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Hydrothermal pretreatment of poultry litter for biogas production[1]

Pré-tratamento hidrotérmico da cama de aviário para produção de biogás

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HIGHLIGHTS:

The pretreated conditions at temperatures below 100 °C showed better energy balances.
The highest single-stage yield was 255.65 NmL CH_4·gVS^{-1}, obtained by pretreatment at 120 °C for 24 min.
The highest two-stage yield was 277.57 NmL CH_4·gVS^{-1} when pretreated at 160 °C for 48 min.

ABSTRACT: Hydrothermal pretreatment (HPT) allows the solubilization of the hemicellulose, leading to increased biodegradability for microorganisms. This paper presents a study based on the evaluation of the variables time (12 to 60 min), temperature (80 to 200°C), and solid/liquid ratio (4 to 8 g mL^{-1}) for the HPT (autohydrolysis) of synthetic poultry litter (rice straw: poultry manure 1:5) using the Doehlert matrix. Twelve HPT conditions followed by anaerobic digestion were evaluated with a focus on methane production. Firstly, tests were conducted to evaluate biogas production in a single stage in a single reactor, where both the acidogenic and methanogenic phases occur. Subsequently, tests were conducted to evaluate biogas production in a two-stage, consisting of separating hydrogen and methane production phases. The best performance of the biochemical potential of methane was the conditions 6 (24 min, 120 °C, and solid-liquid ratio = 4) in a single stage and 3 (48 min, 160 °C, and SLR = 8) in a two-stage, producing 255.6 and 277.6 NmL CH_4gVS^{-1}, respectively. Using the desirability criteria, two hydrothermal pretreatment (HPT) conditions were evidenced/ condition 1 in two stages (12 min, 80 °C, and SLR = 4)- (D1-2S) and condition two in two stages (12 min, 98 °C, and SLR = 4) - (D2-2S) showed high methane production, 248.9 and 249.3NmL CH_4·gVS^{-1}, respectively.

Key words: chicken manure, autohydrolysis, anaerobic digestion

RESUMO: O pré-tratamento hidrotérmico permite a solubilização da hemicelulose, o que leva a um aumento da biodegradabilidade para microrganismos. Este trabalho apresenta um estudo baseado na avaliação das variáveis tempo (12 a 60 min), temperatura (80 a 200 °C) e relação sólido/líquido (4 a 8 g mL^{-1}) para o pré-tratamento hidrotérmico (auto-hidrólise) de cama de frango sintética (palha de arroz: esterco de frango 1:5) utilizando a matriz Doehlert. Doze condições de pré-tratamento seguidas de digestão anaeróbica foram avaliadas com foco na produção de metano. Primeiramente, foram realizados testes para avaliar a produção de biogás em uma única etapa, realizada em um único reator, no qual ocorrem tanto a fase acidogênica quanto a metanogênica. Posteriormente, foram realizados testes para avaliar a produção de biogás em estágio duplo, consistindo na separação das fases de produção de hidrogênio e metano. O objetivo deste trabalho foi definir as melhores condições para a auto-hidrólise do resíduo, visando aproveitá-lo para a produção de metano. As condições experimentais com melhor desempenho do potencial bioquímico do metano foram as condições 6 (24 min, 120 °C e SLR = 4) em único estágio e 3 (48 min, 160 °C e SLR = 8) em duplo estágio que produziram 255,6 e 277,6 NmL CH_4·gVS^{-1}, respectivamente. Usando o critério de desejabilidade, duas condições de pré-tratamento hidrotérmico (HPT), a condição 1 de desejabilidade em dois estágios (12 min, 80 °C e SLR = 4)- (D1-2S) e a condição dois de desejabilidade em dois estágios (12 min, 98 °C e SLR = 4) - (D2-2S) apresentaram alta produção de metano em dois estágios, 248,9 e 249,3 NmL CH_4·gVS^{-1}, respectivamente.

Palavras-chave: esterco de galinha, auto-hidrólise, digestão anaeróbia

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Introduction

The possible depletion of fossil fuels combined with unstable policies, the need for energy security, and the main compromise assumed with the environment, especially about the reduction of greenhouse gas emissions, are responsible for strengthening the interest in developing energy sources based on the principles of sustainability (ÓhAiseadha et al., 2020; Soeder, 2021). Because of this, lignocellulosic biomasses were promoted to the category of raw material for low-carbon energy generation and with the potential to reduce dependence on fossil fuels (AliAkbari et al., 2021).

Rice production occupies the third position as the main agricultural crop in the world, and as a residue of this crop, there is rice straw. Despite the recalcitrant nature of lignin, rice straw is rich in cellulose and hemicellulose and is considered a promising source of bioenergy (Kavitha et al., 2020). One of the applications attributed to rice straw is its use as poultry litter. One way to mitigate the environmental impact caused by poultry litter is to use this residue in anaerobic reactors for biogas production. The use of the anaerobic digestion process for the production of renewable energy from lignocellulosic biomass is a promising technology that has been consolidated and aroused increased interest. However, the application of biomass as an energy source often requires pretreatment (Kumar et al., 2022)

In this context, this study analyzes a set of energy, economic and environmental indicators associated with the production of biogas from the anaerobic co-digestion of a substrate containing rice straw and hydrothermally pretreated poultry litter in different conditions of time, temperature, and solid-liquid ratio (SLR), aiming to find the best conditions for greater biogas production.

Material and Methods

The rice straw used in this study was provided by a chicken production company located in São Sebastião do Oeste (latitude: 20º12'16" S, longitude: 45º1'8" W, altitude: 780 m), state of Minas Gerais, Brazil. All rice straw was stored in a dry environment, using closed plastic bags without light incidence. The preparation and characterization of the materials for the experiments were all conducted in a controlled environment in a research laboratory specialized in topics in environmental and industrial technology.

The synthetic poultry litter was obtained by the heterogeneous mixture of rice straw and chicken manure in the mass ratio 1:5, both provided by Avivar Alimentos, located in São Sebastião do Oeste. Synthetic poultry litter was a strategy used to replace the company's poultry litter because the naturally produced litter contains antibiotic residues that have not been metabolized in the chicken's body, which could affect the microbial population of the inoculum used in the methane production tests, which would somewhat mask the result found (Paranhos et al., 2020). The proportion was adopted because it is the same used in the composition of the poultry litter of the farm that yielded the rice straw.

The inoculum used in the tests is a mixture of anaerobic sludge and manure from domestic chicken, fed only with feed and crushed corn, with a proportion of volatile solids of 1:1. Anaerobic digestion requires the presence of different types of microorganisms for the degradation of substrate, therefore, the mixture of poultry manure with the Upflow Anaerobic Sludge Blanket (UASB), sludge sought to enhance methane production from the different microbial populations contained both in the UASB sludge and poultry manure. Furthermore, preliminary tests showed that this mixture led to higher methane production when compared to other inoculums (100% chicken manure or 100% UASB sludge) (Paranhos et al., 2020).

Anaerobic sludge used in the research was obtained at the Center for Research and Training in Sanitation at UFMG/Copasa (CePTS), Wastewater Treatment Station in Arrudas, Belo Horizonte, MG, Brazil, and the chicken manure was collected in a domestic cage. The pH of the inoculum was empirically set at 9 (±0.15), according to the potential for methane production. Preliminary tests were conducted in the laboratory (Paranhos et al., 2020), and the best pH found was approximately 9.0. The solution used was sodium hydroxide NaOH (1.0 M). For the two-stage methane production tests, the inoculum was thermally pretreated at 100° C for 120 minutes to eliminate methanogenic bacteria and favor the environment for acidogenic bacteria (Baêta et al., 2016).

The moisture of the materials was measured using a thermogravimetric balance (OHAUS MB25). The extractive content of raw rice straw was determined according to the modified TAPPI T204 om-97 standard, in which cyclohexane replaced benzene. The TAPPI T211 om-02 standard was used to determine the sample's inorganic fraction. The lignin content was determined according to the TAPPI T222 om-98 standard. Acid-soluble lignin was quantified using a UV-Vis spectrometer (Hewlett-Packard®, model 8453).

Cellulose and hemicellulose concentrations were determined from the analysis of the products obtained by the Klason method by chromatographic analysis (HPLC). The refractive index detector identified and quantified the sugars, while the UV-Vis detector was operated in a dual channel, with wavelengths of 210 nm for the determination of organic acids and 274 nm for the determination of Furfuraldehyde (FF) and Hydroxymethylfurfural (HMF). For the mass balance of the rice straw components, Eq. 1 was used, which corresponds to the sum of the concentrations of cellulose (Cel), hemicellulose (Hem), total lignin (Lig), ash, and extractives (Ext).

$$\text{Mass balance}(\%) = \text{Cel} + \text{Hem} + \text{Lig} + \text{Ash} + \text{Ext} \quad (1)$$

The experimental design applied to the pretreatment (autohydrolysis) of poultry litter sought to evaluate the influence of time, temperature, and SLR variables on methane production. The amount of water and substrate, temperature, and pretreatment time used in each reactor were defined respecting the variables previously defined for a Dohelert matrix. Twelve conditions were generated for the HPT assays, plus another three replicates of the center point. The planning matrix resulted in 12 treatments in addition to the central point

(CP) test condition. In addition to the conditions found in the initial planning, further desirability tests were performed, which defined two more conditions as optimal.

The total number of treatments (N in the first test stage can be obtained through Eq. 2, whose k and CP values represent the number of factors and the number of treatments at the central point, respectively. The severity (S_0) of the HPT conditions can be calculated through Eq. 3, where t is the time (min), T is the temperature (°C), T_{ref} is the reference temperature (100 °C), and 14.75 is a fixed, empirically defined parameter related to the activation energy, assuming pseudo-first-order kinetics. Table 1 summarizes the experiment matrix that was used for HPT optimization.

$$N = k^2 + k + CP \quad (2)$$

$$\log(S_0) = \log\left[t \exp\left(\frac{T - T_{ref}}{14.75}\right)\right] \quad (3)$$

In a later stage of the experiments, desirability values were estimated using the Statistica® software to select the experimental condition (S) with the best average performance for methane production.

It should be noted that the rice straw HPT was performed in 316 L steel tubular reactors of the autoclave type with a polytetrafluoroethylene (PTFE) sealing ring and a useful volume of 180 mL. The reactor was immersed in a thermostatic glycerol bath to be heated to the desired temperatures. The rice straw mass used during the tests varied according to the experimental design according to the established solid-liquid ratio values (4, 6, or 8).

Biochemical methane potential tests (BMP) quantify the anaerobic biodegradability of substrates through biogas production. Through the results of these tests, it is possible to optimize the variables of the anaerobic digestion process to achieve better results in methane production (Jimenez et al., 2015). The base protocol for the BMP tests performed is based on the methodology described by Angelidaki et al. (2009) and has since been used in several works already published in the literature (Souto et al., 2010; Paranhos et al., 2023). Tests were set to evaluate batch biogas production using single-stage and dual-stage. Glass flasks with a total capacity of 120 mL were used, with 60 mL for liquid volume and the remaining 60 mL for gas volume (headspace). The solid and liquid fractions generated from the pretreatment were used in the anaerobic digestion tests, characterized as semi-solid due to the percentage of total solids (15%) used in the tests.

In the process of elaborating the BMP, specific amounts of inoculum and substrate (liquid fraction and solid fraction) were added in bottles, according to pre-defined values, respecting the ratio of food per microorganism (0.5 $VS_{substrate}$ $gVS_{inoculum}^{-1}$) and total solids.

Tests for biogas production were performed under mesophilic conditions (34 to 37 °C), and the bottles were purged with nitrogen gas (N_2) to remove oxygen gas (O_2), ensuring the anaerobic environment. The bottles were placed in a shaker incubator under controlled temperature and agitation conditions.

The biogas production was monitored daily, and the pressure accumulated in the bottles was measured with a differential manometer (CCE brand). For the composition of methane in the biogas, a 1.0 mL sample of the gas produced was collected after the pressure measurement and injected with a gastight syringe into a Shimadzu gas chromatograph equipped with a thermal conductivity detector. All methane production values were expressed in NL of CH_4 kg SV^{-1}, presented under normal temperature and pressure conditions (NTP: 273 K; 101.315 Pa).

The energy balances were conducted using the best conditions for methane production, according to the procedures detailed in Paranhos et al. (2022). The total energy produced in the BMP tests, the energy spent to pretreat the synthetic poultry litter, and the energy for biogas purification were considered for calculations. The energy production per kg of chicken (Ep) was estimated using Eq. 4, considering the methane yield obtained in the BMP tests (Nm^3 of CH_4 kg SV^{-1}), the accumulated methane production, and the number of volatile solids (SV) per tonne of poultry litter on a dry basis (PL).

$$Ep = BMP\left(\frac{VS}{1\ \text{ton PL}}\right)\left(\frac{54\ \text{ton PL}}{1\ \text{cycle}}\right)\left(\frac{1\ \text{cycle}}{30000\ \text{chic.}}\right)\left(\frac{1\ \text{chic}}{2.5\ \text{kg}}\right)34.5 \quad (4)$$

where:

Ep - Energy production ($MJNm^3CH_4^{-1}$);

BMP - Biochemical methane production (Nm^3 CH_4 kg SV^{-1});

VS - Volatile solids (kg);

Ton - Tonne;

PL - poultry litter;

Cycle - Cycle in 45 days; and,

Chic - Chicken.

For the calculation of the energy used in the purification of biogas, 10% of the total energy produced by the experimental condition was estimated, and for the production of total energy (Ep_{CHP}) an efficiency of 85% of the CHP system (heat and power combined), represented by Eq. 5. The calculation of the energy spent for the purification of biogas and E_{pCHP}, presented in Eq. 6,

Table 1. Treatments for executing the Doehlert matrix for single-stage and two-stage experiments

Condition	T (min)	T (°C)	SLR (g mL⁻¹)	log (S_0)
C1-αS	60	140	6	2.95
C2-αS	48	200	6	4.62
C3-αS	48	160	8	3.44
C4-αS	12	140	6	2.25
C5-αS	24	80	6	0.79
C6-αS	24	120	4	1.96
C7-αS	48	80	6	1.09
C8-αS	48	120	4	2.26
C9-αS	24	200	6	4.32
C10-αS	36	180	4	3.91
C11-αS	24	160	8	3.14
C12-αS	36	100	8	1.55
CP13-αS	36	140	6	2.73
CP14-αS	36	140	6	2.73
CP15-αS	36	140	6	2.73

α - Parameter that indicates can be replaced by 1 (single) or 2 (two) to indicate the type of stage; C - Experimental condition; CP - Condition at the center point; t - Time; T - Temperature; SLR - Solid-liquid ratio; S_0 - Severity is based on the 85% efficiency of the CHP system, similar to the efficiency of a combustion engine. The thermal and electrical energies were obtained from Eq. 7 and 8; 0.65 and 0.35 are the energy conversion factors produced by the CHP system to electrical and thermal energy, respectively (Laser et al., 2002). Furthermore, the calculation of HPT energy was performed according to Eq. 9, where Cp_{PL}, Cp_{water}, T_{PL}, and T_{water} are the specific heats and temperature of the poultry litter and water, respectively, as well as T_{HPT} and SLR are the temperature and solid-liquid ratio of the HPT condition analyzed.

$$Ep_{CHP} = 0.85Ep \quad (5)$$

$$E_{purification} = 1.0Ep_{CHP} \quad (6)$$

$$E_{thermal} = 0.65Ep_{CHP} \quad (7)$$

$$E_{electric} = 0.35Ep_{CHP} \quad (8)$$

$$E_{HPT} = Cp_{PL}\left(T_{HPT} - T_{PL}\right) + \left(Cp_{water}SLR\right)\left(T_{HPT} - T_{water}\right)1000 \quad (9)$$

where:

$Ep_{(CHP)}$ - Production of the total energy of the CHP system ($MJNm^3\ CH_4^{-1}$)

Ep - Energy production ($MJNm^3\ CH_4^{-1}$);

$E_{purification}$ - Energy spent for the purification of biogas (MJ/TonnePL);

$E_{thermal}$ - Thermal energy (MJ kg per chicken);

$E_{electric}$ - Electrical energy (kWh kg per chicken);

$E_{(HPT)}$ - Energy spent for the pretreatment ((MJ/TonnePL);

Cp_{PL} - specific heats of the poultry litter (1.76×10^{-3} MJ $(kg°C°)^{-1}$);

Cp_{water} - specific heats of the water ($4,19 \times 10^{-3}$ MJ $(kg°C)^{-1}$;

T_{HPT} - Temperature of the pretreatment(°C);

T_{water} - Temperature of the pretreatment(°C); and,

PL - poultry litter.

The calculations of the energy required in the HPT consider the energy required to heat the water and the substrate to the temperature of the condition found in the experimental design, considering that the heat capacity of the poultry litter is 0.001672 MJ $(kg\ °C)^{-1}$ and the water is 0.00419 MJ $(kg\ °C)^{-1.}$

The economic balances were conducted according to Adarme et al. (2019). The net energy productions were performed after disregarding the biogas purification energy and the HPT energy of the synthetic poultry litter from the conditions that produced the most methane in the BMP tests. Eq. 10 was used to calculate the net energy recovery (E_{net}) of the poultry litter, considering that the estimated cost (R\$ kWh^{-1}) of industrial energy is 0.47916 (Adarme et al., 2019).

$$Cost = 0.47916E_{net} \quad (10)$$

where:

Cost - (R\$ kWh^{-1}); and,

E_{net} - Net energy recovery.

The economic evaluation considers the operating costs of the biomass HPT and the savings generated by replacing the energy purchased from a concessionaire with the energy produced, which in this case, is used to maintain the production of chickens. In addition, the sale of a possible surplus of this energy is evaluated.

The costs considered in this work were obtained and adjusted in the national context, for example, considering the value of electrical energy in Brazil. The costs of pretreatment and methane purification were considered, as these processes were included in the study boundary. However, this study did not consider the cost of investing in equipment. In addition, transport values were not considered since the waste produced by the company is located on the same property where its reuse was suggested.

The volume of waste calculated/used is the same volume produced by the company in the production of chickens today. Meanwhile, electricity and heat generated were considered revenue, in addition to the carbon credit, representing an economic profit, possibly tradable, obtained from reductions in greenhouse gas emissions.

Finally, the environmental assessment is based on replacing energy from fossil fuel sources with renewable energy from biogas to reduce greenhouse gas emissions. Estimated CO_2 emission reduction using a greenhouse gas equivalence calculator (EPA, 2022) was considered. The idea is to convert emissions or energy data to the equivalent amount of carbon dioxide CO_2. Thus, it is considered the replacement of the use of electrical energy with the energy produced by anaerobic digestion.

The data it were evaluated by Pareto chart of standarized effects, using the software Statistica.

Results and Discussion

The rice straw analyzed had a hemicellulose concentration of 27.6% on a dry basis, in agreement with the values presented by Chen et al. (2011) and Castro et al. (2017), who found average values of 22.3 and 23.8%, respectively. Paranhos et al. (2020) showed the correlation between higher methane production and a higher amount of hemicellulose in the substrate. It can be said that a high hemicellulose concentration improves the biomethanisation of waste, as hemicellulose is the main source of C5 sugars. The value found for lignin on a dry basis was 29.29%, which is in agreement with Paranhos et al. (2020). In contrast to hemicellulose, there is a negative linear correlation between methane production and lignin content. This is because lignin is the main contributor to biomass recalcitrance and is one of the main components affecting the enzymatic conversion of lignocellulosic biomass (Paranhos et al., 2020). The value found for cellulose was 39.9%, which is consistent with the values between 29.7 and 41.1% presented by Arai-Sanoh et al. (2011), as well as the volatile and total solids contents (Paranhos et al., 2020). The percentage of ash in rice straw was 12.24%, which was also compatible with the values reported in the literature by Paranhos et al. (2020) and Castro et al. (2017). Ash represents the inorganic part after complete combustion and may indicate the presence of silicon species. In biomass residues, the ash content is expected to be 5 to 20% of the total mass (Fernandes et al., 2013). The

Table 2. Composition of rice straw on a dry basis

Variables	Percentage (%)
Hemicellulose	27.60 ± 1.6
Lignin	29.29 ± 2.1
Cellulose	39.90 ± 1.8
Ashes	12.24 ± 0.4
Extractives	3.310 ± 0.1
Volatile solids	77.78 ± 2.1
Total solids	87.37 ± 0.2
Mass balance	112.90

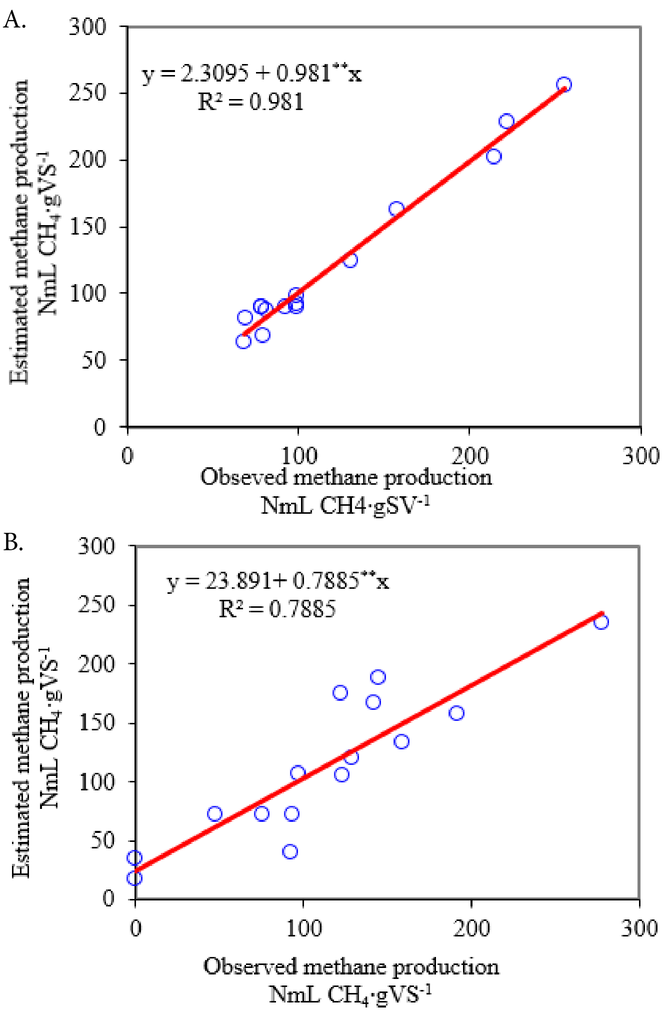
variations found in the concentrations compared to other works can be attributed to the different characteristics of soil and climate of the region, cultivation type, processing type, and characterization methods. For the raw rice straw analyzed in this study, the values presented in Table 2 were found.

The raw rice straw before hydrothermal pretreatment had total and volatile solids concentrations of 87.37 and 77.78%, respectively. The lack of fit in the analysis of the single-stage test results was insignificant since the adjusted R^2 was 94.68%, and the R^2 was 98.1%. For the two-stage tests, the adjusted R^2 was 40.78%, and the R^2 was 78.85%. Figures 1A and B show the linear regression between estimated and observed methane production.

The Pareto chart data show the variables' effect in single- and two-stage tests. For the single-stage results, the SLR and the temperature were significant and negative; that is, the higher the SLR and pretreatment temperature, the lower the methane production. On the other hand, time was not significant for methane production in single-stage tests. None of the three variables were significant for the two-stage tests, as seen in Figures 2A and B.

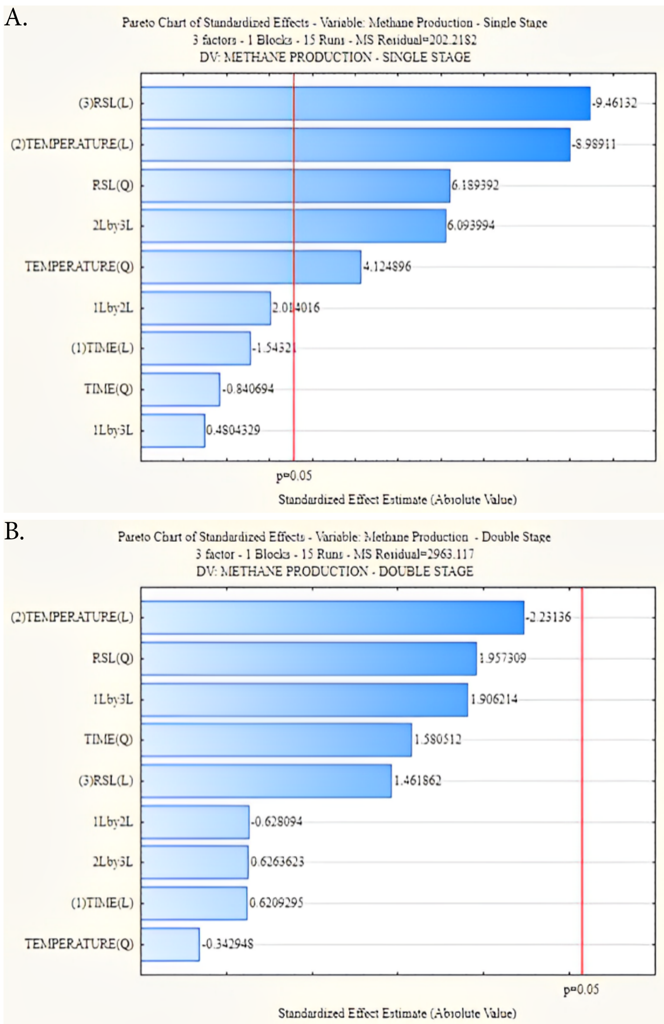
The methane production under HPT conditions ranged from 68.37 to 255.65 NmL $CH_4 \cdot gVS^{-1}$ in the single-stage tests, and in the two-stage tests, the methane production ranged from 0 to 277.57 NmL $CH_4 \cdot gVS^{-1}$. The pretreatment severity was the same for the single and two-stage tests, ranging from 0.4903 in the mildest temperature conditions to 4.6256 in the most severe pretreatment conditions.

Most of the pretreatment conditions applied were not able to cause an increase in methane production when compared to methane production tests using the unpretreated substrate, which produced 270 NmL $CH_4 \cdot gVS^{-1}$. On the contrary, it was possible to notice a reduction in biogas production in most pretreatment conditions. The data presented in Table 3 show the average performance of the methane production of each experimental condition, in single- and two-stage, the variation of the methane produced in the different stages, in addition to the two conditions obtained by the desirability test.



* Significant at p ≤ 0.01 by the F-test

Figure 1. Linear regression of estimated methane production according to observed methane production



SLR- Solid-liquid ratio; p* - Significant by the F-test at p ≤ 0.05

Figure 2. Standardized effects estimates of the factors in chart single- and two-stage methane production

Table 3. Performance of methane production by experimental condition

Condition	T (min)	T (°C)	SLR (g mL^{-1})	log (S_0)	Methane production (NmL CH_4 gVS^{-1}) S1	S. D-1S (%)	S2	S. D-2S (%)	Variation
C1	60	140	6	2.95	79.62	0.44	141.85	1.93	+78.16
C2	48	200	6	4.62	68.78	1.4	-1.30	1.48	-101.89
C3	48	160	8	3.44	98.91	0.75	277.57	1.07	+180.63
C4	12	140	6	2.25	78.44	0.22	159.14	4.34	+102.88
C5	24	80	6	0.79	214.61	1.35	123.43	0.00	-42.49
C6	24	120	4	1.96	255.65	1.37	144.53	4.09	-43.47
C7	48	80	6	1.09	157.74	1.33	191.81	3.12	+21.50
C8	48	120	4	2.26	222.05	5.09	97.25	0.02	-56.20
C9	24	200	6	4.32	68.37	0.00	-116.85	0.08	-270.91
C10	36	180	4	3.91	130.83	0.06	91.92	2.68	-29.74
C11	24	160	8	3.14	98.99	0.65	128.89	1.03	+30.21
C12	36	100	8	1.55	80.94	0.59	122.16	0.05	+50.93
CP13	36	140	6	2.73	92.09	0.16	47.26	4.27	-48.68
CP14	36	140	6	2.73	78.52	0.15	93.21	1.51	+18.71
CP15	36	140	6	2.73	99.22	0.48	75.40	0.99	-24.01
D1	12	80	4	0.39	125.54	0.86	248.90	4.79	+98.26

S.D -1S - Standard deviation single-stage; S.D-2S - Standard deviation two-stage; C - Condition; t -Time; T - temperature; SLR - Solid-liquid ratio; S- Severity; CP - Central point

To estimate the energetic, economic, and environmental viability of HPT, the values of the pretreatment conditions that reached the highest methane production were used, as shown in Table 3. Table 4 presents the different energy balances for the selected conditions.

The conditions C7-2S (48min, 80°C, SLR=6, and two-stage), D1-1S (desirability condition one - 12 min, 80°C, SLR=4, and single-stage), D1-2S (desirability condition one - 12 min, 80°C, SLR=4, and two-stage), D2-1S (desirability conditions two - 12 min, 98°C, SLR=4, and single-stage), and D2-2S (desirability conditions two - 12 min, 98°C, SLR=4, and two-stage), are capable of supplying the energy demand of the HPT process and producing a surplus volume, being also those with a lower degree of severity. Although some conditions have relatively high methane production, HPT is not always viable due to high energy costs.

Thus, the energy generated by burning methane cannot supply the energy demand in the pretreatment, as occurs with C6-1S, C8-1S, and C3-2S. Under these conditions, high temperatures are necessary for the HPT of the biomass, demanding water vaporization, unlike the other conditions that operate below 100 °C. The conditions D1-2S, D2-2S, and C7-2S presented the best final net energy balances.

Furthermore, for all conditions, it is necessary to consider at least 10% of the total energy production for biogas purification. The data in Table 6 show the correlation (r2) between the net energy generated from HPT, severity, time, and temperature obtained from the Doehlert experimental design. The data in Table 5 show that severity greatly influences the final energy balance since its correlation index is greater than 0.96. Note that temperature strongly correlates with net energy, unlike time, which proved to be non-significant.

Table 5. Correlation analysis by Pareto test for net energy, severity, time, and temperature

	E_{net}	log (S_0)	T (°C)	t (min)
E_{net}	1.0000	-0.9642 *	-0.9558 *	-0 .6277
	p = 0.000	p = 0.000 *	p = 0.000 *	p = 0.096
log (S_0)	-0.9642 *	1.0000	0.9702 *	0.7207 *
	p = 0.000 *	p = 0.000	p = 0.000 *	p = 0.044 *
T (°C)	-0.9558 *	0.9702 *	1.0000	0.5335
	p = 0.000 *	p = 0.000 *	p = 0.000	p = 0.173
t (min)	-0.6277	0.7207 *	0.5335	1.0000
	p = 0.096	p = 0.044 *	p = 0.173	p = 0.000

E_{net}- net energy ; S-Severity T- Temperature; t- Time; * - Significant variables with p ≤ 0.05

In the D1-2S condition, with better energy balance (Table 4), the separation of the acidogenesis and methanogenesis stages improved methane production due to greater acidification in the first stage of anaerobic digestion. Consequently, there was greater production of acids more easily degraded by microorganisms in the later stages of anaerobic digestion.

Another relevant aspect to be highlighted is that the conditions that presented the best energy balances were those with temperatures lower than 100 °C. This is because water vaporization is unnecessary, requiring less energy for heating in the HPT.

Considering that there is a production of 54 tonnes of poultry litter waste per 45-day cycle (the average time for the development of chicken from the initial phase to slaughter)

Table 4. Energy balance of the eight best methane production conditions

Energy (MJ t_{res}^{-1})	Condition C6-1S	C8-1S	C3-2S	C7-2S	D1-1S	D1-2S	D2-1S	D2-2S
Ep	3147.05	3801.77	5143.92	3013.12	2149.41	4261.57	2920.14	3806.15
$E_{Purification}$	314.70	380.17	514.39	301.31	214.94	426.15	292.01	380.61
E_{HPT}	829.24	829.24	2739.72	594.76	427.16	427.16	758.93	758.93
$E_{thermal}$	5394.22	5394.22	10788.45	0.00	0.00	0.00	0.00	0.00
E_{net}	-3391.12	-2801.87	-8898.64	2117.05	1507.31	3408.253	1869.19	2666.60
log (S_0)	-1.97	2.27	3.45	1.09	0.49	0.49	1.02	1.02
R$$_{TPL}^{-1}$	-451.39	-372.96	-1184.5	281.8	200.64	453.67	248.81	354.95

T_{Res} - Residue tonne; E_p - Purification energy; E_{HPT} - Pretreatment energy; $E_{thermal}$ - Thermal energy; E_{net} - Net energy; R$$_{TPL}$ - Value obtained by the energy of 1 tonne of poultry litter; S - Severity; C - Condition; D - Desirability condition

Table 6. Energy balance per kg of the chicken after pretreatment

Energy	Condition							
	C6-1S	C8-1S	C3-2S	C7-2S	D1-1S	D1-2S	D2-1S	D2-2S
Ep (MJ kg per chicken)	-2.44	-2.02	-6.41	1.52	1.09	2.45	1.35	1.92
Δ (%)	-26.14	-21.60	-68.59	16.32	11.62	26.27	14.41	20.55

E_p - Energy production; C - Condition; D - Desirability condition 1S - single-stage; 2S - two-stage; Δ - Difference between Ep and 9.34 (MJ kg per chicken) obtained in Marchioro et al. (2018)

Table 7. Estimated CO_2 emission for pretreatment conditions

Emission (CO_2)	Condition							
	C6-1S	C8-1S	C3-2S	C7-2S	D1-1S	D1-2S	D2-1S	D2-2S
Natural gas *	150.04	495.72	107.61	77.29	77.29	77.29	137.32	137.32
CHP and biogas *	0.04	0.15	0.03	0.02	0.02	0.02	0.04	0.04

* - CO_2 Carbon dioxide; ; C - Condition; D - Desirability condition; 1S - Single stage; 2S - two-stage; CHP - Combined Heat & Power; *Tonne of CO_2 equivalent per tonne of waste

and that each batch of this material is used an average of five times before being replaced, daily production of 0.24 tonnes of poultry litter is reached. Table 6 presents the daily energy production per kg of chicken for the best HPT conditions and the percentage difference (Δ%) resulting from the consumption of 9.34 MJ kg^{-1} of chicken presented in a Marchioro et al. (2018) study.

C6-1S, C8-1S, and C3-2S present negative results since their energy production is lower than the expense demanded by their pretreatment condition. In other words, these conditions prove to be energetically and financially unfeasible. The other conditions, all with temperatures below 100 °C, can compensate for the energy demand of the pretreatment and reduce part of the energy demand of the aviary.

Regarding the environmental assessment, Table 7 presents the equivalent CO_2 emissions using natural gas and substituting it with the thermal energy produced by the company. Note that the CO_2 emission is much lower when replacing natural gas with biomass energy.

Figure 3 presents the total, electrical and thermal energy production of each HPT condition. Condition C3-2S had the highest electrical energy production, followed by condition C8-1S, with productions of 0.32 and 0.24 kWh kg^{-1} and thermal 2.40 and 1.77 MJ kg^{-1} of chicken. Figure 4 presents data showing the surplus energy production. Condition D1-S2 was the one that presented the highest extra production of electrical and thermal energy.

According to Marchioro et al. (2018), the energy spent by burning firewood for each kilogram of chicken is, on average, 3.25 MJ. Thus, for the D1-S2 condition, with a production of 1.6 MJ kg per chicken, the resulting thermal energy can replace half of the energy obtained by burning firewood. For the other conditions, the percentage of firewood replacement varies from 21 to 39%.

It is worth mentioning that replacing the burning of firewood with the use of biogas generated by the anaerobic digestion process. in addition to presenting financial savings, also has the advantage of reducing CO_2 emissions. In this sense, considering the conditions D1-2S and D2-2S, it would be possible to produce the equivalent of 373 and 334 kWh of electric energy per chicken production cycle, that is, using the energy produced in an integrated system of the company itself would be possible avoid the emission of 0.264 and 0.237 tonnes of CO_2 per chicken production cycle, respectively.

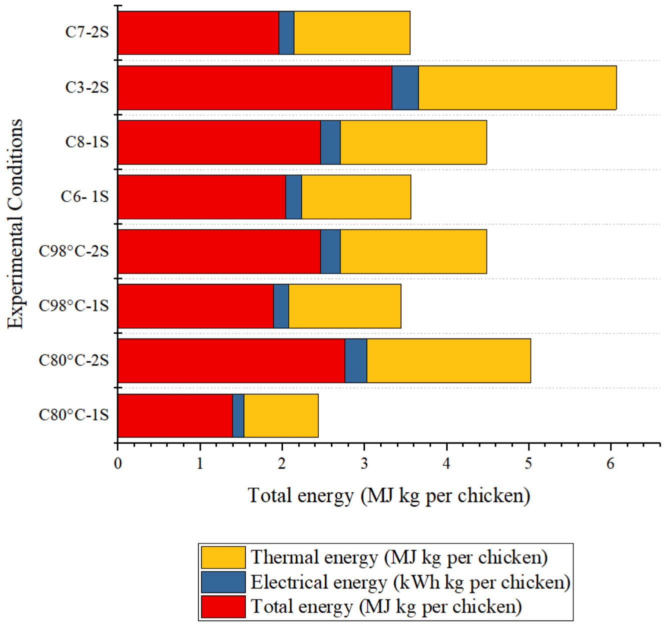
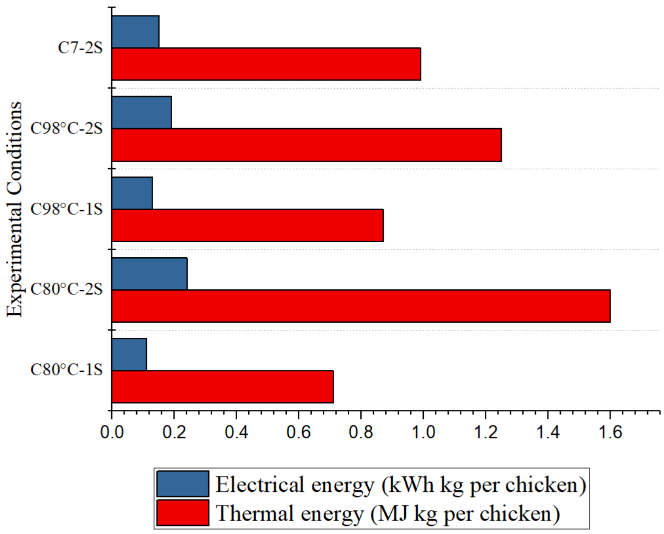


Figure 3. Total, electrical, and thermal energy production of each pretreatment condition



C -condition; 1S - single-stage; 2S - two-stage

Figure 4. Energy surplus of each pretreatment condition

Conclusions

1. The experimental conditions with the best performance of the biochemical potential of methane were 24 min, 120°C, and solid/liquid ratio = 4 in single-stage and 48min, 160°C,

and solid/liquid ratio = 8 in two-stage, which produced 255.6 NmL CH_4 gVS^{-1} and 277.6 NmL CH_4 gVS^{-1}, respectively.

2. The pretreatment of synthetic poultry litter under conditions D2-2S (condition two in two stages [12 min, 98 °C, and SLR = 4]) and D1-2S (condition one in two stages [12 min, 80 °C, and SLR = 4]) resulted in a methane production of about 249 NmL $CH_4 \cdot gVS^{-1}$.

3. The pretreatment of poultry litter under experimental conditions D1 (condition one) or D2 (condition two) in two-stage produced energy for the pretreatment of the poultry litter and a surplus of energy to produce chickens.

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