy Content and Energy Output

The energy content or High Heating Value (HHV) of coffee husk on a dry basis (13.09 MJ/kg TS; 15.04 MJ/kg VS) was calculated based on the elemental composition (Tables 2 and 3). According to the literature, theoretical HHVs of coffee husk are usually around 13–21 MJ/kg [15–19]. If we consider that the predicted overall coffee husk harvest in 2023 amounted to 54.94 million 60 kg bags, equivalent to approximately 3.3 million tons of coffee waste annually, this would yield a potential electrical energy of 11.12 TWh each year [57]. Thus, it can be inferred that coffee husks show great potential as a green and sustainable energy source, simultaneously mitigating pollution and offering a practical approach to coffee waste management.

The energy output has been estimated from BMP_{Exp} data by using Equation (7). The energy output values were 3.2 KJ/g CH, 2.5 KJ/g CH and 3.9 KJ/g CH for C1-35 °C, C2-20 °C, and C3-20 °C-w/pretreatment, respectively. These values correspond to 902.2 KWh/T CH, 685.4 KWh/T CH, and 1086.1 KWh/T CH, respectively. Assuming that 3.3 million tons of coffee waste are generated annually, these values would yield 2977.3, 2261.9, and 3584.3 GWh of potential electrical energy per year, respectively. Considering that to hydrothermally pretreat 1 ton of raw coffee husk, an energy input of 420 MJ/T CH would be needed [35,58,59], the net energy using the C3-20 °C-w/pretreatment condition resulted in a surplus of 3199.25 GWh of energy per year that could be used in other stages of coffee processing or to supply electricity for 494 million residences per year in the southeast region of Brazil where the per capita consumption is 2.60 KWh/hab. per year.

According to the results, utilizing psychrophilic AD of thermochemically pretreated carbonaceous material presents a promising approach to enhancing AD at room temperature, providing environmental benefits. Nevertheless, the incorporation of a pretreatment process escalates the expenses of the AD plant, and this expenditure is exacerbated when a combined pretreatment is implemented. This involves the necessity for extra equipment, materials, technology, and skilled personnel. Therefore, a thorough techno-

economic analysis is essential for evaluating both individual pretreatment and combined pretreatment approaches.

4. Conclusions

The experimental findings suggest that biomethane production can occur at psychrophilic conditions, yet it demonstrates enhanced efficiency when coffee husk, a type of lignocellulosic biomass, undergoes a thermochemical pretreatment (i.e., 120 °C, 0.5% HCl (v/v), 30 min of exposition time). This superior performance is even observed when compared to AD processes carried out at mesophilic temperatures. Furthermore, it was estimated that it could yield a potential electrical energy of 3199.25 GWh/year that could meet the energy needs of 494 million residences annually. Therefore, the utilization of thermochemical pretreatment on lignocellulosic biomass emerges as a potential approach for implementing AD at ambient temperature. Moreover, coffee processing facilities could have the opportunity to utilize this energy potential for both electrical and thermal energy, contributing to the improvement in their own operational sustainability. In sum, this could eliminate the necessity for external energy input and offer compelling economic benefits, making it a crucial consideration.

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Abbreviations

The following abbreviations are used in this manuscript:

TS	Total Solids
VS	Volatile Solids
AD	Anaerobic Digestion
BD	Biodegradability
BMP	Biochemical Methane Potential
COD	Chemical Oxygen Demand
COD _{Th}	Theoretical Chemical Oxygen Demand
E ⁰	Energy Content

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