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Biogas Production from the Degradation of Biodiesel Agroindustry Waste

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Abstract

Due to advances in environmental policies in Brazil and demand to reach knowledge and techniques of new ways for obtaining energy, to avoid future blackouts and rationing, the renewable energy market is on the rise, and biofuel is a very promising energy source. In the biodiesel agro-industries, there is a constant increase in the residues generation (glycerin, washing waters, press cake, and oil sludge) resulted from the fuel production process, so there is the need for residues management or treatment valuing biodiesel by-products. In this paper, it was evaluated the main types of waste generated at the Caetés Biodiesel Pilot Plant - BR and analyzed the biogas generation potential of this waste. In the laboratory, comparative analyses were carried out between different combinations and percentages of sludge (inoculum containing a high concentration of methanogenic microorganisms to accelerate biomass degradation process) and biodiesel by-products. It was investigated through tests of Biochemical Methane Potential (BMP) biogas generation from samples and simulated the capacity of electric power generation. Based on these data and the calculation of energy efficiency, it can be suggested the use of biodigesters with residues generated in the plant to produce energy in the unit enabling a 20% reduction in power consumption.

Keywords: Agro-industrial Waste; Biogas; Biodiesel; Energy.

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1. Introduction

Biodiesel is considered a promising source of energy to replace petroleum products due to its neutrality related to CO2, significantly reducing greenhouse gas (GHG) emissions.

Due to recent advances in the renewable energy market, driven by the increase in biofuel production in Brazil, the United States and Europe, there is the consequent emergence of a new waste production route: biodiesel agroindustry waste.

In 2004, after the creation of the National Program for Production and Use of Biodiesel (PNPB), there was a wide increase in the diffusion of biodiesel in Brazil; given the vast agricultural potential existing in the country, biodiesel production had a massive growth, which increases the number of plants. Biodiesel plants cause environmental impacts mainly due to residues generation, so it necessary to develop studies to identify and quantify these problems to optimize the biodiesel production process and to search viable alternatives for better use or destination of these residues.

It is necessary to elaborate guidelines directed to the theme of waste in the industrial sector, as well as the regularization of waste generation and its treatment. This problem is currently a major impasse that requires more specific legislation for this type of production.

In view of the existing quantity and variety of waste generated in a biodiesel plant, which meets parameters that allow reuse for energy purposes, a production chain that starts in the field and can be processed in biodigesters for biogas production configures anaerobic digestion as an important energy vector with great versatility as an energy source. Anaerobic digestion presents characteristics that allow chemical energy to be converted into electric, thermal, and vehicular power contributing to the variety of energy matrix in the agroindustry and neighboring communities. This practice is encouraged by the National Policy on Solid Waste (Federal Law No. 12,305/2010) and National Policy on Climate Change (Federal Law No. 12,187/2009) regulated by Decree No. 7,390/2010. By these laws it is established that one of the objectives is the reduction of GHG emissions from various human activities including those related to waste; moreover, it makes official Brazil's commitment to the UN Framework Convention on Climate Change to reduce GHG emissions around 36.1% and 38.9% on projected emissions until 2020 [1].

Considering the production process, there is the problem of the consequent increase in waste generation in the agro-industry. To solve it, some technologies could be used to waste treatment and disposal including anaerobic digestion in reactors. Therefore, in addition to biodegrading the residues present in the reactors, these same residues, in a concomitant association in their physical-chemical structures, may perform certain metabolic functions producing electricity from the biogas generation through this synergy; moreover, there is the material stabilization for future application as biofertilizer in the field boosting agricultural production. Notwithstanding, to promote energy production it is necessary to evaluate the biogas and methane generation potential of these main biodiesel by-products.

2. Background

2.1. Biodiesel, Production Chain and Main Raw Materials

Biodiesel may be produced from any natural oil taken from plants. The most used in Brazil are oilseeds, such as soybeans, cottonseed, palm nuts, sunflower, babassu, peanut, castor bean, jatropha, or from fatty acids, such as animal fat. In addition to soil variety, climate, and types of oilseeds, once there are more than 100 plants with energy potential, each Brazilian region has its natural tendency for biodiesel production; palm trees, as palm nuts and babassu, in the North, or soybeans, in the Center-South. Soybeans present a structured production chain, so they are the most widely used crop in the Brazilian biodiesel production currently, accounting for about 80% of production. Nevertheless, other oilseeds have greater energy potential in terms of productivity; for example, palm nuts possible produce 13 times more biodiesel in comparison with soybeans. Jatropha, cottonseed, sunflower, and peanuts are also considered promising sources [2].

Law 11,097/05 defines biodiesel as a biofuel derived from renewable biomass for use in internal combustion engines with compression ignition or according to regulations for the generation of other types of energy, which may partially or totally replace fossil fuels [3].

2.1.1. Production Chain

Biodiesel production chain shown schematically in Figure 1 presents as main segments of the chain oilseed producers, oil extraction plants, biodiesel producing industries, distributors, gas stations, and consumers [4].

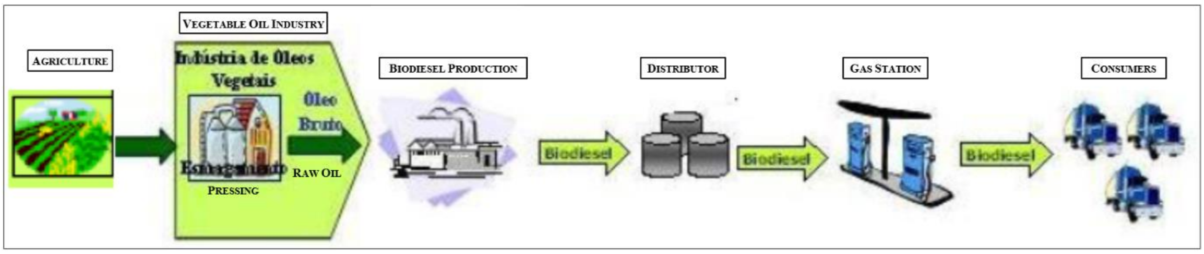

Figure 1: Biodiesel production chain simplified flowchart [4].

The entire agro-industrial chain is a major producer of diversified residues as vegetable residues from harvesting and processing residues, such as bark, straw, lumps, and press cake that may be used energetically. Nonetheless, Brazil uses less than half of its waste; more than 200 million tons of agro-industrial waste are not harnessed [4].

In biodiesel chain's first stage, i.e. harvest, leaves and stems remain in the field. In the next stage, when the oil is extracted, residues such as press cake and bran are considered by-products or co-products depending on these materials' sale value; usually, they are used to feed animals or to fertilize soil. Another possible alternative to benefit these residues is to take advantage of the significant starch and lignocellulosic percentage existing in this residual biomass for bioethanol production through hydrolytic and fermentative processes [5].

In regard to the production process, biodiesel is predominantly produced by a reaction called transesterification, which consists on a triglycerides reaction (vegetable oils or animal fat) with an active intermediate formed by the reaction of a short chain alcohol (methanol or ethanol) and a catalyst producing a mixture of esters (biodiesel) and glycerol, as co-product [6].

2.1.2. Anaerobic Biodegradation

In all the processes of organic matter anaerobic digestion presented three basic phases are involved: hydrolysis, fermentation (also known as acidogenesis), and methanogenesis. Figure 2 shows the biodegradation process scheme.

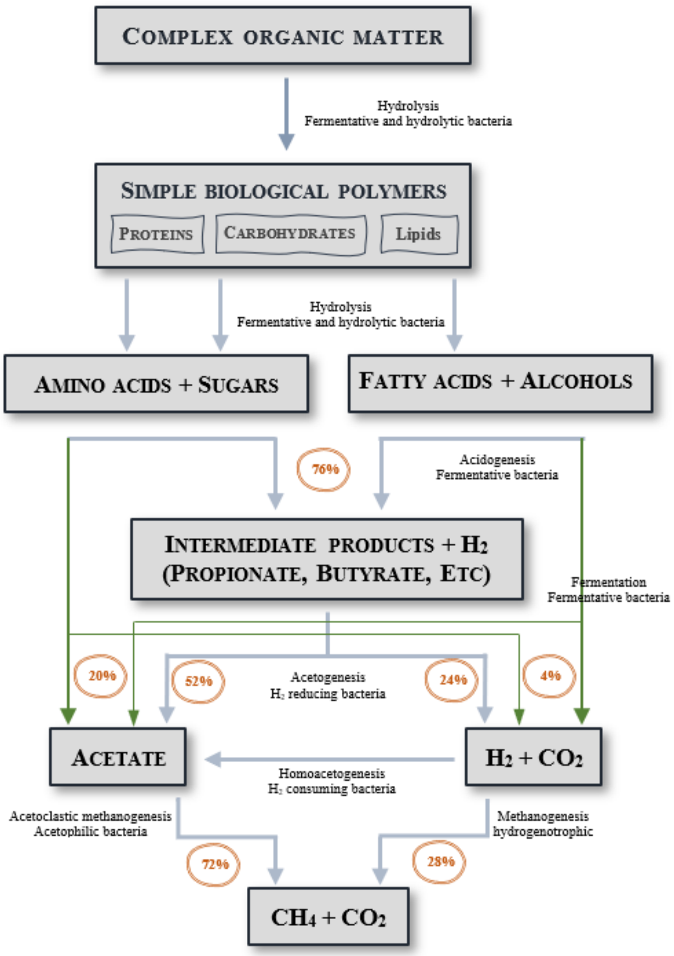

Figure 2: Biodegradation flowchart [1].

2.2. Plant Characterization

The biodiesel plant where the research was carried out is located in the municipality of Caetés, in the middle zone of the state of Pernambuco, which is called Agreste.

It is an experimental plant located in the municipality's Rural Zone, which was implemented in early 2006 with funds from the Federal Government through the Ministry of Science and Technology - MCT.

The municipality of Caetés borders the municipality of Garanhuns and is situated 252 km away from the state capital, Recife. In addition to the geographical distance, the municipality is also socioeconomically distant from the state capital in terms of the Human Development Index (HDI) and consequently in terms of life quality indices.

According to data collected by the Brazilian Institute of Geography and Statistics (IBGE) for the 'Mapping of Poverty and Inequality in Brazilian Municipalities' in 2003, in one hand the municipality of Caetés has an incidence of poverty equals to 68.08%, on the other hand the municipalities of Garanhuns and Recife present an incidence of 43.41% and 39.46%, which reflects the pattern of population power consumption. While Garanhuns registers a total power consumption of 142,760 Mwh, the consumption registered in Caetés falls drastically to a minimum of 8,720 Mwh. A large part of the city's power consumption comes from the rural area (2,510 Mwh) where the studied biodiesel plant is located. It confirms the need to carry out more studies to diversify the energy matrix in the region sustainably, using resources already available at the site; hence, besides to provide a better energy distribution to neighboring populations, it reduces the power cost on the own production unit, i.e. biofuel plant.

The plant, which is regulated by the National Agency of Petroleum, Natural Gas and Biofuels (ANP), has a production capacity of 1m³ of biodiesel per day, totaling an annual production of approximately 360 thousand liters, using vegetable oil from various oilseeds as raw material for production; the most common is cottonseed oil [4]. At the unit, there is an experimental plantation that analyzes different promising oilseed crops for biodiesel production. The cottonseed (Gossypium hirsutum) is the main raw material used in the unit, but this paper investigated in its analysis the jatropha (Jatropha curcas) press cake, which is also a promising crop for biodiesel production since it is available in the harvests that were carried out.

The Caetés plant has a license to operate for research purposes, so the waste generation in the unit is small; however, in processes such as biodiesel purification and alcohol recovery, there is waste generation, which is demonstrated quantitatively in Table 1. Despite the higher production capacity, the plant respects the limit established by the ANP of 1m³/day.

Table 1: Waste annually generated at the pilot plant of Caetés - PE (adapted from [4]).

Residue/By-product	Quantity	Disposition	Treatment	Destination	Destiny	Distance (Km)
Glycerin	30	Tanks	-	Donation/Storage	Own plant	20
Oil Neutralisation Sludge	15	Tanks	-	Storage	Own plant	-
Press cake	240*	Bins	-	Fertilization	Own plant	-
Oil washing water	30	Decantation tanks	-	Fertigation	Own plant	-
Recyclable	Uninformed	Waste shelter	-	Recycling	Own plant	20

3. Methodology

3.1. Study at the Pilot Plant

The research procedures applied in this study consisted of: first, adopting a biodiesel production plant in the state of Pernambuco; second, identifying raw materials used in the biodiesel production process in the unit; third, carrying out technical visits to identify the residues produced, as well as the destination given to each one of them. Then, residues were collected and incubated in reactors. Finally, it was monitored the gas production in a period of 60 days.

3.2. Collection and Sampling of Waste

To perform the research, it was used the residues generated at the Caetés Biodiesel Plant. Residue's collections were made in October 2012, in which 5 L plastic drums were used to store the waste such as glycerin, jatropha press cake, washing waters, and cottonseed oil sludge.

3.3. BMP Test

The evaluation of the residues' biodegradability was made by the Biochemical Methane Potential (BMP). BMP test is intended to assess waste biodegradability based on CH4 total production under optimal degradation conditions [7].

The inoculum used in the tests, i.e. sludge, came from an anaerobic lagoon at COMPESA's Sewage Treatment Station located in the municipality of Recife, at the neighborhood of Mangueira. Once the collection was done, the sludge was applied in the experiment to preserve the microorganisms pool present in the sample. In the laboratory, samples were weighed and crushed to reduce the waste particles' size; it increases the contact surface between the microorganism and the medium accelerating the degradation process. Then, groups of tests were formed. Glass flasks with screw cap were used; on the cap, it was attached gas inlet and outlet valves and a 1 kgf/cm2 manometer with a scale of 0.02 kgf/cm2 to control each flask internal pressure. The bottles were wrapped with aluminum foil to avoid light influence during the biodegradation process. To fill the BMP flasks, a laminar flow chamber with exhaustion was used to enable the flasks handling preserving their characteristics and respecting biosafety rules required in laboratories. The substrates were subjected to degradation in the 250 mL glass flasks in 7 groups, performed in triplicate, as presented in Table 2.

50 mL of inoculum was placed in groups 1, 2, 3, 4, 5, and 6 with the addition of their respective mixtures, except for Group 1 which is the controlling group. Group 7 was formed only by glycerin and press cake to observe the sludge influence in this mixture. All flasks were closed and submitted to the circulation of a gas mixture containing 80% of N2 and 20% of CO2 to promote an anaerobic atmosphere in the flasks. After two minutes of gas mixture circulation, i.e. in and out of the flasks, valves were closed, and the manometer was coupled.

Flasks were kept at 37 °C for 60 days; in this period, there was daily monitoring of pressure and flasks internal temperature.

Table 2: Waste annually generated at the pilot plant of Caetés - PE (adapted from [4]).

Group	Composition	Inoculum	By-product
1	Sludge (50g)	Sludge	Sludge
2	Sludge (50g) + Glycerin (5g)	Sludge	Glycerin
3	Sludge (50g) + Press Cake (5g)	Sludge	Press Cake
4	Sludge (50g) + Washing Waters (5g)	Sludge	Washing Waters
5	Sludge (50g) + Oil Sludge (5g)	Sludge	Oil sludge
6	Sludge (50g) + Glycerin (2,5g) + Press Cake (5g)	Sludge	Glycerin and Press Cake
7	Glycerin (50g) + Press Cake (5g)	Absent	Glycerin and Press Cake

4. Results

4.1. Biogas Generation Analysis

The Methane Biochemical Potential (BMP) test is designed to evaluated residues biodegradability based on total biogas and methane production under optimal degradation conditions in humidity, temperature, anaerobic microbial flora and nutrient availability terms [1]. According [8], BMP test is also suitable when used to clarify substrates types, cosubstates optimal ratio, determine biodegradability degree and also residence time required for complete digestion. To maximize degradation and biogas generation in tests, anaerobic sludge was added as an inoculum to ensure greater microorganisms and nutrients availability to degrade the substrate. Anaerobic sludge from domestic sewage treatment plants used for co-digestion of other residues is proposed in several treatments such as [9]. In order to verify biogas generation influence from the sludge, BMP test was carried out with only sludge. It was observed an accumulated biogas volume of 48.46 NmL after 60 days of testing (Figure 3). There is a potential of biogas generation of 0.96 NmL/g wet sludge considering wet mass used. In consonance with [1], the methane generation is approximately 50% of the value obtained from biogas; therefore, the potential for CH4 generation is 0.48 NmLCH4/g for sludge. In this research, considering 20,000 mgO2/L the sludge DQO analyzed and 50% methane in biogas [1], it has a potential of 24.23 NmL CH4/gDQO, below those found by [10], between 188 to 214 NmLCH4/gCOD, analyzing inoculum from 7 sewage treatment plants.

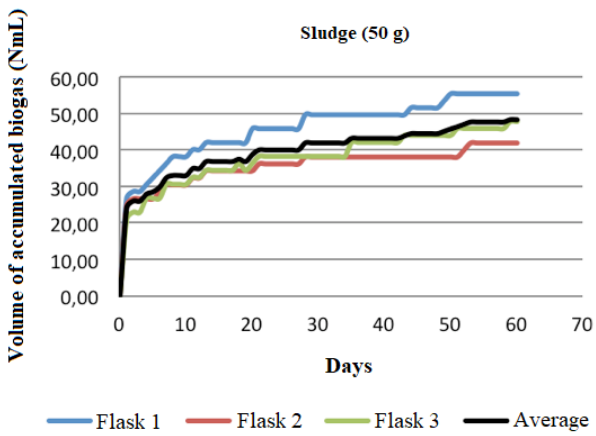

Figure 3: Biogas generation behavior in sludge samples (Group 1).

Figure 4 shows accumulated volume curves in each group studied. The results of accumulated volume and biogas and methane generation potential from the residues obtained are summarized in Table 3.

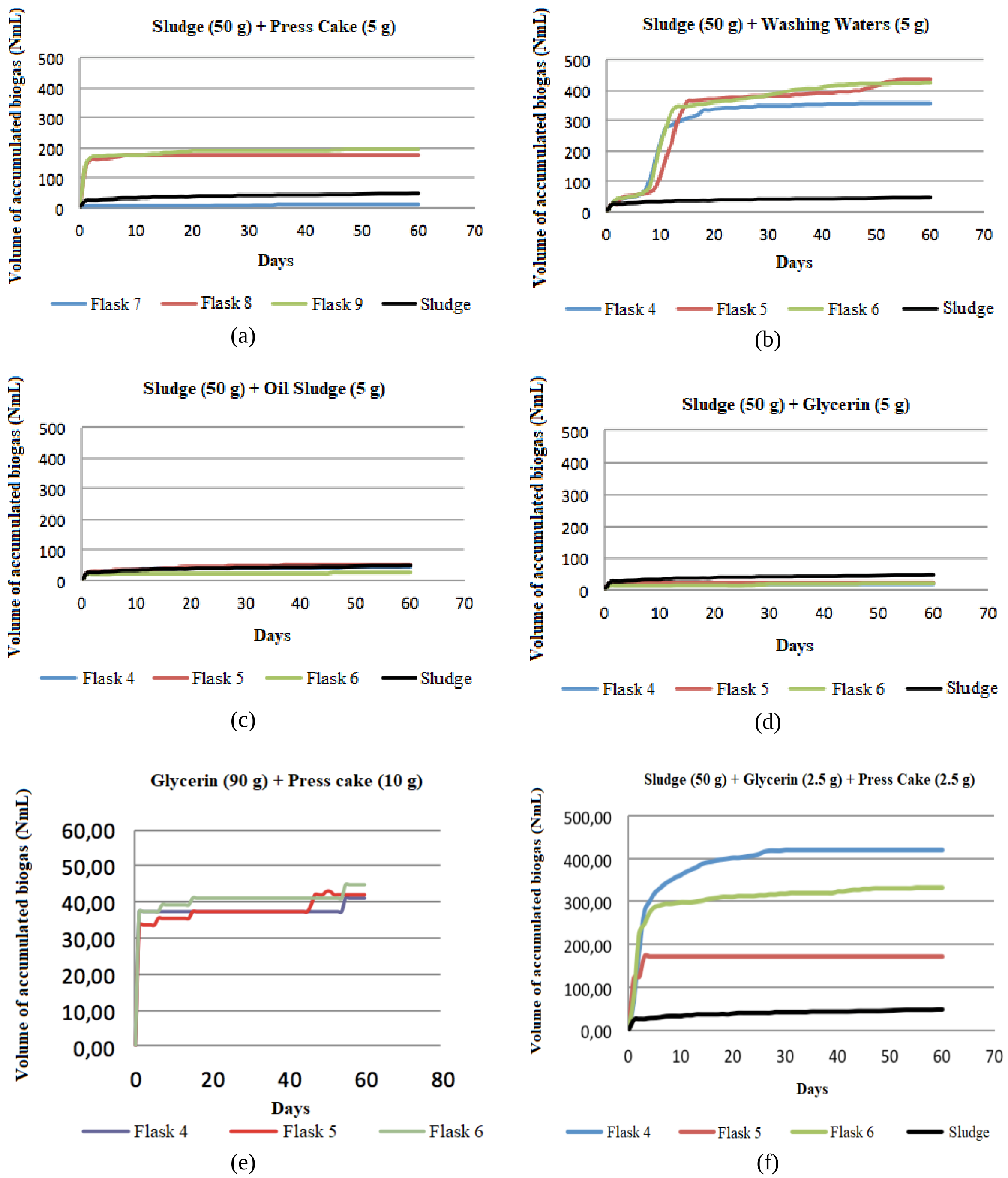

Figure 4: Biogas generation behavior in (a) sludge samples with addition of 10% Press Cake [Group 3], (b) sludge samples with addition of washing waters [group 4], (c) sludge samples with addition of Oil Sludge [Group 5], (d) sludge samples with addition of Glycerin [Group 2], (e) samples with Glycerin with addition of Press Cake [Group 7] e (f) sludge samples with addition of Glycerin and Press Cake [Group 6].

Table 3: Experimental data and biogas and methane potential in which studied groups.

Group	**Composition**	**Accumulated Volume (NmL)**	**Accumulated Valoume – Sludge Accumulated Volume (NmL)**	**Biogas Potential (NmL/g)**	**Methane Potential* (NmL CH4/g)**
1	Sludge (50g)	48,46	-	0.97	0.48
2	Sludge (50g) + Glycerin (5g)	20,53	0	0	0
3	Sludge (50g) + Press Cake (5g)	186.4	137,94	27.59	13.79
4	Sludge (50g) + Washing Waters (5g)	431.52	383.06	153.22	76.61
5	Sludge (50g) + Oil Sludge (5g)	40,73	0	0	0
6	Sludge (50g) + Glycerin (2,5g) + Press Cake (5g)	377.33	328.87	65.77	32.88

* Methane generation potential was defined by 50% of the value obtained from biogas.

Among the groups analyzed, the best methane generation potential performance was Group 4 (90% sludge + 10% washing water) with 76.61 NmL, followed by Group 6 (90% sludge + 5% glycerin + 5% press cake) with 32.88 NmL and the lowest CH_4 generation potential performing was Group 3 (90% sludge + 10% press cake) with 13.79 NmL. Some groups did not show viability in biogas production, such as Group 2 and 5.

The high biogas generation in Group 4 is due to the high water and diluted or pre hydrolyzed oil presence in the washing waters which favored biodegradability of the medium.

Samples of Group 6 were idealized due to the low values resulting from the samples of sludge with addition of glycerin. Therefore, it halved the amount of glycerin and added the same amount of press cake to obtain a better microbial activity in the samples. The synergy between the three residues could contributed to studies of energy production.

Reference [11] obtained for a mixture of 75% poultry manure + 25% orange peel a biogas generation volume of 768 mL. The amount of substrate used is 2.5 times bigger than this paper, so finding a value about 1.8 smaller for the group 4 (431.52 NmL) is expected.

Reference [12] presented a methane generation potential of 79.9 mL with banana substrate and 69.7 mL with grass substrate. The values are close to group 4 (90% sludge x 10% washing water), which is 76.61 NmL.

In the literature, most published studies indicate biogas production increases with the increase in glycerin percentage in the reactor. A close value was found by [4] for similar species to press cake (Jatropha curcas). The author also tested Jatropha mixture with gross glycerin and noted this mixture presented biogas production high capacity.

The biogas accumulated volume generated in Group 2 and 5 tests was lower than only sludge accumulated volume, indicating degradation inhibition. Thus, proportions and conditions used in these tests and with the residues studied, no viability in biogas production was presented and biogas generation potential can be presented as null.

When oil sludge physical characteristics were studied, it was noted a high content of fatty acids making the medium acid for fermentative bacteria; consequently, it was generated a low biodegradation index justifying the negative values presented by these samples. Reference [13] tested different glycerin supplementation percentages, being the percentage of 6% the most favorable for biogas production, providing increased production, and values above this caused inhibition.

Reference [14] studied the MSW organic fraction co-digestion with 5% by glycerin mass and 30% of anaerobic sewage sludge. It was also verified the methanogenic phase inhibition and significant pH reduction.

In addition, it is also necessary to analyze the C/N ratio, whose ideal value recommended by [15] is between 20 and 30 for anaerobic digestion. In glycerin, traditionally this value is much higher. In most studies, glycerin caused an increase in biogas generation potential when there was a low C/N ratio in the substrates, being glycerin an important carbon input.

4.2. Electric Power Generation Capacity

4.2.1. Simulation

Data collected indicate the biodiesel plant consumes 5,600 kW/month or 7.77 kW/month. To obtain energy generated in J/s, the Equation 1 was applied.

$$W = Generated\ Power\ /\ month\ (kJ/\ month)\ x\ 3{,}858\ x\ 10^{-4}\ J/s \qquad (1)$$

The generated power per month is expressed in Equation 2.

$$\text{Generated Power / month} = \text{CH}_4 \text{ Calorific Value (kJ/m}^3\text{) x Volume (m}^3\text{/month)} \qquad (2)$$

Table 4: Energy and power values installed at the Caetés biodiesel plant.

Power		**Installed Power**		
Volume (m^3/month)	**CH_4 Calorific Value (kJ/m^3)**	**Generated Power /month (kJ/month)**	**W**	**kW**
502,01	35,600	17.871.556	6.894	6,89484631

According to [16], CH_4 calorific value is equals to 35,600 kJ/m3; Therefore, the values of power and installed power at Caetés biodiesel plant are presented in Table 4.

Consequently, considering the residues placed in optimal biodegradation conditions and respecting the proportions studied in this paper, the plant may mitigate 20% of its power consumption per day (Table 5).

Table 5: Consumed power per day and percentage of power.

Consumed Power (kWh)	Power that may be generated (kWh)	Generated/consumed Power (%)
35	6,9	19,7

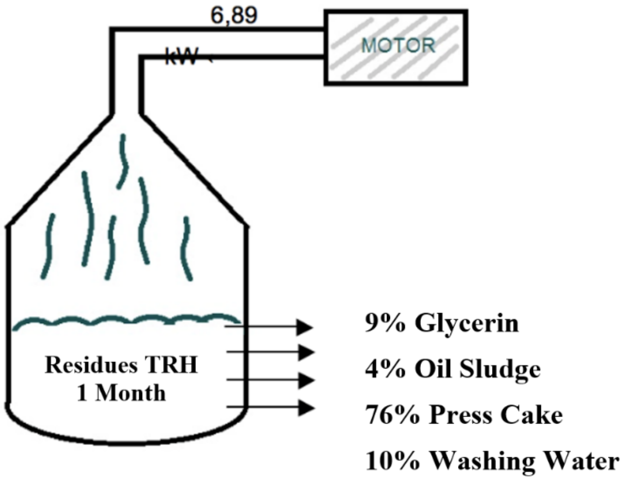

Figure 10: Proportion to be used in the biodigester for biogas production.

5. Conclusion

This study aimed at assessing waste generation in a biodiesel plant in the countryside of Pernambuco, Brazil, and evaluation of residues' biodegradability of which was produced in the plant to estimate biogas and methane generation potential as well as electric power generation capacity to diversify the energy matrix in the region sustainably. Thus, BMP Test presented to be a good mechanism to quantify the potential for biogas generation from agroindustry waste. With the measurements of gases generated and data on the volume of biogas production, it may be obtained parameters for quantification of the production of the mixture.

6. Recommendation

- According to BMP tests, agroindustry waste produced in Caetés biodiesel plant which best methane generation potential performance was washing water, followed by the mixture of glycerin and press cake;

- Based on the data obtained, a 20% decrease in power consumption was observed, and the use of biodigesters with residues generated at the plant for power production to the own unit is a good suggestion.

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