4E ANALYSIS APPLIED TO A BIOREFINERY DESIGN OF SUGARCANE ETHANOL PLANT COUPLED TO AUTOTROPHIC CULTIVATION OF MICROALGAE IN BRAZIL

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ABSTRACT

The integration of microalgae biodiesel production to a sugarcane ethanol plant was simulated using Aspen Hysys. The biorefinery appraises the production of biogas from sugarcane residues (vinasse, filter cake) and the microalgae remnants after extracting lipids. In this way, a 4E (energy, environmental, exergetic, and economic) analysis was conducted for a novel design, in which the post-combustion stream of biogas is used for autotrophic cultivation, along with bagasse flue gas and the gaseous effluent from fermentation as biogenic carbon sources. The proposed design showed that the energy self-sufficiency (steam and power) of the biorefinery could be achieved by incorporating 13% of the biogas into the cogeneration system. In the main case (where all biogas is used in the cogeneration system), biodiesel production reached 20.48 m^3/h, in addition to the current yield of 85 L ethanol/t cane of a standard ethanol plant, besides delivering a similar electricity surplus of 34 MW. The main case maintained a promising sustainability score, with a ratio between energy products and fossil inputs of the main case (10.8) similar to the standard case (12.1), which refers to a stand-alone cane ethanol plant producing electricity surplus. Energy products shared a carbon intensity of 15.75 gCO_{2eq}/MJ, similar to that of the standard case. The hotspot of exergy destruction was the cogeneration system, and the biorefinery was able to preserve 42% of the main exergy inputs (sugarcane and solar exergy) into products. Finally, the economic analysis indicated feasibility, with internal rates of return between 11 and 13%. Although the feasibility might be tenuous for the sector, energy policies focused on decarbonization could benefit the biorefinery through tax incentives at the same time that the regulated carbon market thrives.

1 INTRODUCTION

The energy matrix in Brazil counts significantly with sugarcane bioenergy, which presented a share of 15.4% in the country's primary energy supply in 2022 (EPE, 2023). Sugarcane-ethanol distilleries in Brazil provide mainly bioethanol and electricity, consisting of industrial complexes that are energetically self-sufficient through the utilization of bagasse for cogeneration. In this scenario, ethanol boast a high environmental score, as the main sources of greenhouse gas (GHG) emissions from agricultural operations (such as diesel oil used by vehicles and machinery, contributions from synthetic fertilizers and agrochemicals) imply an emission factor of around 18 g CO_2/MJ (LHV basis) for the bioethanol in some life cycle assessments (Díaz, 2011; Liu *et al.*, 2023). Additionally, ethanol can mitigate circa 69.4 g CO_2/MJ when substituting gasoline (87.4 g CO_2/MJ) in the transport sector, while being able to maintain competitive prices (ANP, 2024). In this way, the government supports decarbonization through two main measures: the mandatory blending of ethanol into gasoline, and a carbon credit program (Renovabio) that allows producers to sell carbon credits according to their environmental efficiency to produce biofuels, while fuel distributors and importers must buy them to comply with the regulatory scheme (Klein et al., 2019). Besides that, the electricity surplus of factories contributes to the country's grid emission factor of circa 88 g CO_2/kWh, as biomass accounts for around 8% of the mix, surpassing even the 6.4% share held by natural gas in 2022 (EPE, 2023). The bagasse

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surplus goes towards 10%, allowing a usual excedent electricity production between 10 - 60 kWh/t cane depending on the level of modernization of the power cycle (Seabra *et al.*, 2011).

Recently, the ethanol industry has been enhancing its efficiency and portfolio as biogas production from filter cake and vinasse (residues from the sugarcane juice treatment and ethanol distillation, respectively) becomes technically and economically feasible. Considering that the processing of sugarcane juice generates 30 kg filter cake/t cane, while the ethanol distillation delivers 12 m^3 vinasse/m^3 ethanol, the biomethane potentials of 54 Nm^3/t filter cake and 8 Nm^3/m^3 vinasse (Janke *et al.*, 2015) can contribute significantly to unlocking the energetic yield of sugarcane.

A promising expansion still underexploited by biorefineries goes towards the carbon capture and utilization of biogenic CO_2 emissions. To that end, autotrophic cultivation of microalgae emerges as a suitable solution. Microalgae typically require 10 to 100 times less area than traditional crops (Mota *et al.*, 2022). In particular, lipid-rich microalgae are prime candidates for the production of next-generation biodiesel (3G biodiesel), offering an alternative to conventional vegetable feedstocks (e.g. soybean for 1G biodiesel) or other less controversial raw materials (e.g., used cooking oil for 2G biodiesel). Despite their relevant lipid productivity (circa 100,000 L/ha.yr for microalgae versus 5,366 L/ha.yr for palm plant) (Mota *et al.*, 2022), the biomass moisture and micro-structure impose high energy load requirements in the form of heat and power so it may be processed into useful products (Chen *et al.,* 2018). Furthermore, microalgae cultivation relies significantly on low-cost carbon sources (Slade and Bauen, 2013), so that a stand-alone microalgae processing factory may become feasible. Thus, the typical CO_2 sources (i.e., fermentation gas or flue gases from biomass combustion) and energy (electricity, heat and cold demands) surpluses provided by sugarcane-ethanol distilleries can address the aforementioned challenges, being interesting the investigation of biorefineries involving modern cane ethanol factories coupled with microalgae biofuels production systems.

Indeed, many designs showcasing such synergy have already been assessed in the literature. In special, Albarelli *et al.* (2018) conducted an analysis covering the cultivation of microalgae using fermentation gas and appraising the anaerobic digestion of vinasse to supply biogas into a cogeneration system. Klein *et al.* (2019) assessed many cases in which microalgae biodiesel and biomethane productions were scaled to substitute diesel in agricultural operations. Both studies embraced the use of straw (a residue left on the soil after harvesting of cane) as an additional fuel for the cogeneration system, although there are technical issues associated with the proper harnessing of this type of biomass.

Thus, this paper analyses the integration of sugarcane ethanol production with autotrophic cultivation of microalgae for biodiesel production. Biogas from cane residues (filter cake and vinasse) is utilized as a source of heat and power to attend to simulated processes, as a way not to recur to fossil or cumbersome outer energy sources. Moreover, the CO_2 in the post-combustion stream of biogas is appraised as a carbon feedstock, alongside the exhaust gas from bagasse combustion and fermentation gas, representing a novelty pursued by this work. Anaerobic digestion of microalgae leftovers after their lipid extraction is also simulated, contributing to the energetic self-sufficiency and maximizing the scale of the 3G biodiesel production. Besides a technic-economic assessment, the environmental performance (in terms of GHG emissions and sustainability in the use of energy resources) and an exergy analysis were also conducted. This way, this paper accomplishes a 4E (energetic, environmental, exergetic, and economic) assessment of a novel biorefinery design.

2 BIOREFINERY SIMULATION

The simulation of the biorefinery was conducted using Aspen Hysys software. The thermodynamic package NRTL-SRK was employed to model the thermochemical and phase equilibrium of streams, which are comprised of up to 33 components. Isentropic efficiencies of pumps and turbines were set at 80% and 75%, respectively. Pressure drops were neglected. Software tools were used to achieve numerical convergence of recycled streams and set correlations. The simplified diagram of the simulation is depicted in Figure 1. The biorefinery is comprised of three major modules, described as follows.

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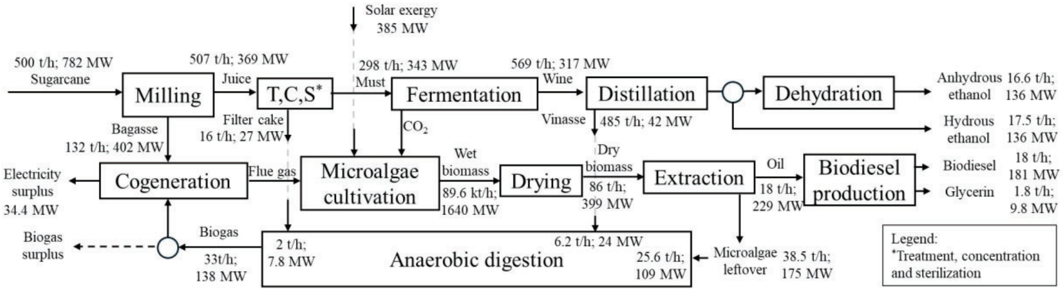

Figure 1: Simplified diagram of the biorefinery and mass and exergy flows of the main case

2.1 Sugarcane ethanol plant and the cogeneration system

The sugarcane-ethanol factory processes 500 t/h of cane into ethanol through the following subsystems: sugarcane milling, juice treatment, concentration, sterilization, fermentation, ethanol distillation, and dehydration. Details about the unit operations as well as the model validation are presented in Castiñeiras-Filho and Pradelle (2020). The key results and yields of such a standard ethanol plant are 264 kg bagasse/t cane, 85.32 L ethanol/t cane, 32 kg filter cake/t cane, and 12 L vinasse/L ethanol. Half of the resulting distilled ethanol (hydrous ethanol, 94 wt% ethanol) is sent to dehydration through an extractive distillation, producing anhydrous ethanol (99 wt%) suitable for blending with gasoline. All bagasse (7.4 MJ/kg, LHV basis) is directed to cogeneration to meet steam demands – 600 kPa (158 ºC) for sterilization and ethanol dehydration, and 250 kPa (127 ºC) for juice concentration and ethanol distillation – as well as general power requirements (28 kWh/t cane) of the ethanol plant. The boiler (88% efficiency, LHV basis) produces superheated steam at 67 bar and 480 ºC, while the heat rejection of the power cycle generates saturated water at 165 kPa. The superheated steam is cascaded through 4 turbines (1 direct drive and 3 electric turbines) while steam is extracted to fulfill the aforementioned heat demands. The electricity surplus of this standard ethanol plant is equal to 65 kWh/t cane.

2.2 Microalgae-biodiesel plant

The autotrophic cultivation of microalgae was carried out with biogenic CO_2 sources. The primary carbon sources are the flue gas of the cogeneration system (10-11 vol% CO_2) and the fermentation gas (95 vol% CO_2). After considering a loss of 10% of the streams carrying the CO_2, the carbon conversion rate into microalgae biomass was set at 58% (Souza *et al.*, 2015). Microalgae composition in dry weight corresponds to 6% proteins, 43% lipids (38.7% as triolein and 4.3% as oleic acid), and 51% carbohydrates. Biomass processing follows a dry route approach, by which the moisture is reduced, the oil is extracted, and the TAGs are finally converted to biodiesel (methyl oleate). The resulting 3G biodiesel is thus produced through a similar pathway applied to vegetable crops (i.e. soybean), well established in the Brazilian market. Moreover, the biodiesel specifications in the simulation meet the requirements for the B10 (diesel fuel with 10 vol% biodiesel) mixture regulated by the Brazilian government (EPE, 2023). It is worth mentioning that microalgae biodiesel has shown successful performance in engines and drop-in capabilities purely or blended with diesel oil (Piloto-Rodriguez *et al.*, 2017). The microalgae cultivation was simulated like ponds for the sake of economic feasibility (Albarelli et al., 2018), resulting in a biomass produced at a concentration of 0.05 wt% (dry basis). Mechanical processes reduce water content to 50 wt%, followed by thermal drying to achieve a biomass concentration of 85 wt%. The oil is extracted with n-hexane, with a solvent-to-biomass ratio of 20:1 (mass basis) (Peralta-Ruiz *et al.*, 2013). After recovering the solvent, the oil is reacted with methanol at a molar proportion of 1:6, respectively, at 50 ºC and 400 kPa, through an alkaline catalyzed process. After phase separation steps, and recovery of the reactant alcohol (methanol) and glycerin as a byproduct, microalgae biodiesel is produced as a main product. Additional electricity consumptions (paddling, centrifugation, etc.) were considered according to Xu *et al.* (2011). More details about the unit operations were reported in Castiñeiras-Filho and Pradelle (2023). In general, the proposed design requires high loads of heat and power for the processing of microalgae into biodiesel. The cogeneration system supplied with bagasse would be able to sacrifice the electricity surplus and cover the additional power demand. However, the heat demand would need other sources so the microalgae-biodiesel-plant

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scale could be sustained. Preferably, such a source should be renewable so that the expansion may maintain the energy self-sufficiency of the global system, akin to a standard ethanol plant. To overcome these concerns practically, the anaerobic digestion of the microalgae residue is considered along with the production of biogas of vinasse and filter cake. This way, biogas plays the role of providing heat and power, as well as serving as a CO_2 source, representing a novel scheme explored in this paper.

2.3 Anaerobic digestion of residues and incorporation of biogas into the cogeneration system

The anaerobic digestion of vinasse, filter cake, and microalgae leftovers was simulated by considering conversion reactors for each residue. The organic compounds in these residues, except for lignin (Janke *et al.*, 2017), are considered susceptible to anaerobic digestion, being accounted for in the estimation of volatile solids (VS) or chemical oxygen demand (COD). The theoretical biomethane potential (TBMP) is thus calculated based on the overall AD reaction (Equation 1) (Sialve *et al.*, 2009).

$$C_aH_bO_CN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 + \left(\frac{4a-b+2c+3d}{8}\right)CO_2 + dNH_3 \qquad (1)$$

Table 1 presents the content of the resulting substrates, the expected conversion rate in AD, and the necessary dilution for solid substrates to achieve an organic load rate of 3.20 $kg_{VS}/m^2.d$ in CSTR reactors (Kunz *et al.*, 2019). The characteristics of vinasse were consistent with those of other simulations (Palacios-Bereche *et al.*, 2021) and experimental data (Janke *et al.*, 2015). Similar validation was verified for filter cake (Janke *et al.*, 2015), which typically consists of organic matter less susceptible to AD. Lastly, microalgae biomass tends to yield biomethane at levels half of the TBMP presented in Table 2 (Barros *et al.*, 2022), resembling the behavior of filter cake or lignocellulosic matter (Janke *et al.*, 2017). Nonetheless, given that the microalgae leftovers come from an intensive pre-treatment process, the disrupted microalgae cells would be more susceptible to AD (Sialve *et al.*, 2009). Thus, a conversion rate of 72% was adopted. Following the application of AD individually to each substrate, a leakage of 2.5% was considered over the biogas production (Szumski, 2023).

The available biogas (13.98 MJ/kg, 1.06 kg/Nm^3) can be combusted. The resulting exhaust gas is mixed with the bagasse-derived flue gas in the cogeneration system, thereby augmenting the local energy supply and allowing the recycling of CO_2 for microalgae cultivation. To integrate the MB system's heating needs with the cogeneration system, steam extractions at 250 kPa (127.4 ºC) and 4,000 kPa (250.3 ºC) were considered. Therefore, the cogeneration system undergoes little modifications to fulfill the MB plant's heat and power demand. The biogas can be entirely directed to the cogeneration system, or a portion of it can be diverted for other usages, provided that sufficient biogas is allocated to the cogeneration to meet the global system's heating requirements.

Table 1: Characterization of resulting substrates for the AD process

Substrate	VS or COD*	TBMP	Conversion	Dilution
Vinasse	17.03 $kgO_2/m^3_{f.m.}$	0.3880 $Nm^3/m^3_{f.m.}$	80%	n/a
Filter cake	215.70 $gVS/kg_{f.m.}$	0.4437 $Nm^3/kg_{f.m.}$	52%	1.775 kg $H_2O/kg_{f.m.}$
Microalgae leftover	779.94 $gVS/kg_{f.m.}$	0.5123 $Nm^3/kg_{f.m.}$	72%	11.47 kg $H2O/kg_{f.m.}$

Note: * VS for filter cake and microalgae leftover, and COD for vinasse; f.m. = fresh matter

2.4 Simulated cases

The following cases are analyzed for comparison purposes: (i) the standard case considers a standalone ethanol plant utilizing all available bagasse for cogeneration and lacking an AD system; (ii) the main case considers the entire biorefinery, including the AD system, and all produced biogas is used in the cogeneration system; (iii) the alternative case considers the use of sufficient biogas for cogeneration and outputs the biogas surplus as a product. The alternative case required 13.3% of the produced biogas (after accounting for the leakage) to be sent to the cogeneration. Thus, the outcomes of the main and alternative case serve as a sensitivity analysis for the indicators, concerning the biogas usage choices.

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3 INDICATORS FOR THE 4E ANALYSIS

This section defines the indicators used to cover the 4E analysis as follows.

3.1 Energetic assessment

A life cycle assessment approach was employed to evaluate the system within a cradle-to-gate scope (Castiñeiras-Filho and Pradelle, 2024). The following energy inputs and main outputs (products or coproducts) were considered for the calculation of the energy ratios (ER) (Equation 2).

$$ER = \frac{ES + \sum_{i=HE,AE,MB,Gly,BS} \dot{m}_i LHV_i}{SCF + N_M + P_M + MeOH + f \, . m_{SC} LHV_{SC}} \tag{2}$$

The ER considers as outputs the electricity surplus and the energy content of the material streams (in terms of LHV): hydrous ethanol (28.42 MJ/kg), anhydrous ethanol (26.36 MJ/kg), microalgae biodiesel (40.04 MJ/kg), glycerin (14.62 MJ/kg), and biogas surplus (13.98 MJ/kg). Inputs include the burdens of the rural activities in the sugarcane field (11,392 MJ/ha.a associated with a yield of 65.9 t cane/ha.a) (Diaz, 2011), ammonia (56.3 MJ/kg N, with ammonia containing 82 wt% N) and SSP (0.24% kg P/kg dry microalgae, 7.5 MJ/kg P_2O_5) as nutrients for microalgae, and the methanol make-up (32.58 MJ/kg) (Xu *et al.*, 2011). If the ER aims to measure the energy preserved in products compared to the fossil energy inputs, as a form of measuring the sustainability of the biorefinery, the factor f, associated with the consideration of sugarcane (2.93 MJ/kg) as an input, is equal to zero. The ER is defined then as the fossil energy ratio (FER). Otherwise, f is equal to 1, ER refers to the net energy ratio (NER), measuring how all energy burdens are preserved in the main products. Solar energy was neglected as it was considered a free input. Another energy metric to be observed is the difference between the numerators and denominators in Equation 2, divided by the cane processing capacity (500 t/h). For f equal to zero and 1, these metrics are defined as FEB and NEB, respectively, indicating the performance of the biorefinery under the functional unit of a ton of cane.

3.2 Environmental assessment

The GHG emissions were accounted for according to the global CO_2 mass balance and other burdens outside the simulation environment's perimeters. Thus, Equation 3 shows that the emissions considered were those of N (3.94 $kgCO_{2eq}$/kg N) and P (1.24 $kgCO_{2eq}$/kg P_2O_5) nutrients for microalgae (ANP, 2024), methanol make-up (2.2 $kgCO_{2eq}$/kg MeOH) (METHANOL INSTITUTE, 2022), sugarcane field contributions (2,153 kg CO_{2eq}/ha.a), and biogenic methane of the biogas leakage. The GHG was attributed proportionally to the energy imbued in the products (energy allocation). Finally, the net GHG emissions were calculated according to each energy product's capability to displace a fossil burden: ES displaces electricity of the Brazilian grid (88g CO_{2eq}/kWh); ethanol streams displace gasoline (87.4 gCO_{2eq}/MJ); and biodiesel displaces diesel (86.5 gCO_{2eq}/MJ). The BS (alternative case) displaces also electricity from the grid since a motor generator (33% efficiency) is considered for the sake of relating biogas to a solution convenient for any sugarcane ethanol factory in the short term. The net GHG emissions served also to account for revenues derived from carbon credits in the economic analysis.

$$GHG = Em_{N_M} + Em_{P_M} + Em_{MeOH} + Em_{SCF} + Em_{CH_4,BL} \tag{3}$$

3.3 Exergy assessment

Exergy measures the useful work obtained from a system through reversible processes, after which it reaches thermochemical equilibrium with the reference environment. Due to irreversible phenomena, the entropy of the universe increases, implying that exergy is destroyed. For the steady-state simulation conducted, the exergy balance (Equation 4) was carried out for the global system and the following subsystems: milling, extraction, concentration, sterilization, fermentation, distillation, dehydration, microalgae cultivation, microalgae drying, oil extraction, biodiesel production, and anaerobic digestion. The specific physical exergy of material streams (Equation 6) was obtained from the software, while their chemical exergy was calculated with Equation 7, in which the activity coefficient γ_i is equal to 1

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for simplicity (Peralta-Ruiz *et al.*, 2013). The rate of exergy destruction ($\dot{Ex}_d > 0$) in each subsystem and their exergy efficiencies were calculated. Exergy efficiency (Equation 8) considers the $\dot{Ex}_d$ and wasted exergy flows ($\dot{Ex}_w$), which refers to streams dumped to the environment, such as the heat loss in furnaces and the vinasse output in the standard case. The exergy of some material streams for the main case was highlighted to comprehend the ones carrying significant amounts of exergy (Figure 1).

$$0 = \sum(\dot{m}_{in} ex_{M,in} - \dot{m}_{out} ex_{M,out}) + \sum\left(1 - \frac{T_0}{T_b}\right)\dot{Q} + \sum \dot{W} - \dot{Ex}_d \tag{4}$$

$$ex_M = ex_{ph} + ex_{ch} \tag{5}$$

$$ex_{ph} = (h - h_0) - T_0(s - s_0) \tag{6}$$

$$ex_{ch} = \frac{1}{MM}\left[\sum x_i\, ex^0_{ch,i} + RT_0 \sum x_i \ln(\gamma_i x_i)\right] \tag{7}$$

$$\psi = 1 - \frac{\dot{Ex}_d + \dot{Ex}_w}{\sum \dot{Ex}_{in}} \tag{8}$$

3.4 Economic assessment

The economic performance of the biorefinery was conducted through an incremental cash flow analysis in comparison to the standard case. The cash flow considers a lifespan of 20 years (Palacios-Bereche *et al.*, 2021; Albarelli *et al.*, 2018), two years of investment with the allocation of 60% of total investment in the first year (Tercero *et al.*, 2014), and an annual discount rate of 10% (Palacios-Bereche *et al.*, 2021, Hoffman *et al.*, 2017). Investment costs were acquired from literature data and considering economies of scale. Three major expansions are considered for the investments regarding capital expenditures (CAPEX): the expansion of the cogeneration system (Furtado, 2024; Palacios-Bereche *et al.*, 2021), encompassing differences between the biorefinery and the standard ethanol plant costs; the AD module, comprising the separate scaling of AD of vinasse (Moreira *et al.*, 2022), filter cake, and microalgae leftovers (Janke *et al.*, 2017), and the desulfurization of biogas (Palacios-Bereche *et al.*, 2021); and the microalgae-biodiesel (MB) plant. The MB plant had its investment for microalgae cultivation estimated at 3.40 USD/m^2 for a 400 ha base scale, considering a conservative exponential scaling factor of 0.9. A biomass productivity of 25 g/m^2.d was assumed to scale the cultivation system (Hoffman et al, 2017). The harvesting, drying, and oil extraction steps (Tercero *et al.*, 2014), and the biodiesel production investments (Heo *et al.*, 2019) were calculated and aggregated to the MB plant's CAPEX. The investment values were updated to 2023 by the CEPCI. A sensitivity analysis considered varying the CAPEX in -/+30% to cover the cost uncertainties. Table 2 summarizes key metrics resulting from the investment estimates. Market data from Brazil was used for determining the variable costs and selling prices. A uniform depreciation of the total investment over the first 10 years of operation and a tax rate of 34% were also considered. The annualized (20 years, 10%) net present value (NPV) and the internal rate of return (IRR) were calculated to evaluate the feasibility of the biorefinery.

Table 2: Main parameters for the economic analysis

Major Expansions	Unitary CAPEX	Simulation's scale	O&M
Cogeneration[a]	1055 USD/kW *	70,564 kW	3% CAPEX
AD module[b]	149.82 USD/(Nm^3/d)$_{\text{biogas}}$*	648,000 Nm^3/d	3% CAPEX
MB plant[c]	529,374 USD/(m^3/d)$_{\text{biodiesel}}$ *	491 m^3/d	1% CAPEX
Main costs and prices for variable costs and revenues			
SSP	688 USD/t	Biodiesel	0.896 USD/L
Ammonia	919 USD/t	Electricity surplus	59.4 USD/MWh
Methanol	526 USD/t	Biogas surplus	0.133 USD/Nm3
Cooling water	0.33 USD/GJ	Glycerin	280 USD/t
CO$_2$ credit	20 USD/t		

Notes: * the average scaling factor for cogeneration, AD module, and microalgae-biodiesel plant are 0.73, 0.6, 0.85, respectively. The results were constructed with data obtained from (a) (Furtado, 2024; Palacios-Bereche et al., 2021), (b) (Moreira *et al.*, 2022; Janke *et al.*, 2017; Palacios-Bereche *et al.*, 2021), (c) (Tercero *et al.*, 2014; Hoffman *et al.*, 2017; Heo *et al.*, 2019). More details are listed in Castiñeiras-Filho and Pradelle (2024).

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4 RESULTS AND DISCUSSION

The proposed biorefinery produced 47.65 t/h of microalgae biomass (dry basis), 17.99 t/h of oil, and 20.48 m^3/h of biodiesel in the main case. The system presented a gross specific consumption of 4.11 $kgCO_2$/kg microalgae, which is conservative compared to other efficiencies for the CO_2 capture assumed in previous works like 3.3 $kgCO_2$/kg microalgae (Albarelli *et al.*, 2018). Considering that the ethanol outputs totalize to 42.71 m^3/h, there is a significant increase in the overall biofuels production volume. The biodiesel capacity production would rival that of 1G biodiesel factories in Brazil, which present an average capacity of 24.3 m^3/h (EPE, 2023). The biogenic sources of CO_2 (196 t/h) that allow such a sizing present each the following shares: 24.6% from the biogas flue gas, 59.2% from the bagasse flue gas, and 16.2% from fermentation gas. A closer look at the biogas sources partakes showed that 12% came from vinasse (7 Nm^3/m^3, 482 m^3/h of vinasse), 6% from filter cake (105 Nm^3/t, 16t/h of filter cake in wet basis), and 82% from the microalgae leftovers (570 Nm^3/t, 38.5 t/h of microalgae residue in wet basis). Therefore, not only did the biogas represent a relevant boost for the cost-effective CO_2 availability, but also the microalgae residue was responsible for the greater share, complying with the key roles of serving energy demands (heat and power) and as a raw material.

The electricity surplus was equal to 34.4 MW, slightly higher than in the standard case. The MB plant consumed 17.4 MW of electric power while the AD module consumed around 3.6 MW. Although relevant, these additional electrical power consumptions are together comparable to that of the already existing power demand of 22 MW (electrical and direct drive) required by the standard ethanol plant.

4.1 Energy efficiency and sustainability in the use of energy resources

The main case for the biorefinery resulted in a NER of 1.105, which is thus 63% higher than the standard performance of an ethanol plant (Figure 2). Therefore, despite the use of additional inputs (micronutrients for microalgae and methanol) and the halving of the bioelectricity surplus, the energy delivered by the MB compensates and promotes a higher energy efficiency for the global system. It is worth highlighting that the defined NER neglects solar energy as an input in the ratio's denominator, and thus a value higher than 1.0 means just that the biorefinery is able to imbue solar energy into useful products compared to the inputs represented mainly by sugarcane's energy flow. In other words, the exploitation of sugarcane crops becomes enhanced since a usual ethanol plant delivering a NEB of -1.0 GJ/t cane could be upgraded to a NEB of 0.35 GJ/t cane. The FEB values for these schemes are 1.9 and 3.27 GJ/t cane, respectively, indicating a promising boost in the sustainability of the system. The ratio however declines from 12.14 to 10.79, showing sort of an inefficiency by the biorefinery with respect to a standard ethanol plant. Anyway, the performances are adequate considering that sugarcane ethanol plants tend to present FER around 9.0 while other 1G ethanol, like corn ethanol in the U.S., presents such metric around 1.3 (Macedo *et al.*, 2007).

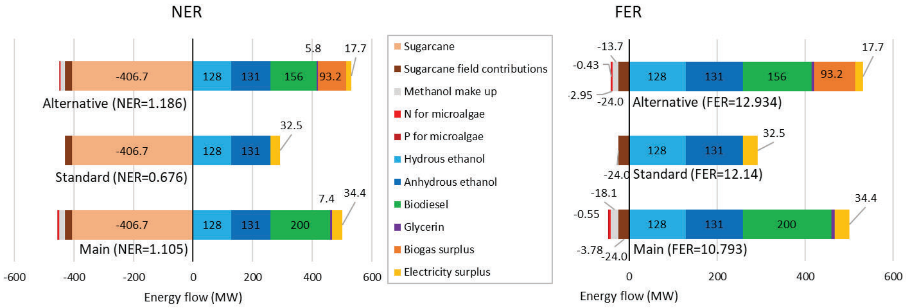

Figure 2: Energy ratios (NER and FER) of the cases.

The alternative case presented a lower electricity surplus (17.7 MW) derived from the cogeneration system, since the scaling of the MB plant was set just so to fulfill the total heating demand with biogas. In this way, biodiesel production was reduced by 44 MW. Those decreases were compensated by the biogas surplus of 93.2 MW. Overall, the alternative case's FER (12.9) was slightly higher than the main

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case (12.1). Finally, the alternative case presented the highest NEB (0.6 GJ/t cane) and FEB (3.52 GJ/t cane). By considering that the biogas surplus would be used in a motor generator for electricity production (33% efficiency), the NEB and FEB would fall at best (other burdens are neglected) to 0.15 and 3.07 GJ/t cane, respectively. In this case, where a final use is considered for biogas, the main case for the biorefinery would slightly outperform in terms of energetic performance and sustainability.

4.2 GHG emissions and carbon intensity of bioenergy

For the main biorefinery design, the emission hotspot (58.4%) remained the contributions from the sugarcane field (16 t CO_{2eq}/h), akin to a standard ethanol plant (Figure 3).

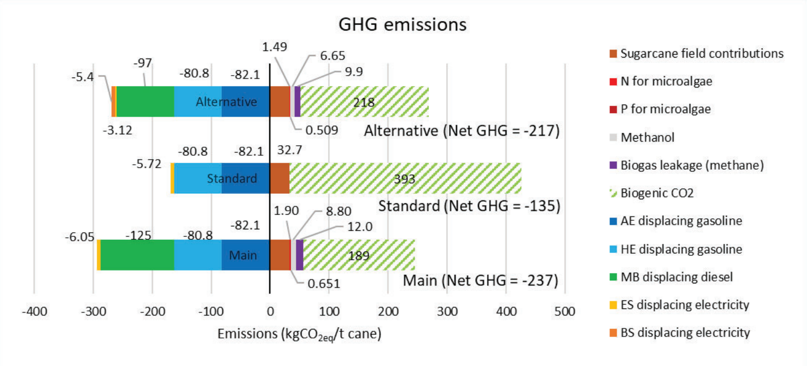

Figure 3: GHG emission sources of the cases

The MB plant presented emissions of 1.28 t CO_{2eq}/h due to nutrients for microalgae and 4.4 t/h due to the use of methanol for the transesterification reaction, representing both sources a share of 20.2% in the total emissions. The remaining share of 21.4% was due to biogenic methane in the biogas leakage (5.28 t CO_{2eq}/h). Therefore, the total GHG emissions of the system could still be tackled by the continuous improvement of the sugarcane field cultivation, management, and harvesting operations (Liu *et al.*, 2023). The Renovabio program in Brazil stimulates the efficiency of agricultural operations. To concretely achieve such reductions, the producers can plan the logistics to reduce fuel consumption and avoid the practice of burning sugarcane before harvesting, for example, which is practically phased out in São Paulo state. Another relevant action would be the use of fertilizers (urea, SSP, etc.) with lower environmental impacts, not only in the sugarcane field but also for supplying N and P nutrients for microalgae. However, such actions depend on the advancements in green chemistry by the industrial sector, signifying a stronger structural change in supply chains. Addressing the impact of methanol could also be done through similar means, as this basic chemical, like the N fertilizers, has its production typically anchored in natural gas. Attention should also be given to biogas leakage since a fugitive emissions higher than the assumed one (e.g., higher than 8%) could spoil significantly the environmental benefits of biogas. Finally, fugitive emissions due to undesired methanogenesis in cultivation ponds were neglected in the analysis as the organic matter is very diluted. Thus, it is pertinent to recommend proper control and monitoring, not only to optimize microalgae productivity, but also to prevent an undesired arising of biogenic methane from the cultivation medium. By using the energy allocation, the main biorefinery case presented an emission factor of 15.75 gCO_{2eq}/MJ for its bioenergy products, similar to the emission factor of products from a standard ethanol plant (15.57 gCO_{2eq}/MJ). The 3G biodiesel output contributed to the carbon credit of 237 $kgCO_{2eq}$/t cane, higher than the 135 $kgCO_{2eq}$/t cane of the standard case. Conversely, the alternative case presented an emission factor (13.55 gCO_{2eq}/MJ), 13% lower than the standard case, and a lower carbon credit of 217 $kgCO_{2eq}$/t cane than the main case. This fact arises from the high share of renewables in the Brazilian electricity grid, which turns the emissions displaced by electricity much lower than the amount of diesel displaced by biodiesel. It is worth highlighting that the adopted emission factor of 88 g CO_2/kWh for the grid can be as high as 350 g CO_2/kWh, depending on the dispatching of thermoelectric generation by the grid's operator. In

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such cases, to reduce GHG emissions, the delivery of electricity surplus would have to match the margin of operation of the system, so as to displace the use of fossil resources recurred by the grid operator.

4.3 Exergy analysis

The exergy flows of the main case are highlighted in Figure 1. Overall, all cases process 782 MW of exergy related to sugarcane. The coupling of the MB plant allowed an increment of 385 MW of solar exergy in the main case. The exergy flows imbued in products (497 MW) represented 42% of these inputs. Another interesting observation is the capability of the AD plant to preserve 49.8 MW in biogas, considering the exergy flow of 69 MW corresponding to vinasse and filter cake. Considering all residues (244 MW consisting mainly of chemical exergy), the exergy preserved in biogas was equal to 138 MW.

The total exergy destruction of the main case was 532 MW, and the exergy efficiency was equal to 39.5%. Such values for the standard case were 352 MW and 35.9%, respectively, while for the alternative, they were 445 MW and 46.2%, respectively. Overall, the cases that destroyed more exergy were naturally the ones with larger production scales, since the thermodynamic state and composition of material streams were similar among all cases. This also resulted in similar exergy efficiencies for some subsystems in different cases. Anaerobic digestion presented little difference, which can be explained by the different partakes of the substrates in each case. Distillation and juice treatment of the standard case presented lower exergy efficiencies compared to the other two cases because vinasse and filter cake were considered to be dumped as exergy waste in the former case. The main hotspot of exergy destruction and inefficiency (Figure 4) was the cogeneration system, which can be addressed to irreversible phenomena derived from the combustion reaction and the finite temperature differences. Anaerobic digestion and biodiesel production involve irreversible chemical reactions as well, contributing to their low exergetic efficiency in relation to other subsystems.

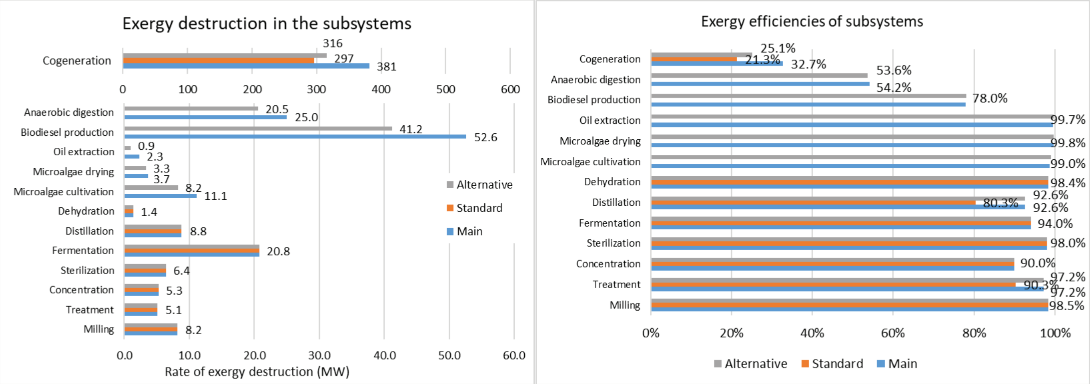

Figure 4: Rate of exergy destruction (left) and exergy efficiencies (right) of the subsystems

4.4 Economic assessment

While the annual revenues from ethanol products of the standard ethanol plant are around USD 89 million (this value was not considered in the incremental cash flow), the biodiesel revenue reached USD 73 million. Thus, biodiesel production can significantly contribute to the biorefinery's total portfolio. The breakdown of values for the main and alternative cases is shown in Figure 5. The main case presented a profit of USD 7.88 million per year and an IRR of 11.21%, making it economically feasible given a discount rate of 10%; these values for the alternative case were USD 11.72 million per year and 13.11%, respectively. The main shares among the costs were the capital investment for the MB and AD systems, besides taxes. In either scenario, it is shown that the availability of low-cost CO_2 and energy sources (steam and power) are crucial. Varying the total CAPEX in -/+30% resulted in an IRR of 8.68 and 19.64% for the main case, and for the alternative case, 10.63 and 21.39%. In the high CAPEX scenario for the main case, a tax incentive of 50% or a carbon price of USD 60/t CO_2 could promote the economic feasibility for a 10% discount rate. Thus, energy policies could offer tax incentives under the scope of supporting the environmental benefits. Also, carbon market development (carbon credits represented circa 5% of revenues in the reference cases) can contribute to the economic feasibility.

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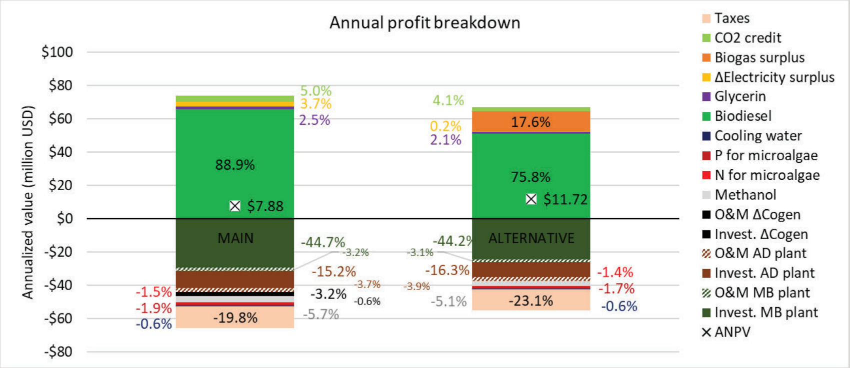

Figure 5: Annual profit breakdown for the main and alternative cases

Finally, profitability becomes tenuous if the sector demands discount rates higher than 12% (Albarelli *et al.*, 2018; Klein *et al.*,2019). In the alternative scenario, the biogas was considered to be sold near its break-even cost of 0.13 USD/Nm^3. The result still depends on the margin requested by the downstream usage. For example, by aggregating other cost components to upgrade biogas into biomethane (Moreira *et al.*, 2022), the simulated scenario can represent the selling of biomethane at circa 11 USD/GJ at the biorefinery's gate, making it competitive in the Brazilian market, in which natural gas prices for industrial users reached circa 19 USD/GJ in 2023. Dedicated electricity generation using the biogas surplus would also need to tolerate the resulting biogas cost for its economic feasibility.

5 CONCLUSIONS

A novel simulated biorefinery, integrating a sugarcane ethanol plant, a microalgae biodiesel plant, and the appraisal of biomass residues for biogas production, demonstrated promising outcomes in the 4E analysis. In the main case, the biorefinery exhibited a better exploitation of the sugarcane input, being capable of delivering 0.35 GJ/t cane in the form of products and mitigating 237 kgCO$_{2eq}$/t cane. The exergy analysis could identify the importance of appraising residues for biogas production for the sake of exergy efficiency, as well as suggest that efforts can be directed to the cogeneration system to reduce exergy destruction. The economic analysis demonstrated the feasibility of the system given a risk corresponding to a discount rate of 10%. In general, the main and alternative cases presented advantages compared to the standard one. The market scenario and feasible final uses for biogas should be considered for individual plants so as to optimize scale, economic performance, sustainability, and emissions. Finally, future studies should be conducted in laboratory or pilot scales to develop appropriate microalgae strains and comprehend their practical behavior in the cultivation environment (biomass productivity, lipid content, and CO$_2$ capture efficiency). A sensitivity analysis of the indicators with these relevant variables is proposed for future works as a valid effort in the simulation environment, besides the incorporation of multicriteria analysis comprising other key responses, regarding, for example, the use of an exergy approach to measure environmental impacts. The practical feasibility of incorporating sugarcane cane straw into the cogeneration system could also boost the biorefinery performance and should be investigated. Finally, the synergy of the biorefinery with the lignocellulosic ethanol production and bagasse use allocation could be analyzed.

NOMENCLATURE

4E	Energetic, environmental, exergetic, and economic
AD	anaerobic digestion
AE	anhydrous ethanol
B10	diesel oil blend with 10 vol% biodiesel
CAPEX	capital expenditures (US$)
CEPCI	Chemical Engineering Plant Cost Index
COD	chemical oxygen demand
Em	emission mass flow rate(kgCO$_{2eq}$/h)
ER	energy ratio (-)
ES	electricity surplus (kW)

$\dot{Ex}$	exergy flow rate (kW)
$\dot{Ex}_d$	rate of exergy destruction (kW)
ex_M	specific exergy of a material stream (kJ/kg.K)
f	boolean variable (-)
FEB	fossil energy balance (kJ)
FER	fossil energy ratio (-)
Gly	glycerin
GHG	greenhouse gas
h	specific enthalpy (kJ/kg)
HE	hydrous ethanol
IRR	internal rate of return (%)
LHV	lower heating value (kJ/kg)
$\dot{m}$	mass flow rate (kg/s)
MB	microalgae biodiesel
$MeOH$	energy burdens of methanol make-up (kW)
NEB	net energy balance (kJ)
NER	net energy ratio (-)
N_M	energy burdens of the nitrogen source for microalgae cultivation (kW)
NPV	net present value (US$)
NRTL	Non-Random Two Liquid
O&M	operation and maintenance costs(US$)
P_M	energy burdens of the phosphorus source for microalgae cultivation (kW)
$\dot{Q}$	heat transfer rate (kW)
s	specific entropy (kJ/kg.K)
SCF	sugarcane field contributions (kW)
SRK	Soave Redlick-Kwong
SSP	single superphosphate
T_0	reference environment temperature (K)
TAG	triacylglycerides
T_b	boundary temperature (K)
TBMP	theoretical biomethane potential (Nm^3 /$kg_{f.m}$)
TCS	Treatment, concentration, and sterilization
USD	U.S. dollar currency (US$)
vol%	volume fraction
VS	volatile solids
$\dot{W}$	power (kW)
wt%	weight fraction
x_i	molar fraction of a species 'i'
γ	activity coefficient (-)
ψ	exergy efficiency (-)

Subscript

0	reference state at 101.3 kPa and 298 K
CH_4,BL	biogenic methane in the biogas leakage
ch	chemical
d	destroyed
eq	equivalent
i	general index relative to a stream
in	inlet
out	outlet
ph	physical
SC	sugarcane
w	waste

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