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Biogas Production from Mesophilic Anaerobic Digestion to Treat Lignocellulosic Wastes in Mezcal Production

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Vinasse and bagasse are residues from the production of mezcal, an alcoholic beverage. Treating these wastes is very important to avoid the contamination of water bodies and soils by their discharge into the environment. One of the processes to treat this type of waste is anaerobic digestion. In this study, mesophilic anaerobic digestions were carried out with different organic loads and a retention time of 30 days, where bagasse was thermally pretreated to decrease cellulose crystallization and reduce lignin content, which is highly resistant to chemical, biological, and enzymatic degradation, constituting a barrier for cellulose utilization during the process such as enzymatic hydrolysis and subsequent fermentation. The process carried out with a lower bagasse proportion of 5% resulted in a more significant reduction of COD, SSV, and a methane percentage of 70%, 49%, and 63%, respectively, while maintaining a pH between 6 and 7.5 and an alkalinity of 2,000 mg/L. These results indicate that the process was not inhibited when the content of bagasse was low, reaching the methanogenesis stage in the anaerobic digestion.

1. Introduction

Currently, the circular economy is of great importance, and it requires the valorization of second-generation raw materials, such as lignocellulosic biomasses. Lignocellulosic biomasses are promising resources for obtaining biofuels; their characteristics influence the energy efficiency of anaerobic digestion and the process operation mode. However, in most cases, it is necessary to apply pretreatments to these lignocellulosic biomasses by physical, chemical, and biological means before being subjected to processes for obtaining biofuels and energy (Yee et al., 2017).

Mexico is rich in natural resources that are transformed into different products by industry, such as alcoholic beverages like mezcal. These processes generate waste that contaminates water bodies and soils due to the lack of treatment for proper disposal. The agricultural industry contributes most to anthropogenic methane emissions and other gases, producing around 32% of methane worldwide. This industrial sector produces alcoholic beverages. It uses agave plantations and has contributed to being an essential source of economic, social, and ecological benefits for the population. Unfortunately, the lack of management and disposal of waste, such as stalks, bagasse, and vinasse, causes contamination of rivers and soils and deteriorates them due to their low pH. The decomposition of waste, such as stalks and bagasse, generates methane released into the atmosphere and contributes to climate change. Therefore, these environmental and sanitary problems must be solved due to their adverse effects on the communities where these activities are carried out.

Mezcal production units are called "vinatas" in traditional or artisanal technology. The state of Durango, Mexico, is one of the top five agave-based beverage producers in the country, with the municipality of Nombre de Dios being the most important in this industry. In this state, only wild populations of Agave duranguensis are used, particularly in the municipalities of Nombre de Dios, Súchil, and Durango (Colmenero et al., 2011).

All these wastes can be treated through anaerobic digestion to obtain by-products that can be used, such as the case of biogas, which is a type of bioenergy that can replace familiar energy sources, especially in isolated

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rural areas where access to electricity is limited (Kashyap et al., 2003). Specific bacteria carry out this type of anaerobic fermentation, and in addition to biogas, a stabilized biosolid is obtained (Campos et al., 2012). The substrates that are treated in anaerobic digestion must be prepared in such a way that microorganisms can easily digest them, hence the importance of subjecting the lignocellulosic product of bagasse to pretreatment before the hydrolysis stage to delignify the biomass and increase the accessibility of cellulose, thus improving bioconversion (Abraham, 2020; Yoo, 2020). These pretreatments will help the anaerobic digestion process be carried out in a shorter time; however, operating conditions such as retention time and temperature influence the process.

This research applied a mesophilic anaerobic digestion process to treat vinasse and bagasse of Agave durangensis from the mezcal industry with an activated sludge inoculum. The bagasse and vinasse residues were pretreated thermally and chemically, respectively. Digestions with a lower organic load of bagasse resulted in higher methane percentages.

2. Materials and methods

2.1 Materials

The substrates of vinasse and bagasse of Agave durangensis were sampled from a local winery in Nombre de Dios, Durango. Using a Felisa model, FE-396 autoclave for bagasse pretreatment at a temperature of 120 °C, a mixture of sodium hydroxide, carbonate, and sodium bicarbonate was used for vinasse pretreatment until both pH's of 8 and 9 were reached. It was sampling the activated sludge inoculum from a biological wastewater treatment plant. Figure 1 shows the substrates used in this research.

a) b) c)

Figure 1: a) Substrates of bagasse, vinasse and activated sludge, b) Non and pretreated bagasse, c) Non pretreated and pretreated vinasse

2.2 Experimental Setup

It carried out laboratory-scale experiments in glass reactors with a capacity of 250 mL and an operating volume of 150 mL. Mixtures of 90% pretreated stillage at pH 8 and 9 were used with 5 and 10% by weight of pretreated bagasse screened through a #40 mesh and 10% activated sludge inoculum. The experiments were carried out at a temperature of 35 °C ±1 and a retention time of 30 days. A Shel Lab model S14 incubator was used for the digestion, and the gas collection was carried out using plastic syringes of 60 mL capacity. A Landtec model 5000 equipment was used for its measurement. During the experiment, the reactors were analyzed every five days until the stabilization of the process was reached, evaluating two types of factors (pH and organic load), each with two levels.Figure 2 shows a run of the anaerobic digestion experiments or biochemical methane tests.

Figure 2: Anaerobic digestion experiments

2.3 Process kinetics

The monitoring and analysis of the biological kinetics of the process was carried out with the parameters of pH, alkalinity, total solids (TS), total volatile solids (TVS), total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), total volatile acids (TVA), total carbohydrates, reducing sugars, nitrate nitrogen, biogas volume, and % methane. An initial characterization of the vinasse, bagasse, and activated sludge substrates was also carried out. It was analyzing bagasse for lignin, cellulose, and holocellulose. For biogas measurement, collecting a minimum amount of 30 mL was necessary for analysis, so not all bottles were analyzed after five days. In the Landtec Biogas 5000 equipment, analyzed: % methane (CH_4) in volume, carbon dioxide (CO_2), diatomic oxygen (O_2), the balance of other gases that can be found, and concentration in ppm of hydrogen sulfide (H_2S).

3. Results

Table 1 shows the results of the initial characterization of the stillage, with and without pretreatment, with pretreatment 1 neutralizing the stillage to a pH of 8 and pretreatment 2 neutralizing it to a pH of 9.

Table 1: Initial characterization of initial stillage without and with pretreatment

Parameter	Vinasse without pretreatment	Vinasse pretreatment 1	Vinasse pretreatment 2
pH	3.5 ± 0	8 ± 0.01	9.12 ± 0.04
Alkalinity	860 ± 44.9	1,020 ± 52.5	2,750 ± 47.7
COD, mg/L	38,982 ± 165.5	2,064 ± 136.4	3,450 ± 125.6
TS, mg/L	9,463 ± 75.7	7,012 ± 88.9	6,807 ± 92.5
TVS, mg/L	6,810 ± 105.8	2,660 ± 121.5	4,273 ± 101.7
TSS, mg/L	315 ± 2.2	308 ± 2.5	302 ± 1.8
VSS, mg/L	295 ± 1.6	355 ±1.4	371 ± 2.01

Table 1 shows that, by modifying the pH of the stillage, its alkalinity increases, which will help the process withstand the changes that occur during the stages of anaerobic digestion. In addition, the reduction in COD concentration also reduced the organic load of the stillage and could precipitate some organic compounds, causing them to become less soluble. However, these compounds do not decompose or degrade into simpler components; they only change state, going from being dissolved in liquid to solids in sludge. Upon precipitation, the amount of ST and STV decreased in the liquid phase since part of the organic and inorganic matter was converted into precipitated solids. Maintaining TSS and SSV, the organic load in suspended particles is not altered significantly in the neutralization. Table 2 shows the characterization of bagasse without and with thermal pretreatment.

Table 1: Characterization of Bagasse without and with thermal pretreatment

Parameter	Bagasse without pretreatment	Bagasse with pretreatment
Lignine	32.44 ± 0.02	27.3 ± 0.05
Celulose	66.65 ± 0.3	58.05 ± 0.1
Holocelullose	67.15 ± 0.01	80.61 ± 0.02

Based on the data in Table 2, it is evident that the percentages of cellulose and hemicellulose in Agave durangensis are higher than those of Agave tequilana. This phenomenon could be closely linked to the specific environmental conditions each species develops. It is possible that habitat variations, including differences in soil, climate, and water availability, contribute significantly to the chemical composition of the plants.

According to the data obtained from the organic compounds of agave durangensis and compared with previous research on Agave tequilana, Agave durangensis has a higher percentage of cellulose and hemicellulose. This finding suggests a greater availability of carbon sources for the anaerobic system. In addition, other studies (Contreras-Hernández et al., 2018) have reported the presence of flavonoids, which are related to the presence of lignin. These compounds probably affect the system that facilitates the development of microorganisms in the anaerobic digestion process. The results obtained show that the thermal pretreatment is influential since a reduction of 11.84% of lignin was obtained, thus facilitating the anaerobic digestion process and giving the possibility of increasing methane production in the anaerobic digestion process.

Figures 3, 4, 5, and 6 show the results of the behavior of solids during anaerobic digestion for pH's of 8 and 9 and at 5 and 10% bagasse.

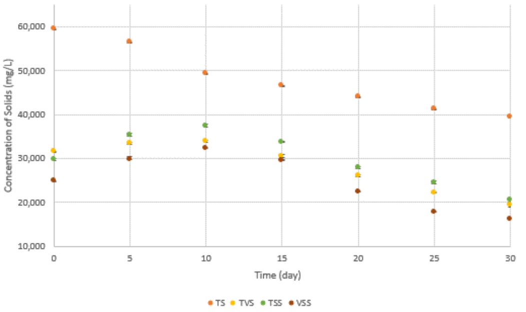

Figure 3: Solids Biological Kinetics (5% bagasse and pH 8)

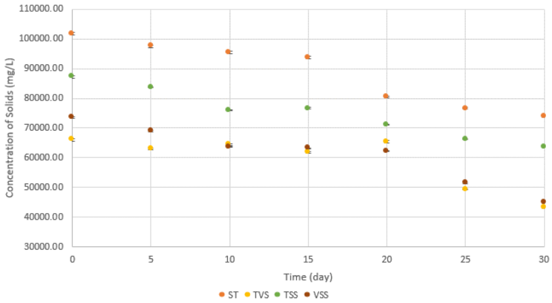

Figure 4: Solids Biological Kinetics (10% bagasse and pH 8)

Observing all the experiments, reductions in solids can be seen; however, at a lower load of 5% bagasse and a pH of 9, the reduction is more significant, in this case 43%. The measurement of solids indicates biological activity and degradation of organic matter since the reduction of solids indicates the production of biogas with high methane content, depending on the initial characterization of the digested substrates.

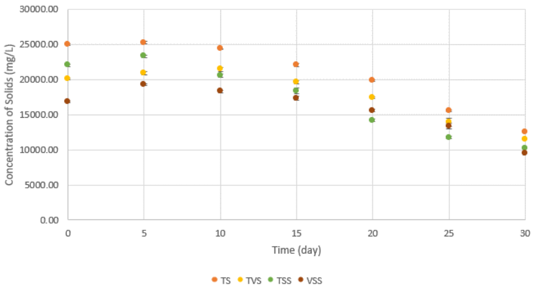

Figure 5: Solids Biological Kinetics (5% bagasse and pH 9)

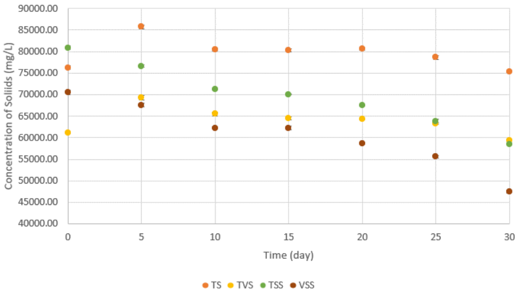

Figure 6: Solids Biological Kinetics (10% bagasse and pH 9)

Table 3 shows the solids reduction at different pH conditions and % bagasse during the anaerobic digestion. The highest reductions in solids occurred at pH 9 and 5% bagasse. In the ANOVA analysis, the p-value for pH was 0.024, and for bagasse percentage, it was 0.034. Both values are below 0.05 and, therefore, significant.

Table 3: Results of solids reduction during the anaerobic digestion process

Parameter	pH 8 5% bagasse	pH 8 10 % bagasse	pH 9 5% bagasse	pH 9 10% bagasse
TS, %	33.8 ± 1.2	27.3 ± 0.5	50.1 ± 0.9	1.28 ± 1.0
TVS, %	38.2 ± 0.9	34.2 ± 1.0	39.9 ± 0.5	2.66 ± 0.7
TSS, %	30.7 ± 0.01	26.9 ± 0.03	53.5 ± 0.03	27.75 ± 0.02
VSS, %	35.2 ± 0.01	38.7 ± 0.04	43.3 ± 0.02	32.68 ± 0.01

Figure 7 shows the behavior of the chemical oxygen demand of the experiments. Observing that COD was reduced in all the experiments, obtaining a higher COD removal of 73% with 5% bagasse and a pH of 9.

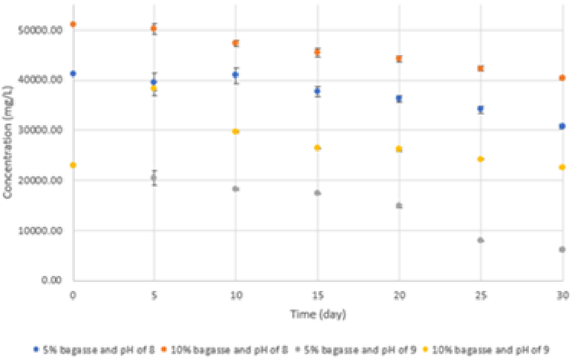

Figure 7: COD behavior during anaerobic digestion experiments

Figures 8 and 9 show the alkalinity and pH of the anaerobic digestion process. Observing that the alkalinity and pH increased during the anaerobic digestion process helped to continue the digestion stages and not inhibit the process. Alkalinities remained above 2,000 mg/L and pH above 6, indicating activity of the methanogenic microorganisms, which is usually in the pH range of 6.5 and 8. Sufficient alkalinity in an anaerobic digester provides buffer capacity and stability to the system.

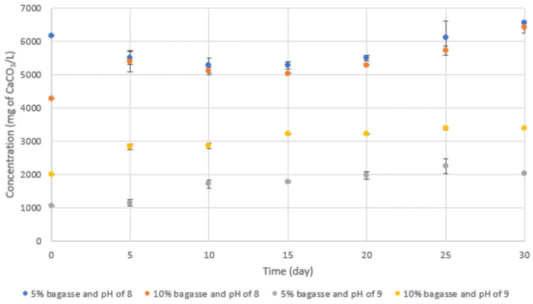

Figure 8: Alkalinity during the anaerobic digestion process

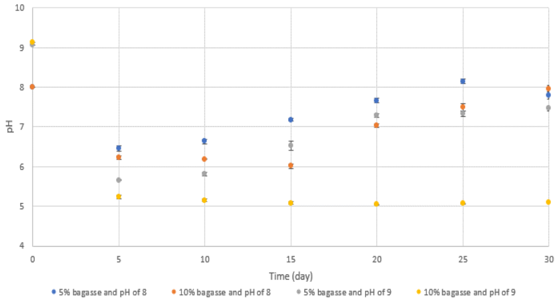

Figure 9: pH during the anaerobic digestion process

Figure 10 shows methane production in the anaerobic digestion processes, where more than 68 % of methane is observed on day 25 at conditions of 5 % and 10 % bagasse at pH 8. However, on day 30, the experiment at pH 9 with 5 % bagasse produced more than 60 % methane. The results indicate the feasibility of producing biogas, specifically methane gas, from mezcal industry wastes subjected to pretreatment and with the addition of activated sludge as inoculum.

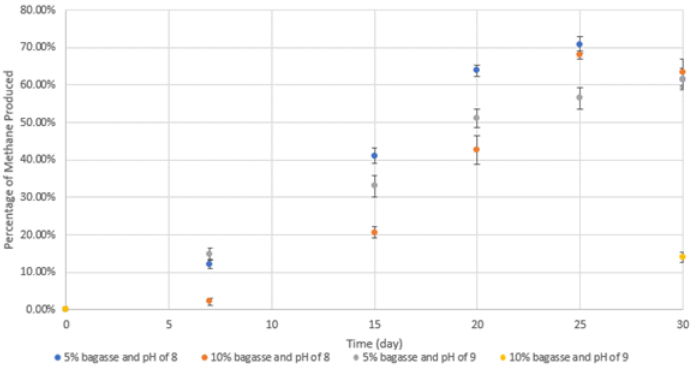

Figure 10: Methane production in anaerobic digestion experiments

4. Conclusions

All experiments generated biogas and methane during the anaerobic digestion. However, the highest production on day 25 were the experiments at pH of 8 and organic loads of 5% and 10% bagasse, reaching a production of over 60% methane and a reduction of 35.2 and 38.7% in volatile suspended solids (VSS), respectively. However, considerable methane production was also observed in the experiment with pH nine conditions with an organic load of 5%, obtaining over 60% methane production and a 43.3% reduction in volatile suspended solids (VSS) after 30 days. Indicating that the anaerobic digestion process was not inhibited because the pH and alkalinities were maintained in the ranges of 6 and 8 pH and alkalinities above 2,000 mg/L. The production of Total Volatile Acids remained in the range of 1704 y 748.8 mg/L Indicating that at a retention time of 30 days at a mesophilic temperature of 35°C, the production of these acids did not inhibit the process. The structure of bagasse before and after pretreatment is essential to conclude that pretreatment modified the lignin structure, which resulted in higher biogas generation during anaerobic digestion. However, these studies were not performed. This study concludes that anaerobic digestion can treat this waste type to obtain methane as biofuel.

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