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Quantification and characterization of the production of biogas from blends of agro-industrial wastes in a large-scale demonstration plant

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ABSTRACT. The use of energy contained in biogas is an interesting alternative to reconcile renewable electric power generation to environmental sanitation. Among the technologies used for recovering energy from biomass, the anaerobic digestion demonstrates ability to treat solid waste and effluents. This research work aims to analyze the influence of physical and chemical factors on the performance of anaerobic digestion reactors and to perform the characterization of biogas in order to assess their quality. The substrate evaluated is the mixture of liquid waste coming from different industrial processes and poultry manure. The characterization of CH_4 , CO_2 , H_2S and O_2 was performed daily in two reactors, R1 and R2, for a period of three months, and the physical and chemical parameters were analyzed biweekly. The parameters analyzed are carbon (C), nitrogen (N), biochemical oxygen demand (BOD), pH, total (TS), volatiles (VS) and fixed solids (FS). Among the results, stands out an average removal of 76% in relation to BOD and H_2S concentration of 156.01 for R1, and of 91.64 ppm for R2, and the $\text{CH}_4:\text{CO}_2$ inverse relationship of 3.15 for R1 and 2.98 for R2, during the monitoring period.

Keywords: renewable energy, waste, gases, sludge, poultry manure.

Quantificação e caracterização da produção de biogás a partir de misturas de resíduos agroindustriais em uma planta de demonstração em larga escala

RESUMO. O uso da energia contida no biogás é uma alternativa interessante para conciliar a geração de energia elétrica renovável ao saneamento ambiental. Entre as tecnologias utilizadas para a recuperação de energia, a partir de biomassa, a digestão anaeróbia demonstra a capacidade de tratamento dos resíduos sólidos e efluentes. Este trabalho de pesquisa tem como objetivo analisar a influência de fatores físico-químicos sobre o desempenho de reatores anaeróbios e realizar a caracterização do biogás, a fim de avaliar a sua qualidade. O substrato avaliado é uma mistura de resíduos líquidos provenientes de diferentes processos industriais e dejetos gerados por aves poedeiras. A caracterização dos gases CH_4 , CO_2 , H_2S e O_2 foi realizada diariamente em dois reatores (R1 e R2) por um período de três meses, e os parâmetros físico-químicos foram analisados quinzenalmente. Os parâmetros físico-químicos analisados foram carbono (C), nitrogênio (N), demanda bioquímica de oxigênio (DBO), pH, sólidos totais (ST), voláteis (VS) e fixos (FS). Entre os resultados destacam-se a remoção média de 76% em relação a DBO, concentração de H_2S de 156.01 para o R1 e de 91,64 ppm para o R2 e relação inversa entre $\text{CH}_4:\text{CO}_2$, sendo esta de 3,15 para R1 e 2,98 para R2.

Palavras-chave: energia renovável, resíduos, gases, lodos, dejetos de aves poedeiras.

Introduction

Until recently, biogas was considered simply as a by-product obtained from the anaerobic decomposition of animal waste and sludge from treatment plants of domestic wastewater. However, the accelerated economic development in recent years and the increase in prices of conventional fuels have encouraged researches into the energy production from alternative and economically attractive sources (Goldemberg & Paletta, 2012).

The sources for the biogas generation cover various raw materials types, such as wastes from households and agriculture, sewage sludge and

wastewater (Kapdi, Vijay, Rajesh, & Prasad, 2005). In the composition of biogas, methane (CH_4) has an aggression potential to the environment around 20 times that of carbon dioxide (CO_2), being then characterized as the main responsible for the increase in the concentration of greenhouse gases (Sanquetta, Balbinot, & Ziliotto, 2004).

The CH_4 produced by degradation of organic matter could be channeled and burned in power generators engines, in order to minimize environmental impacts, and enhance the biogas. The advantages of the use of biogas can be considered in the electric power generation as

well as being a possible solution in the treatment of waste.

Biogas is a colorless, odorless and highly flammable gas that produces no soot and, therefore, has atmospheric pollution potential lower than that of the butane present in the cooking gas (Oliveira & Higarashi, 2006). Biogas is composed by different gases such as CH₄ (60-70%), CO₂ (30-40%), N₂ (< 1%) and H₂ (10-2000 ppm). CH₄ represents the calorific power value contained in the gas equal to 37781.6 kJ m⁻³ and power generation capacity of 5 kW hour m⁻³ (Torres & Osorio, 2009).

Biogas can be used in its original composition, but depending on the application, it is necessary to remove CO₂ and sulphidric acid (H₂S), as humidity and high pressure (Díaz, Ramos and Polanco, 2015). H₂S is responsible for toxicity and corrosion in most devices, when concentrations exceed 50 ppm. The toxicity affects human health, causing headaches, nausea and eye irritation, and, in addition, the combustion of this gas generates emissions of sulfur dioxide (SO₂), with negative environmental effects (Busca & Pistarino, 2003; Greenpro, 2004). Currently, there are various methods of treating for effluent gases, which may be used to minimize these emissions (Pagliuoso & Regattieri, 2008).

All production of biogas from the anaerobic degradation using the upflow anaerobic sludge blanket (UASB) technology is enough to sanitize the entire sludge production from a wastewater treatment plant (WWTP). The pathogenic microorganisms found in the sludge, when not disposed of properly, can be harmful to public health (Borges & Chernicharo, 2009). In this context, it was considered the use of the energy contained in biogas as an interesting alternative to reconcile renewable electricity generation to environmental sanitation.

Regarding the egg poultry manure, these materials are constituted by complex substrates containing particulate and dissolved organic matter as, for example, polysaccharides, lipids, proteins, volatile fatty acids, a high number of inorganic components and high concentrations of pathogenic organisms (Steil, Lucas Junior, & Oliveira, 2012). In a study performed by Minho et al. (2012), the authors evaluated the potential of biogas generation of this slurry mixed with sludge from wastewater treatment (WWTP) and obtained, at the end of 28 days, about 60% of CH₄. Atuanya and Aigbirior (2002) evaluated the feasibility of the UASB reactor for wastewater treatment from poultry and obtained an average content of CH₄ of 57%, whereas in the study of Kalyuzhnyi, Fedorovich, and

Nozhevnikova (1998) the CH₄ concentration was about 80%.

Among the technologies used for energy recovery from biomass, anaerobic digestion has been used in many applications, demonstrating ability to treat solid waste and effluents, also allowing nutrient recycling and energy recovery (Metcalf & Eddy Inc., 2003; Alvaréz & Lidén, 2008). This process occurs through distinct stages, and the initial stage of the degradation is the hydrolysis. During the hydrolysis, there is the transformation of polymers (starch, proteins, and carbohydrates) into monomers, such as amino acids and sugars, by enzymes produced by bacteria. These monomers, in the acidogenic phase, are transformed into volatile fatty acids (VFA) such as butyric, valeric and propionic acids. In the acetogenic stage, these volatile fatty acids are converted into acetic acid, carbon dioxide and gaseous hydrogen, which produce methane by cleavage of acetic acid (acetoclastic methanogenic) and from the reduction of carbon dioxide to molecular hydrogen (hydrogenotrophic methanogens) (Parker, 2005).

It is important to learn about the characteristics and the quantity of biogas produced, since this allows the identification of the constituent gases of biogas in order to optimize the further use of biogas for energy purposes.

The aim of this study was to analyze the physical and chemical factors on the performance of anaerobic digestion of the 'blend', a mix between WWTP sludge and poultry manure, and, further, to perform the characterization of the biogas in order to evaluate its quality.

Material and methods

The reading of gases and collection of material were performed in a biogas plant located in the metropolitan area of Porto Alegre, State of Rio Grande do Sul, Brazil. The blend samples were sent to the Laboratory of Bioreactors at the University Center Univates for physical and chemical analysis.

Initially the blend is produced, a mixture of liquid waste arising from various industrial processes and wastes from poultry manure. The blend is conducted to a container in order to achieve a minimum of 8% of total solids (TS). It is subsequently sieved to eliminate materials that may compromise the subsequent stages of the process, and then led through a pipe to three storage tanks, with capacity of 15 m³ each.

At the considered biogas plant, the feeding is performed through a continuous stream comprising

a storage tank, a piston flow type reactor (R1) with 450, and a vertical upflow reactor (R2) with 900 m³ (Figure 1), plus two gasometers with 1,000 and 1,200 m³ and a reservoir at the end of the process which is intended to the biofertilizer. For the pumping of the input material to the first reactor (R1) there is a timer system that sends blend parcels every 10 min, operating a total of 40 m³ day⁻¹ in both R1 and R2 reactors.



Figure 1. The reactors: on the left is the plug flow reactor R1 (PFR) with 450 m³; and on the right is the vertical upflow reactor R2 (VUR) with 900 m³.

The total hydraulic retention time is 30 days (R1: 10 days and R2: 20 days). R1 has agitation system divided into three zones (surface, middle and bottom) and R2 suffers agitation only when matter is supplied to it. Both are kept at 36°C through a piping system with heat generated from the combustion of surplus biogas.

The characterization of gases was performed daily in both reactors (R1 and R2) for a period of three months, using a gas analyzer Oriun Plus[®], manufactured by MSA AER GmbH Company, which determined the percentage of CH₄, CO₂, H₂S and O₂ present in the biogas.

The collection points in the biogas plant are outlined in Figure 2, where R1 is the Reactor 1 and R2 is the Reactor 2. The sampling points are 1 (at the input of R1), 2 (between the output of R1 and the input of R2) and 3 (at the output of R2). The symbols: a*, b* and c* indicate the effectiveness of

treatment demonstrated by the removal of the organic load, wherein: a* is the value for the analysis of the sample at the R1 input (1) in relation to the R2 input (2), b* is this value for analysis at the R2 output (3) in relation to the input (2), and c* is the value for the analysis of the sample at the R1 input (1) in relation to R2 output (3).

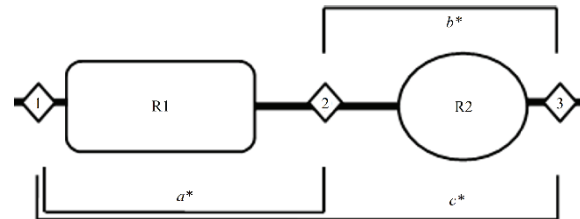


Figure 2. Process flow diagram with the collection points at the biogas plant.

The physical-chemical parameters analyzed were: carbon (C), nitrogen (N), biochemical oxygen demand (BOD), pH, total (TS), volatile (VS) and fixed solids (FS). Samples were collected biweekly at three points: the input of material (point 1) and the outputs of the reactors R1 (point 2) and R2 (point 3). The equipment and method used for each parameter is presented in Table 1.

Table 1. List of parameters and their methods or models of equipment.

Parameter	Equipment	Method or equipment model
BOD	Oxitop	IS 6, TWT
Nitrogen	Digester and distillation	PHA/AWWA
Carbon	Heating plate	PHA/AWWA
pH	pH meter	DM-2P, Digimed
Volatile solids (VS)	Muffle and hothouse	Association of Official Analytical Chemists (AOAC, 1995)
Total solids (TS)	Hothouse	AOAC (1995)

Results and discussion

Physical and chemical analyses

Table 2 presents the values given as average and standard deviation (SD) of BOD, C, N, C:N, FS, TS, VS and pH values of the sample points: 1, 2, 3. The values of the removal for BOD and reductions of C, N, C:N, FS, TS, VS in a*, b* and c* are also shown in this table.

Table 2. Average and standard deviation for the analyzed physical and chemical parameters.

Parameter	(1) R1 input	(2) between R1 output and input R2	(3) output R2	a*	b*	c*
	(average ± SD)					
C (mg L ⁻¹)	26,089.39 ± 10,436.18	18,474.07 ± 6,100.12	18,259.60 ± 9,468.10	23.19 ± 25.60	18.28 ± 36.74	44.30 ± 26.19
N (mg L ⁻¹)	1,780.914 ± 1,561.31	2,750.59 ± 465.21	2,241.19 ± 910.53	-116.8 ± 102.34	24.69 ± 20.79	-41.41 ± 73.31
C: N	22.88 ± 21.02	7.62 ± 3.48	8.86 ± 6.05	51.08 ± 28.85	1.730 ± 45.00	52.60 ± 38.35
BOD (mg L ⁻¹)	38,000.00 ± 17,193.02	10,166.70 ± 3,970.73	5,250.00 ± 4,645.79	69.33 ± 16.47	71.03 ± 32.36	88.01 ± 18.25
pH	6.87 ± 0.63	7.85 ± 0.13	7.88 ± 0.22	-----	-----	-----
FS (%)	41.03 ± 12.98	44.47 ± 9.18	47.78 ± 7.19	-----	-----	-----
TS (%)	7.72 ± 1.69	7.14 ± 1.37	7.65 ± 2.30	-----	-----	-----
VS (%)	58.97 ± 12.98	55.53 ± 9.18	52.22 ± 7.19	-----	-----	-----

The average removal of samples BOD^{a*}, BOD^{b*} and BOD^{c*} were 69.34, 71.03 and 88.01% respectively. It was also obtained a BOD^{c*} removal with efficiency equal to 98% at the end of the process (point 3) in a punctual analysis. The favorable removal obtained from sludge purification is due to R2, which is a reactor of upward flow type. However, it can be seen that R1 has achieved a considerable percentage of removal too. Analyzing the complete system, it was visualized a BOD removal efficiency that was even more satisfactory. In the study performed by Campos, Mochizuki, Damasceno, and Botelho (2005) about the treatment of wastewater from pig manure using the same type of reactor, the efficiency of this parameter was of 75%.

The effluent from the input (point 1) presented a concentration of $26,089.39 \pm 10,436.18 \text{ mg L}^{-1}$ of C and $1,780.91 \pm 1,561.31 \text{ mg L}^{-1}$ of N. The reduction obtained in C^{a*} was of $23.19 \pm 25.60\%$, showing that in some analyzes it was obtained an increase of carbon, as well as in C^{b*}, which presented $18.28 \pm 36.74\%$ of reduction. The best carbon reduction was obtained at the end of the process C^{b*} ($44.30 \pm 26.19\%$). Concerning nitrogen, there was a better reduction in the second sampling point, after treatment in R1, with value of 24.69 ± 20.79 . Subsequently there was an increase for this parameter in the middle.

The concentrations of carbon and nitrogen determine the performance of the anaerobic digestion process. The carbon is the source of energy for microorganisms and nitrogen stimulates microbial growth; therefore, so the process has optimum operation, the C: N should be 30: 1 (Igoni, Ayotamuno, Eze, Ogaji, & Probert, 2008). The C: N ratio of the sampling points 1, 2 and 3 were $22.88:1 \pm 21.01:1$; $7.62:1 \pm 3,48:1$ and $8.86: 1 \pm 6.05:1$; respectively. There was a normal process of anaerobic degradation, with initial and final values for C: N ratio close to optimum value. The C: N ratio was higher at point 3; we infer that the increase of carbon in the medium may have favored the microbial inhibition, reducing the ability of degradation of organic matter (Sgorlon, Rizk, Bergamasco, & Tavares, 2011). The input material presented C:N ratio in the range recommended Luna, Leite, Lopes, Silva, and Silva (2008), between 20: 1 and 30: 1, which is favorable to the biostabilization process. A satisfactory C: N ratio was also obtained at the end of the process, in accordance with Rao and Singh (2004), who explain that the C: N ratio of the stabilized waste varies between 10: 1 and 13: 1.

The average values of TS in the samples 2 and 3 were 7.14 and 7.65%, respectively. The input material contained about 7.72% of TS, which exceeded the level of 5% obtained by Felizola, Leite, and Prasad (2006) in the anaerobic treatment of organic waste.

The content of the VS of the sample points 1, 2 and 3 were 58.97, 55.53 and 52.22%, respectively. The higher the concentration of volatile solids in the daily diet of the digester ($\text{m}^3 \text{ kg}^{-1}$), the higher will be the biogas generation (Oliveira & Otsubo, 2002).

The FS at the sampling points 1, 2 and 3 were equal to 41.03, 44.47 and 47.78%, respectively. These values were consistent with a process of anaerobic degradation where an increasing trend of FS occurs over the time by volatilization of a portion of the total solids, which is in agreement with Nielsen (2011), who describes the increase that occurs on the fixed solids concentration with the passage of time due to the buildup of deposits and recalcitrant compounds in the system.

The average pH of the sample point 1 was 6.87 ± 0.63 , whereas for the sample point 2 it was 7.85 ± 0.13 and, for the sample point 3, 7.88 ± 0.22 . Even though there have been no significant changes in pH, this increase is associated with the buffering effect provided by biostabilization process of organic solid waste (Bouallagui, Cheikh, Marouani, & Hamdi, 2003). According to Gerardi (2003), at pH values between 6.8 and 7.2, methanogenic bacteria present a better performance, occurring the converting from volatile acids into CH₄ and CO₂. The autor Gerardi (2003) explains that the pH of an anaerobic system is significantly affected by the presence of CO₂ in the biogas and pH values from below 6 to above 8 limit the methanogenic activity by presenting a toxic environment.

Characterization of the biogas

The average values and standard deviation of CH₄, CO₂, H₂S and O₂ present in R1 and R2 are shown in Table 3.

Table 3. Average values and standard deviations for the parameters of the gases present in reactors 1 and 2.

Parameters	CH ₄ % - SD	CO ₂ % - SD	H ₂ S ppmv - DP	O ₂ % - SD
Reactor 1	75.76 - 3.09	24.00 - 3.02	156.01 - 53.64	0.23 - 0.26
Reactor 2	74.64 - 2.33	25.07 - 2.28	91.640 - 49.69	0.25 - 0.26

During the three months of monitoring, it was observed that the percentage of CH₄ in R1 was higher than the percentage of this gas in R2, which may be explained by a higher concentration of volatile fatty acids in R1, also confirmed by Felizola et al. (2006).

Luque and Balu (2013), when the ratio between CH₄ and CO₂ reaches an average value of 1.5, the anaerobic treatment process reaches a steady state, that is, conditions under which the biogas produced by the process of anaerobic biostabilization of the organic matter contains, in average, 60 of CH₄ and 40% of CO₂. In this study, the biogas produced in R1 provided a CH₄:CO₂ ratio equal to 3.15, and equal to 2.98 in R2. The biogas obtained was mainly formed by two gases, CH₄ and CO₂, presenting an inversely proportional concentration of one over the other and still leaving traces of other gases characterized in this study (H₂S and O₂).

Conclusion

This research demonstrated that the blends of agro-industrial wastes treated in the studied biogas plant has a significant energy potential, presenting average values for the concentration of methane in the generated biogas of about 75%. The flow of waste from agro-industrial activities can present environmental and health hazard; however, by converting this waste into energy, the health and environment problems are solved, while the energy generated contributes to the sustainable development of society.

The generation of CH₄ is inversely proportional to CO₂ generation. During the monitoring period, the CH₄:CO₂ ratio was of 3.15 for R1 and 2.98 for R2. Other parameters were assessed from the generated biogas. Concentration of O₂ presented values of 0.23 for R1 and 0.25 for R2, while for H₂S, the values were equal to 156.01 in R1 and 91.64 ppmv in R2.

Concerning the evaluations of physical and chemical parameters, results obtained for the removal of BOD were satisfactory, presenting values of 69.34, 71.03 and 88.01% of removal in the analyzed sample points, whereas for the other parameters (C, N, pH, TS, FS and VS), the obtained values were consistent with the anaerobic degradation. The C: N ratio in the sampling points was equal to 22.88:1, 7.62:1 and 8.86:1, while the best reductions of C and N were found in the sampling points 2 and 3, with a reduction of 44.30 and 24.69%, respectively. The values of pH varied between 6.87 and 7.88, and the content of TS, VS and FS ranged from 7.14 to 7.72%, 52.22 to 58.97% and 41.03 to 47.78%, respectively.

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