BIOGAS PRODUCTION FROM GLICEROL PRETREATMENT LIQUOR

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ABSTRACT

Biogas, a renewable energy source rich in CH_4 (50-85%), has diverse applications in electricity and heat generation and serves as a biofuel, particularly in the form of biomethane. Recent studies indicate that incorporating glycerol into anaerobic digestion processes can enhance biogas production. This research aims to utilize the liquor derived from glycerol pretreatment of sugarcane bagasse, a by-product of second-generation ethanol (2G ethanol) production, in a Biochemical Methane Potential (BMP) test. The liquor is obtained by heating sugarcane bagasse to 195°C with a mixture of 50% (w/w) glycerol and 10% (w/w) solids for 30 minutes, producing a liquid fraction rich in hemicellulose, lignin, and glycerol. Anaerobic digestion is conducted at 35°C, and gas samples are collected to measure methane concentration in the biogas. Notably, no lag phase was observed during the BMP test, indicating the absence of substrate inhibition despite high levels of lignin and glycerol. A post-BMP test yielded a methane production rate of 783.04 NmL CH_4/gVS, surpassing results from tests on vinasse, another by-product of ethanol production. Thus, the glycerol-pretreatment solution shows significant promise as a substrate for methane production through anaerobic digestion.

Keywords: Glycerol; Methane production; Anaerobic digestion; Energy balance.

1 INTRODUCTION

The biorefinery concept offers an efficient strategy for converting biomass into bioenergy, biofuels, and value-added bioproducts, thereby minimizing waste and maximizing economic returns. In Brazil, the sugarcane biorefinery sector is highly advanced, producing a variety of sugars, first-generation ethanol (1G ethanol), and generating heat and bioelectricity through the combustion of sugarcane bagasse and straw. This sector is energy self-sufficient and sells surplus energy. Despite cogeneration, there remains an excess of lignocellulosic biomass that can be used to produce second-generation ethanol (2G ethanol) and biogas, further strengthening the sector and integrating the 1G2G production chain [1].

Additionally, it is feasible to integrate this process with biodiesel production. Biodiesel, produced via transesterification, is a renewable and biodegradable alternative to diesel, with lower carbon dioxide and sulfur emissions [2]. The increasing production of glycerol, a byproduct of biodiesel, presents both environmental and economic challenges. Therefore, converting glycerol into valuable products is essential for the sustainability of the biodiesel industry [3].

Crude glycerol can be directly used in the pretreatment of lignocellulosic biomass, a critical but expensive step in producing fermentable sugars. Various pretreatment methods, such as organosolv processes, have been evaluated, demonstrating high selectivity and efficiency. Glycerol is attractive due to its low cost and effective biomass desconstruction properties, promoting delignification while preserving cellulose. This makes glycerol an effective pretreatment agent for producing second-generation ethanol from lignocellulosic biomass [4-7].

This process not only yields cellulose-rich fibers but also generates a pretreatment liquid fraction with high concentrations of hemicellulose, lignin, and glycerol, presenting an opportunity for biogas production. Recent studies have shown that incorporating glycerol into anaerobic digestion processes accelerates biogas production, providing a more environmentally sustainable solution for managing biodiesel byproducts [8]. Therefore, this work aims to explore biogas production through the crude glycerol pretreatment liquid fraction.

2 MATERIAL & METHODS

The study employed experimental techniques to evaluate the biochemical methane potential (BMP) according to the VDI 4630 standard, as detailed in VOLPI et al. (2022)[9]. The substrate used in the BMP tests was derived from the pretreatment of sugarcane bagasse at 195°C with a mixture of glycerol: water (50:50), with 10% (w/w) solids for 30 min, yielding a liquid fraction rich in hemicellulose, lignin and glycerol. The substrate-inoculum mixture was prepared at a 1:2 ratio. The inoculum originated from an Upflow Anaerobic Sludge Blanket (UASB) reactor located at a poultry slaughterhouse. The flasks were incubated at 35°C, and the pressure and CH_4 concentration in the biogas produced were measured daily using gas chromatography.

A revised stacked sigmoidal function (Eq. 1), derived from the Boltzmann double sigmoid model [9], was employed to simulate the volumetric production of CH_4 over time. This approach acknowledges that complex substrates typically result in a series of successive CH_4 production peaks due to variations in the biodegradability of individual substrates.

$$V_{CH_4}^{STP}(t) = V_{CH_4}^{max} \times \left(\frac{p}{1 + e^{\left(\frac{4r_1.(t_1 - t)}{V_{CH_4}^{max}.p}\right)}} + \frac{1-p}{1 + e^{\left(\frac{4r_2.(t_2 - t)}{V_{CH_4}^{max}.(1-p)}\right)}} \right) \qquad (1)$$

where $V_{CH_4}^{STP}(t)$ is the specific CH_4 production in time (NmLCH4.gVS^{-1}), $V_{CH_4}^{max}$ is the maximum specific volumetric production achieved in the experiment (NmLCH4.g VS^{-1}), p is the proportion between the ordinate values of the first and second stacked sigmoid, t_1 and t_2 are the times at which the production of the first and second sigmoidal patterns reach their maximum rate (day), and r_1 and r_2 are the maximum production rates of CH_4 for the first and second sigmoidal patterns, respectively (NmLCH4.gVS^{-1}.d^{-1}).

The energy balance was calculated by incorporating energy contributions from the Biochemical Methane Potential (BMP) processes, as well as accounting for energy consumption during biogas purification and the typical efficiencies of a Combined Heat and Power (CHP) system. The energy output per ton of substrate was estimated using Equation 2.

$$E_{p_{CH_4}} = V_{max} \times \frac{TVS}{ton\ residue} \times 34{,}5\ MJ.Nm^3CH_4^{-1} \qquad \text{(Equation 2)}$$

where V_{MAX} (mL.gSV^{-1}) represents the cumulative production of methane, and TVS denotes the total solids yield per ton of residue.

The electricity consumed for biogas purification was estimated at 10% of the total electricity generated by cogeneration, as specified by Mainardis et al. (2019)[10]. Considering the standard efficiencies of a CHP system, the Electrical Power (EP) was converted into thermal energy (ET) and electrical energy (EE) using Equations 3 and 4.

In these equations, the combustion engine efficiency is represented by 0.85, the conversion factor from EP to ET is 0.66, and the conversion factor from EP to EE is 0.33, as indicated by Cano et al. (2015)[11].

$$E_T = E_p \times 0.85 \times 0.66 \qquad \text{(Equation 3)}$$

$$E_E = E_p \times 0.85 \times 0.33 \qquad \text{(Equation 4)}$$

3 RESULTS & DISCUSSION

Figure 1 depicts the cumulative methane production over time. The data reveals two distinct stages of anaerobic digestion. This phenomenon can be attributed to the composition of the liquor, which contains both readily degradable monomeric sugars and more complex carbohydrates, lignin, and glycerol. The cumulative methane volume surpasses that reported by Volpi et al. (2022)[9] (610 NmLCH4.gSV-1) using deacetylation liquor from the alkaline pretreatment of sugarcane bagasse. This disparity is likely attributable to the presence of glycerol in the liquor of the present study. Existing literature supports the notion that glycerol enhances anaerobic digestion [12].

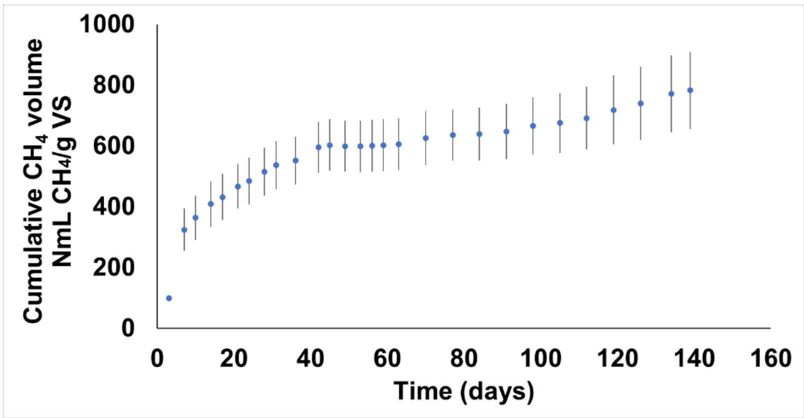

Figure 1 Cumulative CH 4 volume from BMP of liquor digestion.

Table 1 displays the obtained kinetic data. Notably, from the kinetics, specifically the value of t1, it becomes evident that there was no inhibition of the inoculum by the substrate, as evidenced by the absence of a lag phase. The maximum production rate was observed between days 8 and 9 of operation.

Table 1 Kinetic model parameters of anaerobic digestion using a modified Boltzmann double sigmoid model.

Model parameters	
Vmax (NmL CH_4/g VS)	783.04 ± 89.91
p	0.77 ± 0.01
t1 (day)	8.85 ± 0.69
t2 (day)	110.86 ± 0.97
r1 (NmL CH_4/g VS day)	15.23 ± 1.62
r2 (NmL CH_4/g VS day)	2.77 ± 0.68
NRMSE	2.940
r^2	0.993

From the anaerobic digestion of the liquor, thermal energy recovery amounted to 859.13 MJ per ton of substrate, while electrical energy recovery reached 462.61 MJ per ton of substrate.. This energy recuperated from anaerobic digestion holds significant potential for utilization during various stages of second-generation ethanol production, particularly during pretreatment, which demands elevated temperatures. Therefore, apart from facilitating energy retrieval for the process, it offers a practical outlet for crude glycerol, an abundant byproduct of biodiesel production.

Table 2 Thermal and electric energy from anaerobic digestion.

Thermal energy (MJ.ton^{-1} substrate)	Electric energy (MJ.ton^{-1} substrate)	Electrical Power (MJ.ton^{-1} substrate)
859.13	462.61	1727.76

4 CONCLUSION

The utilization of glycerol-pretreated liquor demonstrates significant promise as a substrate for methane production through anaerobic digestion. The absence of a lag phase suggests no inhibition of the inoculum by the substrate. Beyond offering a practical application for glycerol, a biodiesel production byproduct and, anaerobic digestion of the pretreated liquor can generate energy, which can be further harnessed within the process.

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