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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 mL CH<sub>4</sub>/g VS; 161.04 mL CH<sub>4</sub>/g COD), while the C1-35°C test exhibited a 24.03% increase (124.99 mL CH<sub>4</sub>/g VS; 133.77 mL CH<sub>4</sub>/g COD), both in comparison to the C2-20°C test (94.96 mL CH<sub>4</sub>/g VS; 101.63 mL CH<sub>4</sub>/g COD). Notably, the C3-20°C-w/pretreatment trial yielded superior outcomes, accompanied by an associated energy output of 4262.2 KWh/year, sufficient to meet the annual energy demands of 588 residences. This marks an increase of 100 and 217 residences compared to mesophilic and psychrophilic AD of CH without pretreatment, respectively.

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

#### 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, etc.) 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. However, they also offer versatile utility, including their potential as a feedstock for clean energy production [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]. Brazil is the world's largest coffee producer, followed by Vietnam, Colombia, and Indonesia. In 2020, Brazil produced more than 60 million bags of processed coffee, that is, it is responsible for 35% of world production [6].

The Brazilian coffee production cover an extensive area accommodating both Arabic and Conilon coffee species. In Brazil, Arabic coffee thrives in cooler regions, typically at altitudes above 500 meters, 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 [13]. 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 [7–10]. 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 [9,11,12]. 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 a great potential for applications in anaerobic digestion (AD) [7,9].

AD mineralizes organic compounds to methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), and stands as the most ancient technology for harnessing energy from the biological breakdown of organics [14]. At present, the primary role of AD biodigesters is to capture CH<sub>4</sub> emissions arising from the decomposition of organic matter, such as that from agricultural activities. In doing so, mitigating the release of greenhouse gases into the environment[15]. 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 [15]. Many studies on lignocellulosic biomass-fed AD operate at 35-55°C, where reactions generally proceed more efficiently [16]. 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 the seasonal variations [17,18,41,42] . Psychrophilic AD has the potential to replace mesophilic or thermophilic AD, providing a promising solution for year-round sustainable biogas production. Applying not just 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 [17,18,41,42].

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 [17,18]. 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  $18^{\circ}$ C to  $26^{\circ}$ C, this research aims to compare the AD of coffee husk for CH<sub>4</sub> production at mesophilic (35°C) and at psychrophilic (20°C) operational conditions, as well as, at psychrophilic (20°C) temperatura but using biomass thermochemically pretreated as biomimetic strategy for the fermentation lignocellulosic biomass. Results might provide a solution to agricultural waste management at ambient temperature for farmers.

# 2. Materials and Methods

# 2.1. Coffee husk and inoculum

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 grinded to get 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 solids (TS and VS) contents were measured according to the USEPA method 1684, while, the measurement of pH was analyzed by procedures described by APHA method 4500B. The elemental composition (C, H, O, N, S) analysis was performed by 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	6.05
Total volátil solids (%VS)*	92.32	85.12
рН	-	7.3
C(% VS)**	44.99	_
H(% VS)**	5.75	_
O(% VS)**	47.31	_
N(% VS)**	1.76	_
S(% VS)**	0.16	_
C/N	25.56	-

<sup>\*</sup> By total solids basis. \*\* By volatile solids basis.

#### 2.2. Experimental Setup

#### 2.2.1. Adaptation and degassing stage

Biomethane potential (BMP) assays were carry out to determine the  $CH_4$  production of CH residues at mesophilic (C1-35°C) and at psychrophilic (C2-20°C) operational conditions, as well as, at psychrophilic (20°C) but using biomass thermochemically pretreated (C3-20°C-w/pretreatment). Prior to the BMP assays, an adaptation stage was stablished to develop and intensify the lignocellulose (cellulose and hemicellulose) degrading activity in the culture [19]. The adaptation stage comprehend 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 states in the VDI 4630 norm [20]. Prior the operation, the glass bottle was flushed with nitrogen gas (N<sub>2</sub>), sealed, and incubated at  $35\pm1^{\circ}$ C. Feeding was carry out once and the stage was stopped till daily methane production ceased (data not shown) to deplete the residual biodegradable organic material present in it (methane production per day became less than 0.5% of the cumulative methane) [20–24,36]. The adjusted mass was calculated using the Equation (1) and (2).

$$\frac{M_{AS} \times VS_{AS}}{M_{CH} \times VS_{CH}} = 0.1 \tag{1}$$

$$V_{AS} + V_{CH} = 1200 (2)$$

Where  $M_{AS}$  and  $VS_{AS}$  is the mass and volatil solids content of the inoculum;  $M_{CH}$  and  $VS_{CH}$  is the mass and volatil solids content of the coffee husks;  $V_{AS} + V_{CH}$  is the total working volume.

# 2.2.2. BMP tests

After six weeks of acclimation, glass bottles (500 mL) were fixed with a inoculum to substrate ratio of 0.5 based on a volatile solid (%VS) [1]. For each test was performed using three biological replicates. Then, each glass bottle was connected to a glass graduated eudiometer, 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 C3-20°C-w/pretreatment test, coffee husk was exposed to a thermochemical pretreatment (120°C, 0.5% HCl (v/v), 30 minute of exposition time) prior to the BMP assay [25,26].

#### 2.2.3. Monitoring Biogas Production

The BMP performance of each test was evaluated in terms of  $CH_4$  production rate, cumulative  $CH_4$  production (mL) and  $CH_4$  yield (mL  $CH_4/g$  VS).  $CH_4$  production was recorded twice a week. Samples from the eudiometer headspace were taken to determine the amount of  $CH_4$  in biogas by gas chromatography (Shimadzu mark GC-2030 model) equipped with thermal conductivity detector.

For the gas volume normalization under standard temperature ( $T_0$  =273.15 K) and pressure ( $P_0$  = 1 atmosphere) (STP), the actual room temperature ( $T_r$ ) and atmospheric pressure ( $P_r$ ) were recorded at the same time as the gas volume (V) was measured according to Equation (3) [38]. All methane yields were expressed as mL of CH<sub>4</sub> at STP conditions per gram of organic substrate added (g VS).

$$V_{STP} = \frac{VT_0P_r}{T_rP_0} \tag{3}$$

# 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. Accordingly with Cangussu et al., [30] coffee husk has a high content of crude protein (7–17%). For biomass that contain proteins, the modified Buswell's formula is generally used. The expression representing the stoichiometric formula and the methane yield is represented in Equations (4) and (5) [31–33].

$$C_n H_a O_b N_c + \left(n - \frac{a}{4} - \frac{b}{2} + \frac{3c}{4}\right) H_2 O \rightarrow \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right) C H_4 + \left(\frac{n}{2} - \frac{a}{8} + \frac{b}{4} + \frac{3c}{8}\right) C O_2 + c N H_3$$
 (4)

$$BMP_{Th} (mL CH_4/g VS) = \frac{22400 \left(\frac{n}{2} + \frac{a}{8} - \frac{b}{4} - \frac{3c}{8}\right)}{12n + a + 16b + 14c}$$
 (5)

Where  $n = \frac{\%C(\% \ by \ weight)}{12}$ ,  $a = \frac{\%H(\% \ by \ weigh)}{1}$ ,  $b = \frac{\%O(\% \ by \ weigh)}{16}$  and  $c = \frac{\%N(\% \ by \ weigh)}{14}$ ; BMP<sub>Th</sub> is the theoretical biomethane potential.

The stoichiometrically calculated chemical oxygen demand ( $COD_{Th}$ ) was determined using the theoretical Equation (6) [34].

$$COD_{Th} \left( gCOD_4 / gVS \right) = \frac{(2n + 0.5a - 1.5c - b) \times 16}{12n + a + 16b + 14c} \tag{6}$$

The adjusted Dulong formula (Equation (7) and (8)) was utilized to predict the energy potential and the maximum (CH<sub>4</sub>) yield [35]. This prediction relies on the energy value of the input material, which is also determined from its elemental composition [35,36]. 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.

$$E^{0}\left(\frac{MJ}{kgVS}\right) = 337C + 1419\left(H - \frac{1}{8}O\right) + 93S + 23.26N\tag{7}$$

$$BMP_{E^0}\left(\frac{mLCH_4}{gVS}\right) = \frac{E^0 \text{ (based on }\%VS)}{37.78} \tag{8}$$

Where  $E^0$  is the energy value of the substrate (MJ/kg), methane energy content =  $37.78 \text{ MJ/m}^3$  at STP.

Biodegradability was calculated as shown in Equation (9).

$$BD_{CH_4} = \frac{BMP_{Exp}}{BMP_{Th}} \times 100 \tag{9}$$

Where  $BMP_{exp}$  (ml  $CH_4/g$  VS) is the accumulated  $CH_4$  yield;  $BMP_{Th}$  is the theoretical  $CH_4$  yield at STP; and  $BD_{CH_4}$  is the anaerobic biodegradability (%).

The methane yields experimental data obtained in the BMP tests was used to determine the energy output by using Equation (10):

$$E_{CH\_4\_Exp}\left(\frac{KJ}{gVS}\right) = BMP\_Exp \times \mathcal{E} \times \Lambda_m \tag{10}$$

Where  $E_{CH_{4Exp}}$  is the Energy output in (kJ/g VS removed), BMP<sub>Exp</sub> is the cumulative CH<sub>4</sub> yield (mL CH<sub>4</sub>/g VS),  $\mathcal{E}$  is the lower heating value of CH<sub>4</sub> (35.800 kJ / m<sup>3</sup> CH<sub>4</sub>),  $\Lambda_m$  is the energy conversion factor of methane (0.9).

# 2.2.5. First-order kinetic model

This model is commonly employed when hydrolysis represents the rate-limiting stage in AD, particularly in cases where lignocellulosic feedstock serves as the substrate. This assumes that the gas production follows first order kinetics in which biogas accumulation was simulated using exponential rise to a maximum [27–29]. Therefore, the production of methane was assumed to follow Equation (11) and was simulated via non-linear regression analysis by using the 'Solver' function in Microsoft Excel Software, 2007. Then, the model predicted CH<sub>4</sub> yields which were plotted with their respective experimental CH<sub>4</sub> yields.

$$BMP_{Pred} = BMP_{Exp}[1 - e^{-kt}] \tag{11}$$

Where BMP<sub>Pred</sub> is the cumulative predicted CH<sub>4</sub> production (mL/g VS); BMP<sub>Exp</sub> is the maximum CH<sub>4</sub> production (mL/g VS); e is Exp(1)=2.718282; k is the first order kinetic constant (day  $^{-1}$ ); t is the digestion time (days). The kinetics of biogas production were evaluated using the following parameters: BMP<sub>Pred</sub>, BMP<sub>Exp</sub>, k, Adjusted R  $^2$  and root mean square error (RMSE).

# 3. Results and discussion

### 3.1. Changes in biogas and methane productivity

The biogas production and CH<sub>4</sub> 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 4-12 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 mL on day 7, while C1-35°C and C3-20°C-w/pretreatment tests reach 439.29 mL and 368.61 mL on day 4 and day 7, respectively. In these days, similar performance was observed with the CH<sub>4</sub> productivity, where C3-20°C-w/pretreatment test presented a maximum value with 73% increase (139.15 mL CH<sub>4</sub>) when compared with C2-20°C (101.69 mL CH<sub>4</sub>), while C1-35°C just achieved 54% increase (186.87 mL CH<sub>4</sub>). The cumulative biogas and cumulative CH<sub>4</sub> production are shown in Figure 1b. Results revealed that the use of CH thermochemically pretreated influenced positively in the increase of biogas production (C3-20°C-w/pretreatment). This reach 3539.90 mL, 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 mL). Likewise, their respective cumulative methane productivity were higher by 12.8% (1376.36 mL) and 15,3% (1417.38 mL). 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 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 [43]. However, mesophilic operation does not outperform that of psychrophilic operation with pretreated CH, this exceptional outcome

0.85

0.43

0.02

0.001

can be ascribed to the availability of cellulose, hemicellulose, and fermentable substances that become readily accessible to microorganisms when a feedstock is pretreated [37,39,40]. According to [25], 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 [25,37,39,40].

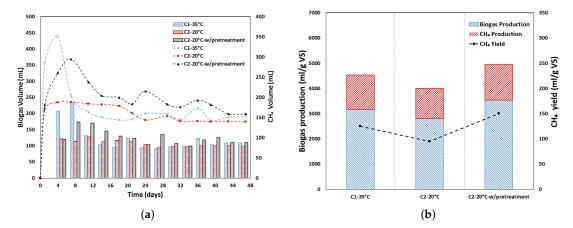


Figure 1. (a) Biogas volume rate (Dashed line) and methane volume rate (Vertical bars). (b) Cumulative biogas (dashed line) and methane v(vertical bars) productivity.

# 3.2. Stoichiometry, Theoretical COD, Theoretical biomethane potential and biodegradability

The chemical formula of the CH was found as  $C_{0.55}H_{0.85}O_{0.43}N_{0.02}$  regarding to the elements C, H, O and N from the stoichiometric equation (Equation 5) (Table 2). H<sub>2</sub>S was desconsidered since it was abscent in the biogas mixture (data not shown). As is shown in Table 3, BMP<sub>Th</sub>, as calculated from the elemental composition, exceeded the BMP<sub>Exp</sub>. Buswell's equation predicted a  $BMP_{Th}$  of 405.52 mL  $CH_4/g$  VS (434 mL  $CH_4/g$  COD), while the corresponding  $BMP_{p0}$  with modified Dulong's equation was 402.26 mL CH<sub>4</sub>/g VS (430.50 mL CH<sub>4</sub>/g COD). However, experimental  $BMP_{Exp}$  among all conditions ranged from 94.96 to 150 mL/g VS (Figure 1b). As discussed in [24], BMP<sub>Th</sub> approaches tend to overstate the CH<sub>4</sub> production in comparison to 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 protoplasm synthesis of microbes [55]. According to previous authors, CH has a large variability values for cellulose (14.7–46.1%), hemicellulose (10.2–29.7%) and lignin (10.1–34.2%) [30]. 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 [46,54].

Contribution mass(g) Weight Fraction (%) Molecular weight(g/mol) Coefficients (mol) 6.59 12 0.55

1

16

14

32

Table 2. Coefficients of the elements

0.848

6.938

0.258

0.023

14.667

Component

Carbon

Hydrogen

Oxygen Nitrogen

Sulfur

44.99

5.79

47.31

1.76

0.16

100%

Table 3. Summary of key energy production parameters

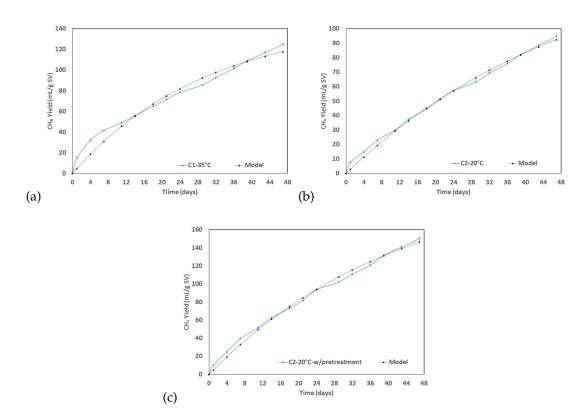
Parameter	Theoretical energy content	C1-35°C	C2-20°C	C3-20°C-w/pretreatment	
Substrate formula		$C_{0.55}H_{0.85}O_{0.43}N_{0.02}$			
BMP <sub>EXP</sub> (mL CH <sub>4</sub> / g VS)		124.99	94.96	150.47	
COD <sub>TH</sub> (g COD/ g VS)	0.93				
$BMP_{EXP-COD_{TH}}$ (mL CH <sub>4</sub> / g VS)		133.77	101.63	161.04	
$BMP_{TH}$ (mL $CH_4/g$ VS)	405.52				*
$BMP_{TH}$ (mL $CH_4/g$ COD)	434.00				
$BMP_{F^0}$ (mL $CH_4/g$ VS)	402.26				
$BMP_{F^0}$ (mL $CH_4/gCOD$ )	430.50				
$E^0$ (MJ/ kg VS)	15.04 (4.2E+09 KWh/Mt VS *)				
$E^0$ (MJ/ kg COD)	16.09 (4.5E+09 KWh/Mt *)				
BD (%)	,	30.82	23.42	37.11	_

Calculated by using the conversion factor of 3.6 MJ/kWh and COD<sub>TH</sub>.

The C3-20°C-w/pretreatment test resulted in an increase of 36.89% (150.47 mL CH<sub>4</sub>/g VS; 161.04 mL CH<sub>4</sub>/g COD), whereas the C1-35 $^{\circ}$ C test showed a 24.03 $^{\circ}$  increase (124.99 mL CH<sub>4</sub>/g VS; 133.77 mL CH<sub>4</sub>/g COD), both compared to the C2-20°C test (94.96 mL CH<sub>4</sub>/g VS; 101.63 mL CH<sub>4</sub>/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 decrease under untreated conditions at mesophilic AD (30.82%), followed by psychrophilic AD (23.42%) conditions. The order of biodegradation could be understood as inversely related to 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 [44,54]. 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 [45], CH<sub>4</sub> yield was significantly lower in the absence of any pretreatment (i.e., 100 mL CH<sub>4</sub>/g VS). However, when subjected to thermal hydrolysis pretreatment, there was an improvement in the ultimate CH<sub>4</sub> 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 [44], 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 mL  $CH_4/g$  COD).

#### 3.3. First-order kinetic model

The model fitness statistics are detailed in Table 4. By plotting experimental data and simulation of first-order model was depicted Figure 2. The methane yield and hydrolysis constant covered a ranges of values from 149.07 mL to 221.90 mL and from 0.019 d<sup>-1</sup> to 0.033 d<sup>-1</sup>, respectively. All results fit very well with the measured data with Adj.  $R^2 > 0.97$  for all BMPs. The coefficient of determination ( $R^2$ ) between the cumulative methane production curve and first-order kinetic curves was highest for C2-20°C test, i.e. 0.996. For C3-20°C-w/pretreatment test, the value obtained was similar (0.994) while for C1-35°C test,  $R_2$  was comparatively low (0.970). The first-order kinetic constant k was highest when coffee husks were fermented at 35°C (0.033 d<sup>-1</sup>), showing rapid degradation of 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 d<sup>-1</sup>) 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.** Experimental versus predicted values of ultimate CH<sub>4</sub> yield of coffee husk (a) at mesophilic conditions (b) at psychrophilic conditions (c) at psychrophilic conditions with thermochemical pretreatment. Black dots correspond to the predicted CH<sub>4</sub> yield and the blue line correspond to the experimental CH<sub>4</sub> yield

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

BMP tests	BMP <sub>Exp</sub> (mL . gVS <sup>-1</sup>	BMP <sub>Pred</sub> (mL . gVS <sup>-1</sup> )	k (per day)	Time (days)	Adj. R <sup>2</sup>	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/pretreatn	nent 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 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 [47–51]. 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 tons of coffee waste annually, this would yield a potential electrical energy of 12.04 MWh each year [52]. Thus, it can be inferred that coffee husk 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 (10). The energy output values were 2.9 KJ/g CH, 3.9 KJ/g CH and 4.6 KJ/g CH for C1-35°C, C2-20°C and C3-20°C-w/pretreatment, respectively. These values correspond to 1072.8 KWh/T CH, 815.1 KWh/T CH and 1291.6 KWh/T CH, respectively. Assuming that 3.3 tons of coffee waste are generated annually, these values would yield a potential electrical energy of 3540.4 KWh/year, 2689.8 KWh/year and 4262.2 KWh/year, respectively. These electrical outputs could supply electricity for 488.371

and 588 residences per year in the southest region of Brazil where the per-capita comsumption is 2.60 KWh/hab. per year, respectively. Another best practice application could involve meeting additional energy requirements in agriculture. This might include delivering thermal energy for grain dryers, supplying electrical energy for coffee processing machines, and utilizing  $CH_4$  as a fuel source for various agricultural machinery, among other applications. Based on the findings, employing psychrophilic AD of thermochemically pretreated CH could serve as a viable alternative for conducting anaerobic digestion at ambient temperature, offering advantages in terms of both cost-effectiveness and environmental considerations.

#### 4. Conclusions

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.,  $120^{\circ}$ C, 0.5% HCl (v/v), 30 minute 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 4262.2 KWh/year that could meet the energy needs of 588 residences annually. This represents an increase of 100 and 217 residences compared to mesophilic and psychrophilic AD of CH without pretreatment, respectively. 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 of 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 Volatil Solids
AD Anaerobic Digestion
BD Biodegradability

BMP Biochemical methane potential COD Chemical Oxygen Demand

 $COD_{Th}$  Theoretical Chemical Oxygen Demand

Energy Content

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