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Effects of vinasse concentration on biogas production: An experimental work and case study in the context of RenovaBio in Brazil

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ABSTRACT

Vinasse composition varies throughout the year, which may affect methane production. To assess the effects of the chemical oxygen demand (COD) on methane yield, we fed a reactor with increasing organic loading rates ranging from 1.15 to 4.56 g COD l^{-1} day^{-1}. In the second part of this study, we compared two scenarios for the state of Sao Paulo: 1) average vinasse COD; 2) ideal vinasse COD (38.8 g l^{-1}). We found that the maximum methane yield was obtained at an OLR of 2.66, equivalent to a COD of 38.8 g l^{-1}, and could increase the sugarcane mill energy production by 15.6 %. Considering the state of Sao Pauo, if all the vinasse was used to produce biogas, 3.9 million tons CO_{2eq} (CBIOs) emission would be avoided yearly. Concentrating all the vinasse to the ideal COD would increase it by 3.2 %. Therefore, vinasse concentration would have little effects on a state-scale.

1. Introduction

In Brazil, sugarcane and its derived products alone accounts for nearly 20 % of the country's energy matrix (Ministry of Mines and Energy, 2021). The nation currently produces over 600 million tons of sugarcane annually across 10 million hectares, with over 90 % of ethanol production concentrated in the Center-South region, and more than half of this output originating from the state of São Paulo (UNICA, 2022).

The sugarcane industry's extensive processing to multiple products leads to substantial on-site byproduct generation (Jendiroba, 2006). Vinasse (fermentation and distillation residue), the main byproduct, is a dark brown effluent, composed of 93 % water and 7 % of organic matter and minerals (Sica et al., 2020a). Although it is used as a fertilizer to replace potassium fertilizers for sugarcane crops (Sica et al., 2020b), the improper disposal of vinasse can result in environmental pollution (Laime et al., 2011; Romanholo Ferreira et al., 2011). Moreover, a significant portion of São Paulo's sugarcane plants are situated in areas with moderate to high pollution vulnerability and shallow groundwater, leading to the introduction of technical standards like P4.231 by São Paulo's State Sanitation Technology Company (CETESB) in 2005 (CETESB, 2005).

This regulation dictates that potassium should not exceed 5 % of soil cation exchange capacity, resulting in increased application costs due to the need for applying vinasse at greater distances (Freire and Cortez, 2000). Several strategies to improve vinasse treatment and application sustainability are emerging within the Brazilian ethanol industry. These include: i) evaporation-driven concentration to reduce transported volumes (Freire and Cortez, 2000; Sica et al., 2017); and ii) anaerobic digestion (AD) to produce biogas and enhance energy balances (Salomon and Lora, 2005; Sica et al., 2020b).

While both treatments can function independently, concentrating vinasse prior to AD offers economic and environmental advantages. This approach may increase AD efficiency, reduce the reactor size and costs, and reduce the volume of biofertilizer effluent, subsequently mitigating environmental impact and management expenses (Sica et al., 2020b). Yet, integrating these processes demands substantial investments due to the vast volumes of vinasse generated, as 10 to 15 l of vinasse are generated for every liter of ethanol produced (Moraes et al., 2015). In 2020/2021, São Paulo produced 14.4 billion liters of ethanol, resulting

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in 144 to 216 billion liters of vinasse from around 170 ethanol plants (UNICA, 2022).

Amid this context, Brazil's RenovaBio Program, initiated in 2017, incentivizes vinasse AD by granting carbon credits. These credits, known as CBIOs, are equivalent to one ton of avoided carbon dioxide (CO_2) emissions due to biofuel production. Fuel distributors are obligated to purchase CBIOs, and these credits are accessible to interested investors (ANP, 2019; Grassi and Pereira, 2019). Notably, Moraes et al. (2014) estimated that biogas reactors processing all of Brazil's vinasse could generate 6.9×10^3 GWh per year, energy that is equivalent to 7.5 % of the energy produced at the world's largest hydroelectric plant located in Itaipu, Brazil.

Thus, the adoption of technologies such as AD is gaining traction in Brazil and further research is imperative to optimize these practices. Sica et al. (2020b) demonstrated that concentrating vinasse can enhance AD efficiency, highlighting its reliance on initial chemical oxygen demand (COD) and organic load rate (OLR). Moreover, vinasse composition fluctuates throughout the harvest season potentially causing variations in digester loading over the year (Godoi et al., 2019). Therefore, investigating correlations between initial vinasse composition and biogas production is crucial for predicting the potential methane production and optimizing this process. However, there is a lack of studies assessing how different COD concentrations will affect methane yield and how these effects will imply in practice the amount of CBIOs granted for the methane production from vinasse.

The objective of this study was to assess the effects of different vinasse COD concentration would affect methane yield and the potential amount of CBIOs granted for the biogas production of vinasse. Thus, in the first part of this study, we carried out an experimental work aiming to identify the optimal OLR to attain peak efficiency in an upflow anaerobic sludge blanket (UASB) reactor and calculate the potential energy production increase in an ethanol plant by performing the AD of concentrated vinasse. Our hypothesis was that *by concentrating the vinasse, it would enhance the AD efficiency up to a threshold before inhibiting the process and reducing efficiency.* In the second part of this study, we compared two scenarios considering that all vinasse produced in the state of Sao Paulo would be used to produce biogas: 1st scenario) vinasse monthly COD average; 2nd scenario) all vinasse being concentrated to achieve the highest methane yield, based on results from the first part. Then we calculated how much the concentrated vinasse would increase the CBIOs distributed for this purpose in the state of Sao Paulo.

2. Materials and methods

2.1. Vinasse

The vinasse used in this study was collected from an ethanol plant in the city of Iracemápolis, in the state of São Paulo, Brazil, and had an initial COD of 30 $g \cdot l^{-1}$. The material was taken to the Laboratory of Sugar and Alcohol of the University of São Paulo, in the College of Agriculture "Luiz de Queiroz", in Piracicaba, where it was concentrated through evaporation to a COD of approximately 800 $g \cdot l^{-1}$. After that, it was shipped to the Bioconversion Center, at the University of Georgia, Athens (Georgia, USA) where the experiments were carried out. The concentrated vinasse was then diluted with distilled water to different levels of initial COD required for the experiments.

2.2. Experimental work (part 1)

The anaerobic digestion was carried out in a 4.5-l upflow anaerobic sludge blanket (UASB) reactor with a constant retention time of 14 d throughout the experiment. Additional information about the reactor setup and processes are reported in Sica et al. (2020b). The reactor was fed daily with 324 ml of vinasse. Before starting the experiment, the reactor was fed with diluted vinasse for stabilization of AD parameters. After the reactor was stabilized, the digester was fed with vinasse containing 15 $g \cdot l^{-1}$ COD in the first week. The concentration of vinasse was increased by 5 g COD l^{-1} every two weeks until reaching 60 g COD l^{-1} in the 19th week of the experiment. The OLR was increased proportionally with increasing COD concentrations (Table 1).

2.2.1. Analytical methods

Effluent samples were collected and analyzed three times weekly to determine COD removal. The volume of biogas produced was measured daily using a wet-tip gas meter (wettipgasmeter.com), while methane (CH_4) concentration was measured once a week by gas chromatography (SRI 310 gas chromatograph, SRI Instruments, Torrance CA, USA). The pH of digestate was measured using an Accumet® AP62 portable pH/mv meter (Fisher Scientific, USA).

The effluent volatile fatty acids (VFA) contents were assessed using the methods outlined by Wang et al. (2016). Chemical oxygen demand (COD), total nitrogen (TN), total NH_4^+-nitrogen (TAN), and total phosphorus (TP) measurements were performed on 100-fold diluted samples employing HACH kits: 8000, 10,072, 10,031, 8191, respectively (HACH Company, Loveland CO, USA).

2.2.2. Statistical analysis

A one-way ANOVA was performed for each parameter measured and presented in Table 3. For all parameters, the ANOVA indicated a significant difference between OLR, thus, Tukey's HSD test was performed to assess the differences between means ($p < 0.05$) (SPSS IBM Statistics 28.0). Polynomial regressions for the relationship between initial vinasse COD content and COD removal and methane yield were conducted using SigmaPlot 14.0. Principal component analysis (PCA) was executed in SPSS IBM Statistics 28.0.

2.3. Case study (part 2)

In the second part of this study, we conducted a case study to compare two scenarios:

1) Performing AD on the average vinasse, based on the average monthly COD contents of the vinasse in the state of Sao Paulo (Godoi et al., 2019).
2) Concentrating the vinasse to a COD of 38.8 g l^{-1}, which, based on the results from part 1, it is the COD in which the highest methane yield can be reached.

For both scenarios, we made assumptions as the total monthly ethanol production and vinasse generation, as well as the total COD generated from vinasse in the state of Sao Paulo every month. More information about this assumptions and their sources are presented in Table 2.

3. Results

3.1. Part 1: experimental work

3.1.1. COD removal

COD removal significantly increased with increasing OLR between 1.15 and 2.29 $g \cdot l^{-1}$ day^{-1} and considerably dropped as the OLR surpassed 3.82 $g \cdot l^{-1}$ day^{-1} (Fig. 1). The second-degree polynomial equation (Eq. (1)), yielding $R^2 = 0.9111$, models COD removal during anaerobic vinasse digestion across variable OLR.

$$y = -8.7355x^2 + 45.278x + 27.096 \quad (1)$$

where, y is the COD removal (%) and x is the OLR in g l^{-1} day^{-1}. According to this equation, the maximum COD reduction of 85.77 % would occur at the OLR of 2.59 g l^{-1} day^{-1}.

Table 1
Initial chemical oxygen demand (COD) concentrations of vinasse and the organic load rate (OLR) to the reactor at different weeks after the start of the experiment.

Weeks	1–2	3–4	5–6	7–8	9–10	11–12	13–14	15–16	17–18	19–20
COD ($g\ l^{-1}$)	15	20	25	30	35	40	45	50	55	60
OLR ($g\ l^{-1}\ day^{-1}$)	1.15	1.53	1.91	2.29	2.68	3.06	3.44	3.82	4.20	4.59

Table 2
Assumptions made for the calculations of Scenario 1 and Scenario 2 used for the case study, considering the total ethanol and vinasse production in the state of Sao Paulo and the average vinasse COD at each month of the harvest season.

		Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Total
Total ethanol[a]	1000 m^3	808	1918	1862	2122	2084	1903	920	286	11,903
Total vinasse[b]	1000 m^3	10,100	23,975	23,275	26,525	26,050	23,787	11,500	3575	148,788
Vinasse COD[c]	kg m^3	33	34	29	34	30	31	35	40	33 ± 3[d]
Total COD	1000 tons	333.3	815.2	674.9	901.9	781.5	737.4	402.5	143	4789

[a] Based on the bi-weekly report of the 2021/2022 harvest by the Brazilian Sugarcane Industry and Bioenergy Association (UNICA, 2023).
[b] Considering an average generation 12.5 l of vinasse per liter of ethanol produced (Moraes et al., 2015).
[c] Average values for different months during the sugarcane harvest season, based on (Godoi et al., 2019).
[d] Average value followed by the standard deviation.

Table 3
Volatile fatty acids (VFA), pH, total NH_4^+-N (TAN), total N (TN), the percentage of TN as TAN, and total phosphorus (TP) of digestate during operation of digester at different organic load rates (OLR).

OLR ($g·l^{-1}$ day^{-1})	VFA ($mg\ l^{-1}$)	pH	TAN ($mg\ l^{-1}$)	TN ($mg\ l^{-1}$)	TAN/TN (%)	TP ($mg\ l^{-1}$)
1.15	647.0 bc	7.05 a	212.6 d	334.4 b	63.5	55.5 c
1.53	725.0 bc	6.95 ab	245.4 cd	340.0 b	72.1	61.0 c
1.91	744.0 abc	7.15 a	252.6 cd	325.0 b	77.7	61.3 c
2.29	702.0 bc	7.30 a	324.3 bcd	370.8 b	87.4	57.5 c
2.68	620.0 c	7.25 a	329.9 bcd	442.5 b	74.5	57.5 c
3.06	568.0 c	7.20 a	353.3 bc	523.3 ab	67.5	74.5 bc
3.44	610.0 c	7.15 a	359.0 bc	653.3 ab	54.9	82.3 abc
3.82	732.0 bc	7.10 a	442.9 ab	801.7 a	55.2	98.9 ab
4.20	848.5 ab	6.50 b	451.6 ab	808.1 a	55.8	103.9 a
4.59	947.5 a	5.90 c	516.7 a	818.3 a	63.1	110.2 a

3.1.2. Methane production

Methane production (l-CH_4/g-COD) increased as the OLR increased from 1.15 to 3.06 $g·l^{-1}$ day^{-1}. However, further increase in OLR from 3.06 to 4.59 $g·l^{-1}$ day^{-1} resulted in considerable reduction in methane production (Fig. 2). The second-degree polynomial equation (Eq. (2)), with $R^2 = 0.8792$, represents the efficiency of AD in converting vinasse's COD into methane as a function of OLR.

$$y = -0.0411x^2 + 0.2179x - 0.0094 \quad (2)$$

where, y is the methane production (l-CH_4/g-COD) and x is the OLR in $g·l^{-1}$ day^{-1}. According to this equation, the maximum methane production (0.310 l-CH_4/g-COD) would occur at an OLR of 2.66 $g·l^{-1}$ day^{-1}.

3.1.3. Other parameters

The VFA and pH did not have significant changes with increasing OLR between 1.15 and 3.82 $g·l^{-1}$ day^{-1}. At OLR 4.59 $g·l^{-1}$ day^{-1}, VFA increased to 947.5 $mg·l^{-1}$ and pH dropped to 5.9. The TAN, TN, and TP of the effluent increased as OLR increased (Table 3). The TAN/TN increased from 63.5 % to 87.4 % as OLR increased from 1.15 to 2.29 $g·l^{-1}$ day^{-1}. Further increase in OLR resulted in decrease of TAN/TN to 55.2 % at an OLR of 3.82 $g·l^{-1}$ day^{-1} (Table 3).

3.1.4. Principal component analysis

Considering the relationship of the parameters assessed in this study, a principal component analysis on covariance was performed. The variation of C1 + C2 represented 62.3 % of the total variability. Most of the parameters were on the positive quadrant for both components. COD removal and methane yield were in the negative quadrant for component 2, and on negative and positive quadrants for C1, respectively (Fig. 3).

3.1.5. Simulation of energy production

Using Eqs. (1) and (2), the potential energy production increase at the ethanol plant was calculated. For a vinasse with average COD of 30 g l^{-1} (OLR 2.29 g l^{-1} day^{-1}), the methane production per ton of sugarcane would be 6904 l, representing an increase of 14.6 % of the energy production with bagasse cogeneration in the ethanol plant. By concentrating the vinasse and increasing the OLR to 2.66 and 3.06 g l^{-1} day^{-1}, the methane production would increase to 7393 and 7353 l, respectively, representing an increase of 15.6 % and 15.5 % in the energy generation, respectively (Table 4).

3.2. Case study

The calculations made in the case study indicate that the methane yield for average vinasse COD content in the state of Sao Paulo (Scenario 1) would range from 0.291 (July) to 0.309 m^3 kg COD^{-1} (November). The highest methane yield would be 0.310 m^3 kg COD^{-1}. Considering that all vinasse generated in the state of Sao Paulo is used to produce biogas and does not go to any kind of concentration process, the biogas produced provide to sugarcane mills 3.9 million CBIOs (ton of CO_{2eq}). If the vinasse was concentrated to 38.8 g COD l^{-1}, these values would increase by 3.2 %, reaching 4.06 million CBIOs (ton of CO_{2eq}). Concentrating the vinasse would also increase the amount of methane production per cubic meter of ethanol (from 126 to 129 m^3) and per ton of sugarcane (from 10.1 to 10.3 m^3) (Table 5).

4. Discussion

4.1. Effects of OLR on anaerobic digestion efficiency

In this study, at initial COD levels up to 30 g l^{-1} (OLR 2.26), there was a notable increase in CH_4 production efficiency and TAN:TN ratio (87 %). Anaerobic microorganisms progressively transform complex biodegradable compounds, like long-chain carbohydrates, lipids, and proteins, into CH_4, CO_2, and other gases across four distinct stages: hydrolysis, acidogenesis, acetogenesis, methanogenesis (Chernicharo,

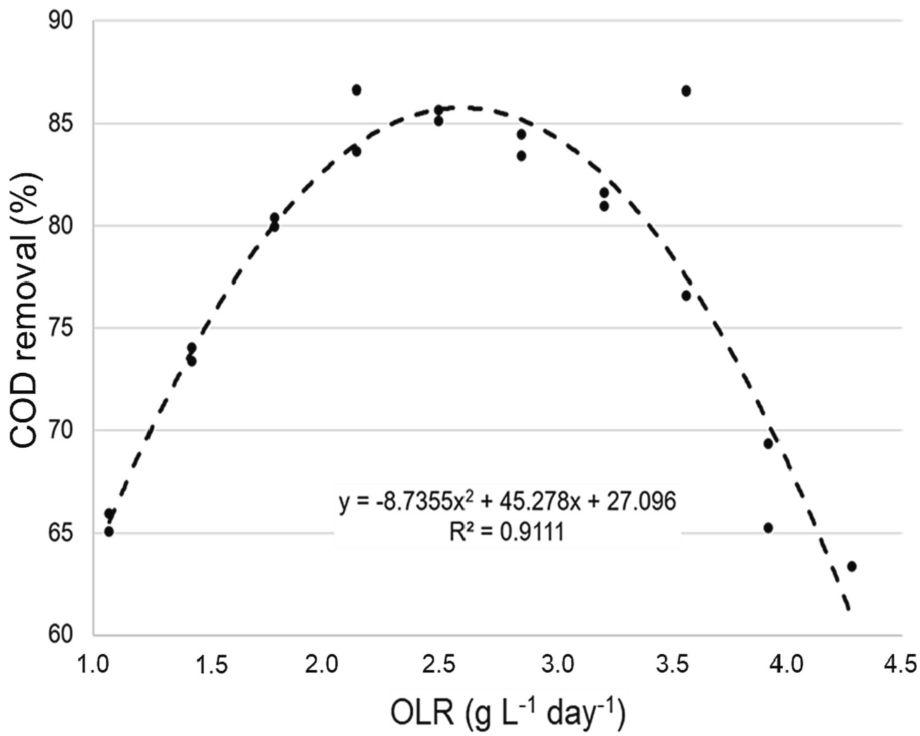

Fig. 1. Chemical oxygen demand (COD) removal (%) of effluent during operation of digester at different organic load rates (OLR).

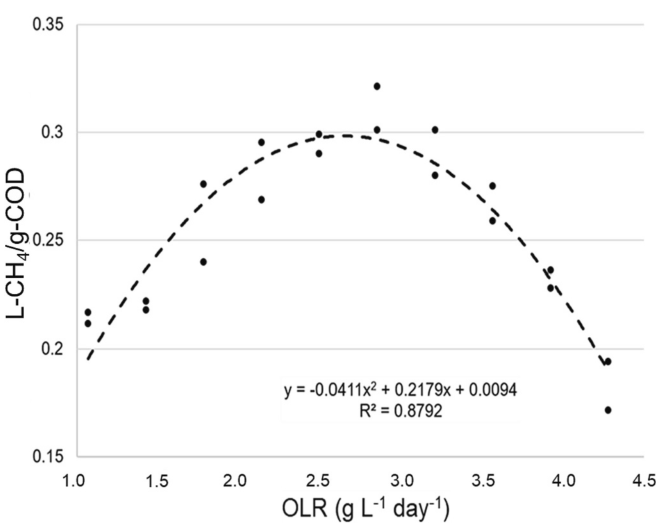

Fig. 2. Volume of methane produced per g of COD removed during operation of digester at different organic load rates (OLR).

2007). Acidogenesis is an intermediate phase which generates ammonium ions and short-chain organic acids including volatile fatty acids (Wang et al., 2016). Considering that at an OLR of 2.26 g l^{-1} day^{-1}, methane production neared its peak. The effluent displayed high VFA and TAN:TN ratios suggesting optimal conditions for the AD process.

Operating the digester at higher COD concentrations initially elevated TAN, TN, and TP levels in the effluent. Increasing the OLR above 3.06 g l^{-1} day^{-1} led to reduced TAN:TN ratio, methane yield, and COD removal. This pattern aligns with the principal component analysis, where TAN, TN, and TP cluster together, while the TAN:TN ratio stands apart. However, the increased TAN, TN, and TP are unlikely to be the inhibiting factor for methane production. Notably, the maximum TAN concentration in the reactor was approximately 500 mg l^{-1}, a value one third of the known inhibitory threshold of 1500 mg l^{-1} (Rajagopal et al., 2013). The TP concentration ranged from 55.5 to 110.2 mg l^{-1}, values much below the preferred concentrations of 414 and 465 mg l^{-1} (Lei et al., 2010; Wang et al., 2015). Hence, supplementing the substrate with phosphorus could potentially enhance the efficiency of vinasse AD and increase the fertilizer value of the effluent. However, further studies are needed to assess the effects supplementing nutrients, as phosphorus, on the methane yield at higher COD concentrations.

The VFA concentration reached the lowest value (568 mg l^{-1}) at the OLR of 3.06 g l^{-1} day^{-1} and significantly increased with increasing OLR, reaching 947.5 mg l^{-1} at the OLR of 4.59. The effluent pH followed a similar trend dropping from 7.3 at an OLR 2.29 g l^{-1} day^{-1} to 5.9 at an OLR of 4.59 g l^{-1} day^{-1}. These results suggest that increasing the OLR did not result in inhibition in the first two phases of AD, namely, hydrolysis and acidogenesis, increasing the organic acids and VFA contents, acidifying the reactor and probably inhibiting the methane production (Silva et al., 2021), however, it reduced the methane yield. Thus, it suggests that to obtain a high AD efficiency with increased OLR, a two-stage AD system is needed with acidogenic and methanogenic processes separated (García-Depraect et al., 2020). Santana Junior et al. (2019) results indicated that by adopting a two-stage AD system, the methane production could 58 % higher than the single-stage system, however, in their experiment, the highest yield was 0.275 ml-CH_4 g-COD^{-1}, slightly lower than the highest yield fond in our study, 0.291 ml-CH_4 g-COD^{-1}.

4.2. COD removal

Previous studies employing vinasse with different initial COD concentrations have shown varying COD removal rates. For instance, Harada et al. (1996) operated a thermophilic UASB reactor at different OLRs up to 28 g l^{-1} day^{-1} and achieved COD removal rates from 39 % to 67 %. In a Brazilian pilot-scale thermophilic UASB reactor (75 m^3), a removal rate of about 72 % was observed for an OLR ranging from 25 to 30 g l^{-1} day^{-1} (Souza et al., 1992). Fuess et al. (2017) and Sica et al. (2020b) obtained 80 % COD removal when feeding a UASB reactor with different initial COD levels. Other studies report higher COD removal rates

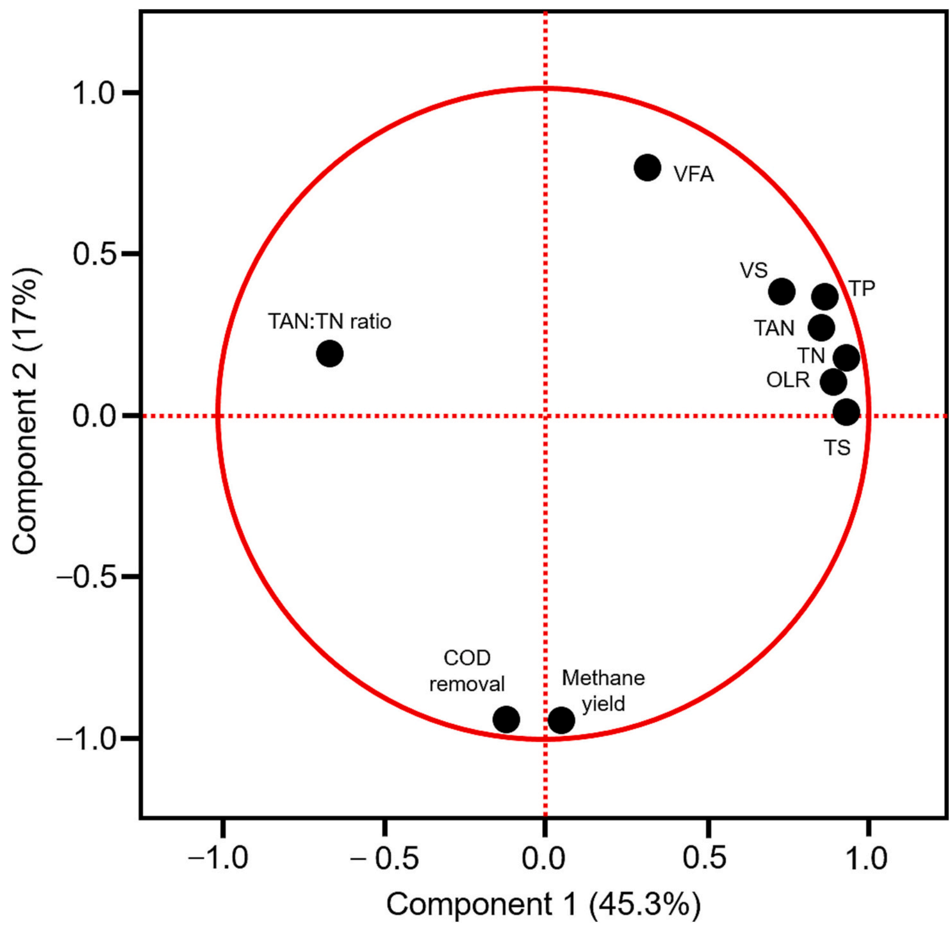

Fig. 3. Principal component analysis (PCA) on covariance of the parameters assessed in this study.

Table 4
Potential COD removal, methane production, and potential energy increase in the ethanol plant at different OLR and vinasse COD concentrations.

OLR ($g\ l^{-1}\ day^{-1}$)	1.53	2.29	2.66	3.06	3.82	4.59
l of CH_4 kg COD^{-1} [a]	220	275	310	290	265	200
COD removal (%)[a]	74	84	85	84	77	60
Volume of vinasse[b] (m^3)	1.5	1	0.74	0.75	0.60	0.50
l of CH_4 ton of sugarcane^{-1}	4891	6904	7393	7353	6091	3598
Kcal from CH_4 ton of sugarcane^{-1} [c]	46,471	65,587	70,238	69,853	57,862	34,185
Potential energy increasing (%)[d]	10.3	14.6	15.6	15.5	12.9	7.6

[a] Calculated according to Eqs. (1) and (2).
[b] Volume of vinasse needed to provide 30 kg of COD.
[c] Considering the calorific power of the methane as 9500 kcal m^{-3} (Lamo, 1991).
[d] Considering 250 kg of bagasse per ton of sugarcane processed (Lamo, 1991) and the bagasse calorific power as 1800 kcal kg^{-1} (Wakamura, 2003), providing an energy of 450,000 kcal from bagasse per ton of sugarcane.

ranging from 82.9 % to 88.5 % when using an influent COD concentration of 31.29 g COD l^{-1} (Craveiro et al., 1986), similar to the values predicted by the polynomial regression reported in this study. This regression indicates a maximum COD removal of 85.1 % for an influent with 35.9 g COD l^{-1} (Eq. (1)).

Theoretical maximum methane yield is 0.350 l g^{-1} COD removed (Nasr et al., 2012). According to Eq. (2), the highest methane production is 0.310 ml-CH_4 g-COD^{-1} when the UASB reactor was operated using vinasse having an initial COD of 38.8 g l^{-1}, equivalent to 82.9 % of the theoretical maximum methane yield. Indeed, according to Eq. (1)., for the highest methane production efficiency COD removal would be 84.1 %. Sica et al. (2020b) reported a similar correlation between COD removal and methane production rate, with results of 0.292 ml of methane per g of COD removed. Harada et al. (1996) reported achieving methane yields of 71.7 % of the theoretical maximum when using a 10-l single-stage UASB reactor, similar to the one employed in this experiment. In another study, Ferraz Júnior et al. (2016) used a two-stage UASB reactor and achieved a higher efficiency of 90.3 %, confirming that the adoption of two-stage anaerobic digesters is a viable approach to increase methane yield. However, further studies are needed to assess the effects of a two-stage AD system on the methane yield at higher COD concentrations.

Therefore, our results are in agreement with our initial hypothesis that *by concentrating the vinasse, it would enhance the AD efficiency up to a threshold before inhibiting the process and reducing efficiency*. However, it is worth noting that these values are considerable at an experimental scale. When we assessed this effects in the scale of the state of Sao Paulo, the increase on methane yield due to vinasse concentration would be only

Table 5

Methane production per COD, total methane production, methane production per ethanol and methane production per ton of sugarcane processed for Scenarios 1 (average vinasse COD presented in Table 2) and 2 (COD for the maximum methane production).

		Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Average
Scenario 1 - average vinasse COD										
Methane production[a]	m^3 kg COD^{-1}	0.303	0.305	0.291	0.305	0.294	0.298	0.307	0.309	0.302
	million m^3	101	249	196	275	230	220	124	44	1439
CBIOs	1000 Ton CO_{2eq}[b]	276	682	537	753	630	603	340	121	3942
Scenario 2 - COD for maximum methane production (38.75 kg m^{-3})										
Methane production[a]	m^3 kg COD^{-1}	0.310	0.310	0.310	0.310	0.310	0.310	0.310	0.310	0.310
	million m^3	103	253	209	280	242	229	125	44	1485
CBIOs	1000 Ton CO_{2eq}[b]	282	693	572	767	663	627	342	121	4068
Increase compared to Scenario 1 (%)		2.3	1.6	6.6	1.6	5.3	4.1	1.0	0.2	3.2
Scenario 1 vs. Scenario 2										
Scenario 1	m^3 CH_4 m^3 $ethanol^{-1}$	125	130	105	130	110	115	134	155	126
Scenario 2		128	132	112	132	116	120	136	155	129
Scenario 1[c]	m^3 ton $sugarcane^{-1}$	10.0	10.4	8.4	10.4	8.8	9.2	10.7	12.4	10.1
Scenario 2[c]		10.2	10.5	9.0	10.5	9.3	9.6	10.9	12.4	10.3

[a] Calculated based on the Eqs. (1) and (2), obtained in this study.

[b] Considering that it is necessary 365 m^3 of methane to replace an equivalent of 1 ton of CO_2 equivalent, based on (Moretti, 2019).

[c] Considering a production of 80 l of ethanol per ton of sugarcane.

3.2 %.

4.3. Increased energy production and potential uses for biogas

In a distillery, approximately 80 l of ethanol is produced per ton of processed sugarcane. Distillation generates around 12.5 l of vinasse per l of ethanol (Silva et al., 2013), resulting in roughly one cubic meter of vinasse per ton of sugarcane processed. Vinasse from sugarcane juice has a COD concentration between 15 and 33 g l^{-1} with an average value of 30 g l^{-1} (Elia Neto and Nakahodo, 1995; Godoi et al., 2019). Consequently, each ton of processed sugarcane generates about 30 kg of COD in vinasse. Our results indicate that the AD of raw vinasse with a COD of 30 g l^{-1} could increase distillery energy production by 14.6 %, in agreement with Moraes et al. (2014) who found that AD could increase energy production at a distillery by 12 %. These results demonstrate that the biogas production of vinasse can be one more process to increase the bioenergy production in the sugar and ethanol plant, diversifying even more its co-products.

Silva Neto et al. (2020) proposed the use of biogas from vinasse to replace fossil fuels, such as diesel, used by tractors, trucks in the sugarcane field, and other equipment in the industry. According to Poveda (2019), if a quarter of the vinasse generated in a sugarcane mill is used for biogas production, the methane produced is enough to replace all the diesel used on agricultural operations. In our study, considering that on average 1 ton of processed sugarcane produces 80 l of ethanol and 1 m^3 of vinasse, based on the values from this study, we have calculated that 10.3 m^3 of methane will be produced per ton of sugarcane processed. For every ton of sugarcane processed in Brazil to produce ethanol, approximately 5 l of diesel are currently used, which can potentially be substituted by 5 m^3 of methane. Consequently, this results in a surplus of 5.3 m^3 of methane per ton of processed sugarcane, which can be seamlessly integrated into the national natural gas network (Nunes Ferraz Junior et al., 2022).

4.4. Vinasse composition and methane production in the context of RenovaBio

In the context of the RenovaBio, ethanol industries producing biogas from vinasse would generate more CBIOs, which are credits equivalent to one ton of avoided carbon dioxide (CO_2) emissions due to biofuel production. Fuel distributors are obligated to purchase CBIOs, and these credits are accessible to interested investors (ANP, 2019; Grassi and Pereira, 2019), becoming another income for the sugarcane industry. Our results indicate that the anaerobic digestion of vinasse could provide around 3.9 million CBIOs just in the state of Sao Paulo. Considering that the value of one CBIO may range from 100 to 200 Brazilian real (R $), it would mean a revenue from 390 to 780 million Brazilian real per year (approximately 78 to 156 million American dollars per year). The anaerobic digestion of vinasse would, therefore, enhance the energy balance of Brazilian ethanol, elevate the sustainability index of biofuels in the country, and reduce the carbon intensity of natural gas distribution systems, as the diesel represents a considerable part of the nonrenewable resources used for ethanol production (Silva Neto and Gallo, 2021).

Based on the results from the experimental work (part 1) of this study, concentrating the vinasse to the COD would increase the total methane production in the state of Sao Paulo from 1439 to 1485 million m^3 per year. This would imply in extra 126,000 CBIOs per year. Considering the same prices mentioned in the previous paragraph, the concentration of vinasse would increase the revenues from 12.6 to 25.2 million Brazilian real per year (approximately 2.52 to 5.04 million American dollars). Thus, considering the Sao Paulo state scale, concentrating the vinasse would imply in little or negligible changes in terms of CBIOs and potential revenues from it. However, further studies are needed in order to assess other factors, as reduction of reactor size and costs on handling the vinasse.

5. Conclusions

This study sheds light on the potential benefits and limitations of vinasse concentration as a strategy for enhancing AD efficiency and energy production. In the experimental work (part 1), we found significant effects of different vinasse chemical oxygen demand concentrations (and organic loading rates) on anaerobic digestion parameters. The highest methane yield (0.310 l g COD^{-1}) was obtained at a COD content of 38.8 g l^{-1}. However, this value is within the average vinasse range in sugarcane mills in the state of Sao Paulo (27 to 40 g l^{-1}). Based on these results, our case study demonstrated that concentrating the vinasse would increase by 3.2 % the total methane production in the state of Sao Paulo, by slightly increasing potential revenues from CBIOs from 390 to 780 to 406–805 million Brazilian real per year. Therefore, our results indicate that in the context of the RenovaBio, concentrating vinasse may not have considerable impacts on CBIOs and revenues. However, it is worth noting that further studies may be needed in order to investigate how supplementation with nutrients, as phosphorus, as well as adopting two-stage reactors will affect the methane yield at higher vinasse COD contents.

CRediT authorship contribution statement

Pietro Sica: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Amanda Olbrick Marabesi:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – review & editing. **Aimee Regali Seleghim:** Conceptualization, Methodology, Validation. **K.C. Das:** Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition. **Antonio Sampaio Baptista:** Writing – review & editing, Resources, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

ANP, 2019. RenovaCalc [WWW Document]. Brazilian National Agency of Petroleum, Natural Gas, and Biofuels. URL. http://www.anp.gov.br/producao-de-biocombustiveis/renovabio/renovacalc (accessed 11.10.19).

CETESB, 2005. Stillage - Criteria and Procedures for Agricultural Application (Technical Standard P4.231) [WWW Document]. São Paulo's State Sanitation Technology Company. URL. https://cetesb.sp.gov.br/wp-content/uploads/2014/12/DD-045-2015-C.pdf (accessed 12.3.19).

Chernicharo, C.A.L., 2007. Anaerobic Reactors (in Portuguese), 2nd ed. Engenharia Sanitaria e Ambiental. Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil. https://doi.org/10.1590/s1413-41522007000300001.

Craveiro, A.M., Soares, H.M., Schmidell, W., 1986. Technical aspects and cost estimations for anaerobic systems treating vinasse and brewery/soft drink wastewaters. Water Sci. Technol. 18, 123–134. https://doi.org/10.2166/wst.1986.0168.

Elia Neto, A., Nakahodo, T., 1995. Physicochemical Characterization of Vinasse (in Portuguese). Piracicaba, Brazil.

Ferraz Júnior, A.D.N., Koyama, M.H., de Araújo Júnior, M.M., Zaiat, M., Djalma Nunes Ferraz Júnior, A., Koyama, M.H., de Araújo Júnior, M.M., Zaiat, M., 2016. Thermophilic anaerobic digestion of raw sugarcane vinasse. Renew. Energy 89, 245–252. https://doi.org/10.1016/j.renene.2015.11.064.

Freire, W.J., Cortez, L.A.B., 2000. Vinasse from Sugarcane (in Portuguese), 1st ed. Agropecuária, Guaíba.

Fuess, L.T., Kiyuna, L.S.M., Ferraz, A.D.N., Persinoti, G.F., Squina, F.M., Garcia, M.L., Zaiat, M., 2017. Thermophilic two-phase anaerobic digestion using an innovative fixed-bed reactor for enhanced organic matter removal and bioenergy recovery from sugarcane vinasse. Appl. Energy 189, 480–491. https://doi.org/10.1016/j.apenergy.2016.12.071.

García-Depraect, O., Diaz-Cruces, V.F., León-Becerril, E., 2020. Upgrading of anaerobic digestion of tequila vinasse by using an innovative two-stage system with dominant lactate-type fermentation in acidogenesis. Fuel 280. https://doi.org/10.1016/j.fuel.2020.118606.

Godoi, L.A.G., Camiloti, P.R., Bernardes, A.N., Sanchez, B.L.S., Torres, A.P.R., Gomes, A. Da C., Botta, L.S., 2019. Seasonal variation of the organic and inorganic composition of sugarcane vinasse: main implications for its environmental uses. Environ. Sci. Pollut. Res. 26, 29267–29282. https://doi.org/10.1007/s11356-019-06019-8.

Grassi, M.C.B., Pereira, G.A.G., 2019. Energy-cane and RenovaBio: Brazilian vectors to boost the development of Biofuels. Ind. Crop Prod. 129, 201–205. https://doi.org/10.1016/j.indcrop.2018.12.006.

Harada, H., Uemura, S., Chen, A.C., Jayadevan, J., 1996. Anaerobic treatment of a recalcitrant distillery wastewater by a thermophilic UASB reactor. Bioresour. Technol. 55, 215–221. https://doi.org/10.1016/0960-8524(96)00003-X.

Jendiroba, E., 2006. Environmental issues in the management of sugarcane agribusiness. In: Segato, S.V., Pinto, A.S., Jendiroba, E., Nobrega, J.C.N. (Eds.), Update on Sugarcane Production (in Portuguese), 1st ed. Livroceres, Piracicaba.

Laime, E., Fernandes, P., Oliveira, D., Freire, E., 2011. Technological possibilities for the destination of vinasse: a review (in Portuguese). Revista Trópica: Ciências Agrárias e Biológicas 5, 16–29.

Lamo, P., 1991. Methane gas production system through treatment of industrial effluents. METHAX/BIOPAQ, Piracicaba (In Portuguese).

Lei, Z., Chen, J., Zhang, Z., Sugiura, N., 2010. Methane production from rice straw with acclimated anaerobic sludge: effect of phosphate supplementation. Bioresour. Technol. 101, 4343–4348. https://doi.org/10.1016/j.biortech.2010.01.083.

Ministry of Mines and Energy, 2021. Brazilian Energy Balance - Summary Report of 2020. Brasília.

Moraes, B.S., Junqueira, T.L., Pavanello, L.G., Cavalett, O., Mantelatto, P.E., Bonomi, A., Zaiat, M., 2014. Anaerobic digestion of vinasse from sugarcane biorefineries in Brazil from energy, environmental, and economic perspectives: profit or expense? Appl. Energy 113, 825–835. https://doi.org/10.1016/j.apenergy.2013.07.018.

Moraes, B.S., Zaiat, M., Bonomi, A., 2015. Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: challenges and perspectives. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2015.01.023.

Moretti, E.R., 2019. Biomethane from Vinasse in the Context of RenovaBIO. State University of Campinas, Campinas.

Nasr, N., Elbeshbishy, E., Hafez, H., Nakhla, G., Hesham El Naggar, M., 2012. Comparative assessment of single-stage and two-stage anaerobic digestion for the treatment of thin stillage. Bioresour. Technol. 111, 122–126. https://doi.org/10.1016/j.biortech.2012.02.019.

Nunes Ferraz Junior, A.D., Etchebehere, C., Perecin, D., Teixeira, S., Woods, J., 2022. Advancing anaerobic digestion of sugarcane vinasse: current development, struggles and future trends on production and end-uses of biogas in Brazil. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2021.112045.

Poveda, M.M.R., 2019. Integração do biogás de vinhaça na matriz energética de Ribeirão Preto. Universidade de São Paulo, Piracicaba, Estado de São Paulo. https://doi.org/10.11606/T.105.2019.tde-26082019-115248.

Rajagopal, R., Massé, D.I., Singh, G., 2013. A critical review on inhibition of anaerobic digestion process by excess ammonia. Bioresour. Technol. 143, 632–641. https://doi.org/10.1016/j.biortech.2013.06.030.

Romanholo Ferreira, L.F., Aguiar, M.M., Messias, T.G., Pompeu, G.B., Queijeiro Lopez, A. M., Silva, D.P., Monteiro, R.T., 2011. Evaluation of sugar-cane vinasse treated with Pleurotus sajor-caju utilizing aquatic organisms as toxicological indicators. Ecotoxicol. Environ. Saf. 74, 132–137. https://doi.org/10.1016/j.ecoenv.2010.08.042.

Salomon, K.R., Lora, E.E.S., 2005. Energetic potential estimate for electric energy generation of different sources of biogas in Brazil. Biomassa & Energia 2, 57–67.

Santana Junior, A.E., Duda, R.M., de Oliveira, R.A., 2019. Improving the energy balance of ethanol industry with methane production from vinasse and molasses in two-stage anaerobic reactors. J. Clean. Prod. 238 https://doi.org/10.1016/j.jclepro.2019.07.052.

Sica, P., Sampaio Baptista, A., Das, K., Piotrovski, J., 2017. Development of physical and chemical processes to increase the efficiency of concentration of vinasse's solids. J. Environ. Sci. Eng. A 6, 90–97. https://doi.org/10.17265/2162-5298/2017.02.005.

Sica, P., Carvalho, R., Beltrame, H., Baptista, A.S., 2020a. Assessment of the Effects of Sugarcane Straw Addition to the Flocculation/Coagulation Process on Vinasse Concentration. Acta Technologica Agriculturae 23. https://doi.org/10.2478/ata-2020-0021.

Sica, Pietro, Carvalho, R., Das, K.C.C., Baptista, A.S.A.S., 2020b. Biogas and biofertilizer from vinasse: making sugarcane ethanol even more sustainable. J. Mater. Cycles Waste Manag. 22, 1–7. https://doi.org/10.1007/s10163-020-01029-y.

Silva Neto, J.V., Gallo, W.L.R., 2021. Potential impacts of vinasse biogas replacing fossil oil for power generation, natural gas, and increasing sugarcane energy in Brazil. Renew. Sustain. Energy Rev. 135 https://doi.org/10.1016/j.rser.2020.110281.

Silva Neto, J.V., Gallo, W.L.R., Nour, E.A.A., 2020. Production and use of biogas from vinasse: Implications for the energy balance and GHG emissions of sugar cane ethanol in the brazilian context. Environ. Prog. Sustain. Energy 39, 1–11. https://doi.org/10.1002/ep.13226.

Silva, A., Rossetto, R., Bonnecine, J., Piemonte, M., Muraoka, T., da Silva, A., Rossetto, R., Bonnecine, J., Piemonte, M., Muraoka, T., 2013. Net and potential nitrogen mineralization in soil with sugarcane vinasse. Sugar Tech. 15, 159–164. https://doi.org/10.1007/s12355-012-0199-0.

Silva, A.F.R., Brasil, Y.L., Koch, K., Amaral, M.C.S., 2021. Resource recovery from sugarcane vinasse by anaerobic digestion – a review. J. Environ. Manage. https://doi.org/10.1016/j.jenvman.2021.113137.

Souza, M.E., Fuzaro, G., Polegato, A.R., 1992. Thermophilic anaerobic digestion of vinasse in pilot plant UASB reactor. Water Sci. Technol. 25, 213–222. https://doi.org/10.2166/wst.1992.0153.

UNICA, 2022. Production andmilling history - Ethanol 2020/2021 [WWW Document]. Brazilian Sugarcane Industry and Bioenergy Association. URL. https://observatoriodacana.com.br/historico-de-producao-e-moagem.php?idMn=31&tipoHistorico=2&acao=visualizar&idTabela=2494&produto=etanol_total&safraIni=2020%2F2021&safraFim=2020%2F2021&estado=RS%2CSC%2CPR%2CSP%2CRJ%2CMG%2CES%2CMS%2CMT%2CGO%2CDF%2CBA%2CSE%2CAL%2CPE%2CPB%2CRN%2CCE%2CPI%2CMA%2CTO%2CPA%2CAP%2CRO%2CAM%2CAC%2CRR (accessed 12.20.22).

UNICA, 2023. Biweekly monitoring of the harvest in the Center-South region [WWW Document]. Brazilian Sugarcane Industry Association. URL. https://www.novacana.com/pdf/10032023110343_Unica-100323.pdf (accessed 11.8.23).

Wakamura, Y., 2003. Utilization of Bagasse Energy in Thailand. Mitig. Adapt. Strateg. Glob. Chang. 8, 253–260. https://doi.org/10.1023/B:MITI.0000005642.56625.9a.

Wang, R., Li, Y., Wang, W., Chen, Y., Vanrolleghem, P.A., 2015. Effect of high orthophosphate concentration on mesophilic anaerobic sludge digestion and its modeling. Chem. Eng. J. 260, 791–800. https://doi.org/10.1016/j.cej.2014.09.050.

Wang, S., Hawkins, G., Kiepper, B., Das, K., 2016. Struvite precipitation as a means of recovering nutrients and mitigating ammonia toxicity in a two-stage anaerobic digester treating protein-rich feedstocks. Molecules 21, 1011. https://doi.org/10.3390/molecules21081011.