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# Exergy analysis of microalgae biodiesel production integrated with a sugarcane ethanol plant

**Pablo Silva Ortiz[1]*, Murilo dos Santos Gabriel[1], Rubens Maciel Filho[1], Adriano Pinto Mariano[1]**

[1]School of Chemical Engineering, University of Campinas, Brazil
e-mail: pabloaso@unicamp.br, murilogabriel210398@gmail.com, rmaciel@unicamp.br, adpm@unicamp.br

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### Abstract

The exergy efficiency of producing microalgae biodiesel using stillage from ethanol fermentation as a cultivation medium was assessed in this work. Thus, mass and energy balances considered the following subsystems of a sugarcane ethanol mill: ethanol and $CO_2$ production from sugarcane juice; biomethane production generated by anaerobic digestion of stillage; microalgae cultivation; conversion of lipids into biodiesel, and cogeneration via sugarcane bagasse and straw. The process integration strategy includes the $CO_2$ utilization produced during ethanol fermentation for the photoautotrophic growth of microalgae; the biodigested stillage as the medium for the heterotrophic growth of microalgae; the burning of biomethane in the cogeneration unit, and the use of electricity and steam cogenerated in the sugarcane mill in the microalgae-biodiesel plant. The microalgae production and conversion plant achieved an exergy efficiency of 29 % with an exergy destruction rate of 159 MW. After process integration, the overall exergy efficiency was 39 % with an exergy destruction rate of 838 MW. This technical performance could represent an indicator following the circular economy concept to increase the profitability of the sugar and ethanol industry. Hence, the issue associated with the stillage disposal (treatment or utilization) from sugarcane ethanol production was addressed from the exergy analysis perspective to explore the potential of this wastewater inherent to the bioenergy sector.

# 1 Introduction

Projections for the next ten years in the sugarcane industry (ethanol and sugar sector) in Brazil point to higher growth in production compared to the past decade [1]. To achieve this goal, the product diversification of the sugarcane supply chain will play a key aspect in enhancing its economic feasibility [2]. Therefore, the sugarcane industry has incorporated the biorefinery and the industrial symbiosis concepts to search for economically and environmentally viable processes integrated into the standard sugarcane mills. The integration of biorefinery processes allows residual/waste biomass to be converted into extract high-value products/by-products (*i.e.,* cosmetics, pharmaceuticals, and food, feed, biofuels, and fertilizers [3].

The recent development of ethanol production technologies concentrates on taking advantage of by-products and residues derived from the production/manufacturing process involved in the ethanol and sugar sector. For example, stillage or vinasse is the final by-product of biomass distillation, mainly from ethanol production from sugar and starch crops or cellulosic material. Its composition is primarily 93% water and 7% solids. Forecasts for Brazil indicated that 490 billion of liters of this material would need to be managed in 2023, considering that each liter of ethanol produced generates around 9 to 14 liters of stillage [4]. Despite most of the stillage utilization being in fertigation practices, this by-product may denote a crucial factor in enhancing the profitability and environmental outcomes of a plant. Thus, upgrade solutions to sugarcane-derived stillage could produce surplus electricity and a reduction in water consumption within a sugarcane mill [5,6].

Currently, the biorefinery process with microalgal biomass represents one of the key areas of interest in the sugar and ethanol industry. Thus, the algal biomass conversion process for biofuel production or high-value products has been explored through the biorefinery and industrial symbiosis concepts. For instance, the integration of microalgae biomass (third-generation) biofuel production process in the sugarcane-based biorefinery has been proven to be a possible technological scenario to maximize the utilization of all components of biomass [7,8]. Most of the studies assessed the biodiesel production from microalgae integrated to the standard sugar/ethanol production processes.

Souza et al. [7] emphasized the technical and economic barriers related to biodiesel production from algae. Highlighting the need for economic incentives and the production of algae-based products with potential benefits, such as carotenoid pigments. Meanwhile, Moncada et al. [8] calculated a positive environmental impact and a high profitability index for the integrated microalgae-sugarcane biorefinery in a payout period of 4 years. Albarelli et al. [9] assessed the integration of first, second, and bioethanol production in a biorefinery system from sugarcane juice, bagasse, and extraction products from microalgae. These authors explored the product diversification in the sugarcane plants over the algae growth and supercritical $CO_2$ extraction via thermal and economic analysis approach. Davis et al. [10] describe in detail a set of process designs and targets to improve the understanding of the economic potential for algal biomass production. The authors also studied the subsequent conversion to biofuels or co-products using cultivation system type '*open pond*' and a sequence of dewatering operations to concentrate the biomass up to 20 wt% solids (ash-free dry weight basis).

In this context, studying the sugarcane-microalgae system performance via simulation tools could be an effective method to explore several biofuels and by-products scenarios by accessing technical feasibility. Hence, the present study aims at assessing from the exergy point of view the integration of first-generation bioethanol production (*autonomous configuration*) from sugarcane juice and biodiesel from microalgae. Thus, technical performance in respect of the global exergy efficiency and irreversibilities rate will be used as thermodynamic criteria to identify potential enhancements in the sugarcane mills.

# 2 Material and methods

## 2.1 Scenario description

In the case scenarios, the ethanol production (first-generation) were considered through data for an autonomous distillery with a processing capacity of 4 million tons of sugarcane (TC) in 210 days per year. The processes involved in the autonomous distillery and the microalgae-sugarcane plant were separated into representative control volumes, as described in the simplified flow diagram of the proposed microalgae-sugarcane biorefinery (Fig. 1). Briefly, cleaning, juice extraction, juice treatment and concentration, glucose fermentation, ethanol distillation, and dehydration are the main steps of the first-generation (1G) ethanol production process. The main operating parameters for each stage of the 1G process for standard mills in Brazil are specified in Bonomi [11] and Silva-Ortiz [12].

Furthermore, the battery limits of the microalgae production and biodiesel plant (dotted line in green) are given in Fig. 1. This control volume involved the anaerobic biodigestion of the stillage, the algal biomass production (microalgae growth in an open pond), and the microalgae biomass conversion into biodiesel through a supercritical $CO_2$ extraction technique. Tab. 1 shows the microalgae biomass composition used to model the system adapted from Davis et al. [10].

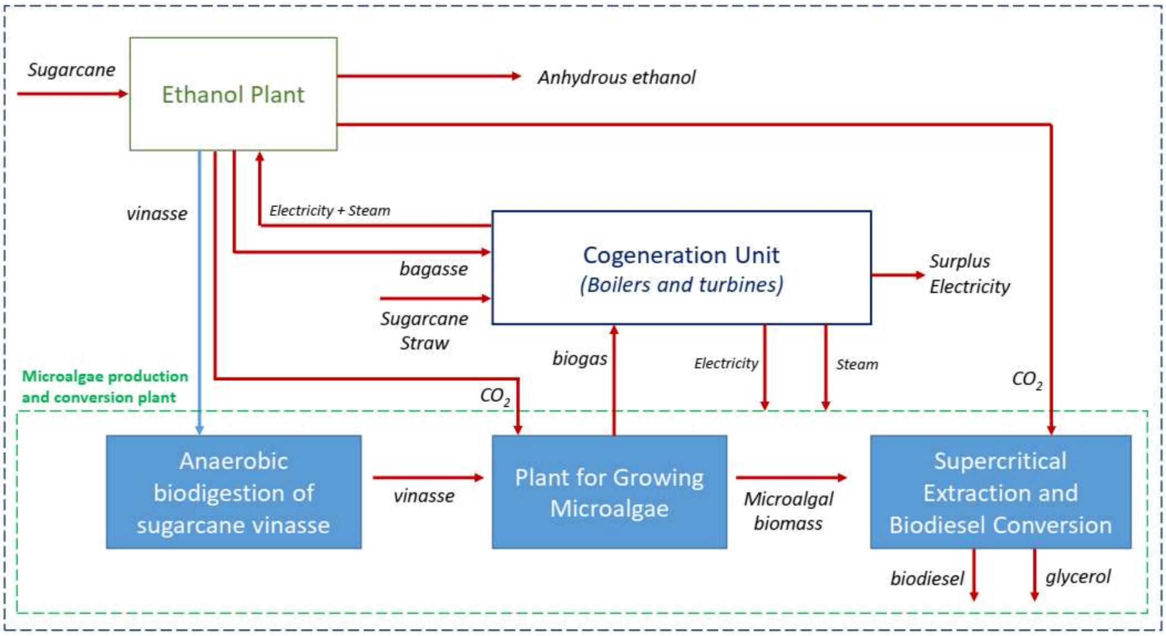



*Figure 1: Simplified flowchart of first-generation ethanol production and the proposed microalgae-sugarcane biorefinery*

Five sugarcane-based biorefinery scenarios/alternatives were evaluated based on the exergy performance indicators.

- S-I Integrated system.
- S-II Integrated system considering algal residue.
- S-III Microalgae production and conversion plant.
- S-IV Microalgae production and conversion plant considering algal residue.
- S-V Base case, Ethanol plant.

*Table 1: Elemental and component compositions for mid-harvest algal biomass*

| ***Culture mode: Scenedesmus acutus* (Davis et al. [10])** | |
|---|---|
| ***Wt% composition (dry basis)*** | (%) |
| Carbon | 54 |
| Hydrogen | 8.2 |
| Oxygen | 35.5 |
| Nitrogen | 1.8 |
| Sulfur | 0.2 |
| Phosphorus | 0.22 |
| Ash | 2.4 |
| Fermentable carbohydrates | 47.8 |
| Non-fermentable carbohydrates | 5.0 |
| Protein | 13.2 |
| Lipids (fuel-relevant lipids as FAME) | 27.4 |
| Non-fuel polar lipid impurities | 2.7 |
| Cell Mass | 1.6 |

In this study, the culture mode selection was based on a review of the characteristics of Scenedesmus, Chlorella, Dunaliella, Nannochloropsis, Spirulina, and Phaeodactylum species. *Scenedesmus acutus* was selected because it presents a high growth rate constant, compatibility/flexibility with the considered location temperature, and available data to enable its modeling.

Table 2 gives the details of the microalgae growth in an open pond, which were taking into account in the mass balance of the microalgae production step.

*Table 2: Modeling parameters (Mass balance)*

| ***General Parameters*** | Value |
|---|---|
| *Geometric cultivation parameters* | |
| Installation area (hectare) | 1076 |
| Module size (hectare) | 40 |
| *Project parameters* | |
| $CO_2$ absorption efficiency in the reservoir (%) | 90 |
| Overall drainage efficiency (%) | 95.5 |
| *Key modeling parameters* | |
| Algae productivity ($g.m^{-2}.day^{-1}$) | 25 |
| Initial concentration on inoculation ($g.L^{-1}$) | 0.1 |
| Collection concentration of reservoirs ($g.L^{-1}$) | 1 |
| Evaporation rate of reservoirs ($cm.day^{-1}$) | 0.1 |
| Tertiary drainage biomass concentration ($g.L^{-1}$) | 200 |

## 2.2 Exergy analysis

The exergy flow of materials consists of kinetic, potential, and internal 'thermal' exergy terms. It was adopted that the variation of kinetic and potential exergy terms was negligible through the system. Hence, the exergy flow of materials was focus on the thermal exergy term, which involves the sum of physical and chemical exergy. A detailed application of the exergy method for a lignocellulosic-based biorefinery is given in Silva-Ortiz et al. [13]. Furthermore, Table 3 displays the specific chemical exergy ($b_{ch}$) of the compounds involved in the assessment.

*Table 3: Specific chemical exergy of the compound*

| ***Compounds*** | ***Molar mass (kg/kmol)*** | ***Formula*** | ***Specific Chemical Exergy (kJ/kg)*** | ***References*** |
|---|---|---|---|---|
| Carbohydrates | 162.14 | $C_6H_{10}O_5$ | 18875 | [14] |
| Glucose | 180.15 | $C_6H_{12}O_6$ | 16280 | [15] |
| Protein | 57.05 | $C_2H_3NO$ | 24488 | [16] |
| Glycine | 75.06 | $C_2H_5NO_2$ | 13981 | [15] |
| Lipids | 801.40 | $C_{57}H_{104}O_6$ | 45861 | [16] |
| Glycerol | 92.09 | $C_3H_8O_3$ | 18539 | [16] |
| Oleic acid | 282.46 | $C_{18}H_{34}O_2$ | 42068 | [16] |
| Water | 18.01 | $H_2O$ | 50 | [15] |
| Ammonia | 17.03 | $NH_3$ | 19840 | [15] |
| Carbon dioxide | 44.01 | $CO_2$ | 451 | [15] |
| Methane | 16.04 | $CH_4$ | 51981 | [16] |
| DAP | 132.06 | $(NH_3)_2(PO_4)$ | 19818 | [16] |
| Sodium chloride | 58.44 | NaCl | 245 | [15] |
| Oxygen | 31.99 | $O_2$ | 124 | [15] |
| Ash | 60.08 | $SiO_2$ | 59 | [14] |

Exergy assessment can be used to analyse, evaluate, and improve the process as a measurement approach of energy quality [15]. A global exergy balance for a system is described by Eq. (1). The terms $B_{IN}$ represents the total exergy inputs and $B_{OUT}$ the sum of the exergy outputs, respectively. Besides, $B_{loss}$ denotes the irreversibilities or the exergy destruction in the operational units.

$$\dot{B}_{IN} - \dot{B}_{OUT} + \dot{B}_{heat} - \dot{B}_{work} = \dot{B}_{loss} \quad (1)$$

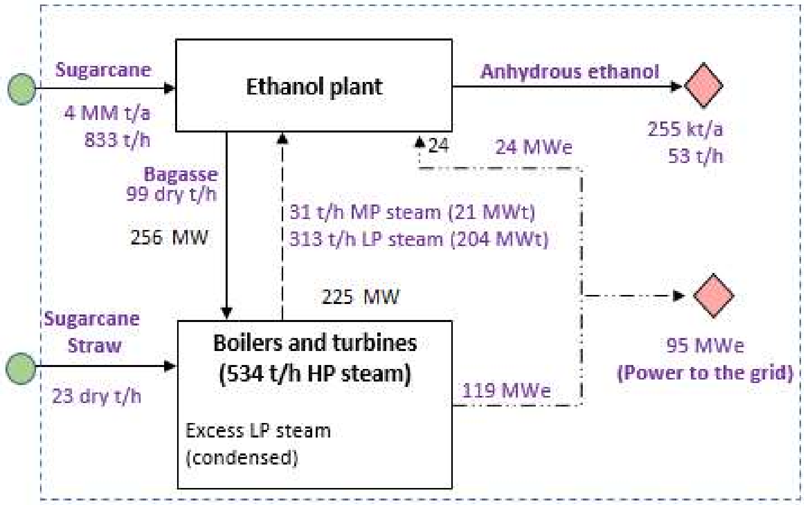
# 3 Results and discussion

## 3.1 Exergy assessment

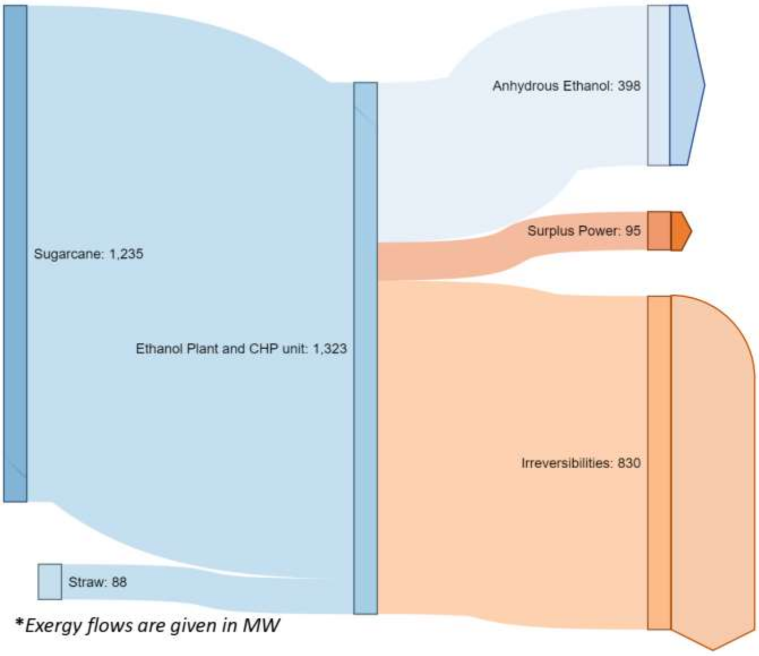
The exergy analysis was carried out founded on the mass, energy, and exergy balances of the different configurations. Thus, the influence of the thermodynamic efficiency of the integration of microalgae production and the biodiesel conversion plant into the first-generation ethanol production process (base case) was assessed to determine the effects of adding/modifying process modules. Indeed, this is a general challenge in the synthesis of energy systems, where there are many technological pathways based on biorefining sequences. This issue could be addressed it thought the Second law of Thermodynamics.

The level of integration of biorefinery systems will also produce different alternatives, which may also influence the technical performance and economic feasibility of energy technologies (*e.g.,* mass, energy, and thermal integration) [8].

Figure 2 shows the mass and energy/exergy balance for an autonomous plant (*base case*) (Fig. 2a). Later, the Grassmann diagram for this sugarcane-based biorefinery is given in Fig. 2b. In this figure, the exergy flows are set in MW for the alternative system S-V.



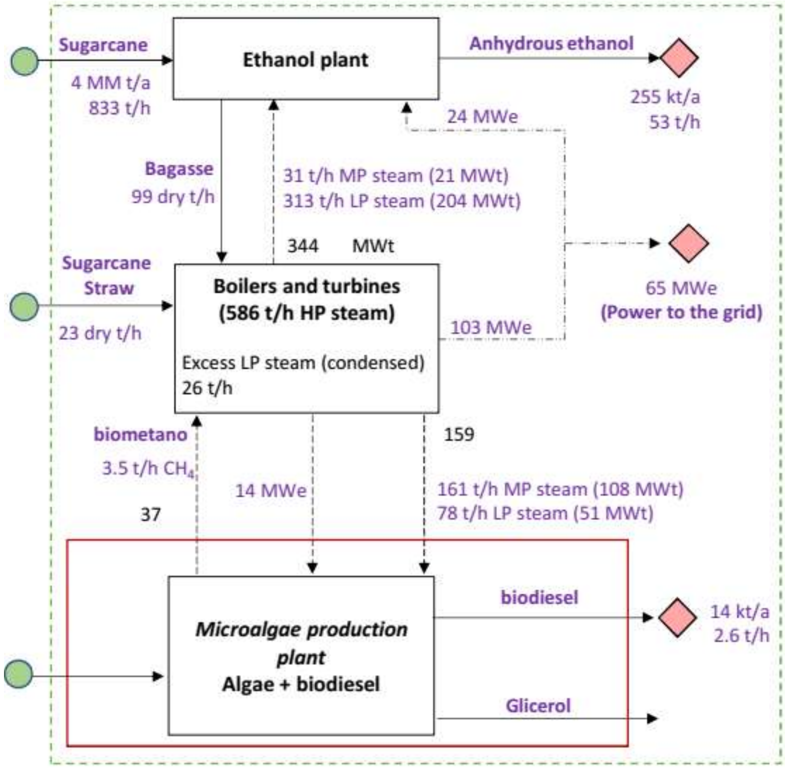

a).



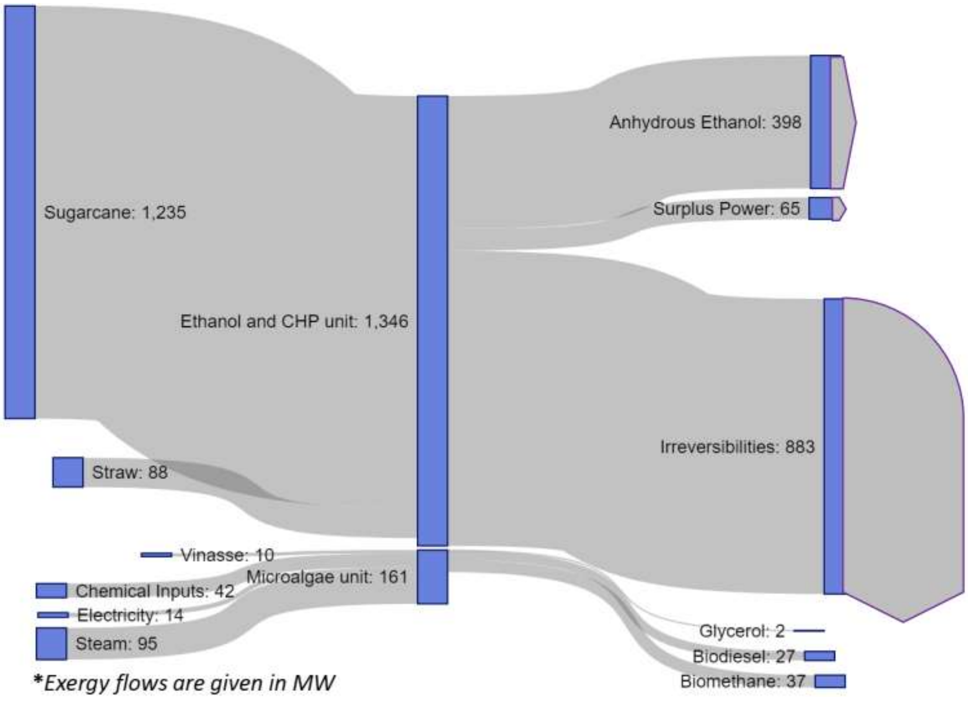

b).

*Figure 2: Mass, energy, and exergy balance, Grassmann diagram of the autonomous plant (SV-base case)*

Figure 3 displays the mass and energy/exergy balance for the integrated system (Fig. 3a). The integrated system involves the base case, microalgae production, and biodiesel conversion plant (S-I). In addition, the Grassmann diagram or the exergies flows in MW for this integrated sugarcane-microalgae biorefinery is given in Fig. 3b.




a).




b).

*Figure 3: Mass energy, and exergy balance, Grassmann diagram of the integrated system (S-I)*

## 3.2 Process Indicators

Figure 4 summarizes the technical process indicators related to the sugarcane-based biorefinery alternatives evaluated. Thus, the exergy efficiency and the destruction exergy rates are used to determine the performance of the processes.

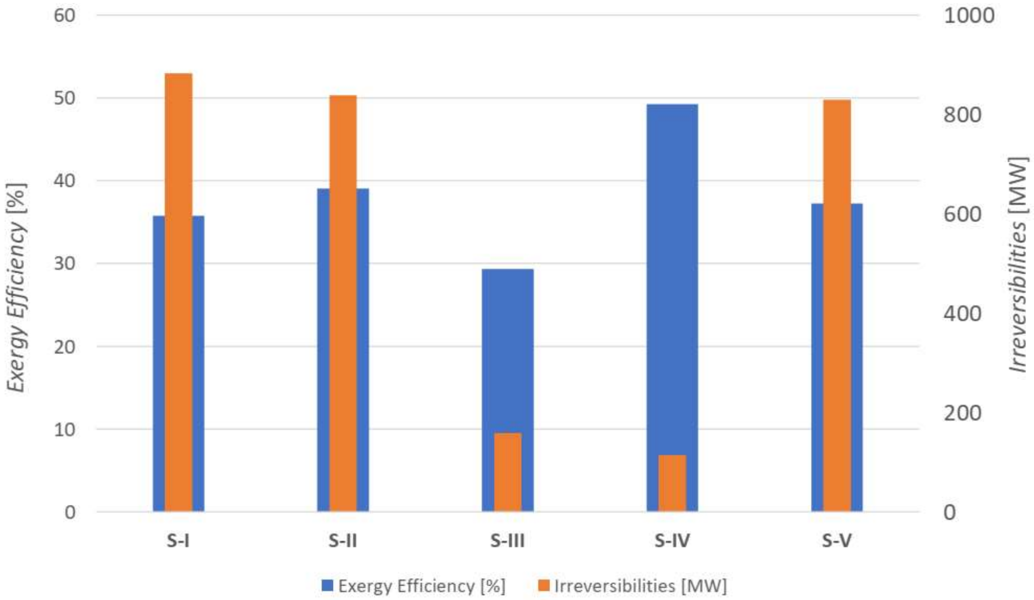



*Figure 4: Process performance indicators*

It is noted that the S-IV present higher exergetic efficiency (49 %) regarding the evaluated alternatives. Hence, adding value to the algal residue (mainly composed of *Carbohydrates 53 %, Protein 13 %, and Lipid 9 %*) could represent a reduction of 45 MW in the irreversibilities. It is also emphasized that the use of the algal residue in the control volume involving the Integrated System allowing achieve an exergy efficiency of 39% (S-II), which is roughly the thermodynamic indicator of the first-generation ethanol plant (S-V).

Thereby, extending the biorefinery/industrial symbiosis concepts into alternative biorefinery scenarios represent the identification of potential pathways that focus on chemical building block (*e.g.*, glycerol, microalgae meal, and biodiesel). Table 4 shows the main flows related to inputs and outputs of the microalgae sugarcane-based biorefinery (alternative S-I).

*Table 4: Main flows (Inputs and Outputs) of the integrated system*

| ***Parameters*** | ***Value*** |
|---|---|
| ***Inputs of the integrated plant*** | |
| Ammonia, (thousand ton/year)[1] | 1.1 |
| Diammonium phosphate (DAP), (thousand ton/year)[1] | 0.5 |
| Raw stillage from the autonomous plant (billion L/year)[1] | 3.5 |
| Biogenic $CO_2$ (thousand ton/year)[1] | 262 |
| Ethanol as a co-solvent for supercritical extraction (thousand ton/year)[2] | 6.9 |
| Sodium bicarbonate for correction of pH (thousand ton/year)[3] | 19 |
| Electricity from the cogeneration unit (MW) | 14 |
| Low and medium pressure steam (MW) | 159 |
| ***Outputs at the integrated plant*** | |
| Glycerol (thousand ton/year)[3] | 1.4 |
| Biodiesel, 99% purity (million L/year) | 14.5 |
| Biogas, 76.5% (v/v) of CH4 for cogeneration (million $m^3$/year) | 26.3 |

[1]Davis et al. [10], [2]Albarelli et al. [9], [3]Klein et al. [17].

The data were obtained through mass and energy balances adapted to the production scale. In the cultivation stage, the data provided by NREL [10] was used to calculate the biomass output. In the biodiesel conversion stage, the efficiency and extraction yield considered parameters reported by Albarelli et al. [9]. In contrast, the inputs and outputs of the pre-treatment and transesterification steps were adapted from Ochoa et al. [18]. Lastly, the treatment of stillage for biogas production used the balance described by Klein et al. [17].

# 4 Conclusions

From the Second Law of Thermodynamic perspective, it was determinate the technical feasibility of microalgae sugarcane-based biorefinery using exergy as an indicator. Hence, the integrated system is ranking as an attractive scenario to be considered into the technological portfolio of a sugarcane mill. Alternatives scenarios were also analyzed under the biorefinery/industrial symbiosis concepts to target the development and implementation of new configurations for the stillage valorization. Thereby, these applications could contribute to the creation of a circular economy based on the potential of chemical building blocks and new products at the biomass supply chain level.

Another aspect of being highlighted is that the supercritical $CO_2$ extraction method via ethanol as co-solvent demonstrated to be an efficient alternative since higher carotenoids and lipid productivity with low-electricity consumption was achieved. In fact, the carbon dioxide flow used in the microalgae production and conversion plant is a key factor in these processes. In this respect, a sensitivity analysis should be addressed to focus on the $CO_2$ recovery, the supercritical extraction, and the calculation of the exergy from the sun in future research.

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# References

[1] Editora Gazeta, Anuário Brasileiro da Cana-de-açúcar 2019. http://www.editoragazeta.com.br/produto/anuario-brasileiro-da-cana-de-acucar-2019/ (accessed July 18, 2020).

[2] UNICA, Etanol, (2020). https://unica.com.br/setor-sucroenergetico/etanol/ (accessed July 18, 2020).

[3] M.G. de Morais, E.G. de Morais, B.B. Cardias, B. da S. Vaz, J.B. Moreira, B.G. Mitchell, J.A.V. Costa. Chapter 13 - Microalgae as a source of sustainable biofuels, in: V.K. Gupta, H. Treichel, R.C. Kuhad, S. Rodriguez-Cout (Eds.), Recent Developments in Bioenergy Research, Elsevier, 2020: pp. 253–271. https://doi.org/10.1016/B978-0-12-819597-0.00013-1.

[4] E.N.V.M. Carrilho, G. Labuto, M.Y. Kamogawa. Chapter 2 - Destination of Vinasse, a Residue From Alcohol Industry: Resource Recovery and Prevention of Pollution, in: M.N.V. Prasad, K. Shih (Eds.), Environmental Materials and Waste, Academic Press, 2016: pp. 21–43. https://doi.org/10.1016/B978-0-12-803837-6.00002-0.

[5] C.E. Rodrigues Reis, B. Hu. Vinasse from Sugarcane Ethanol Production: Better Treatment or Better Utilization?, Front. Energy Res. 5 (2017). https://doi.org/10.3389/fenrg.2017.00007.

[6] B.S. Moraes, M. Zaiat, A. Bonomi. Anaerobic digestion of vinasse from sugarcane ethanol production in Brazil: Challenges and perspectives, Renewable and Sustainable Energy Reviews. 44 (2015) 888–903. https://doi.org/10.1016/j.rser.2015.01.023.

[7] S.P. Souza, A.R. Gopal, J.E.A. Seabra. Life cycle assessment of biofuels from an integrated Brazilian algae-sugarcane biorefinery, Energy. 81 (2015) 373–381. https://doi.org/10.1016/j.energy.2014.12.050.

[8] J. Moncada, J.A. Tamayo, C.A. Cardona. Integrating first, second, and third generation biorefineries: Incorporating microalgae into the sugarcane biorefinery, Chemical Engineering Science. 118 (2014) 126–140. https://doi.org/10.1016/j.ces.2014.07.035.
[9] J.Q. Albarelli, D.T. Santos, A.V. Ensinas, F. Marechal, M.J. Cocero, M.A. Meireles. Product diversification in the sugarcane biorefinery through algae growth and supercritical CO2 extraction: Thermal and economic analysis, Renewable Energy. 129 (2018) 776–785. https://doi.org/10.1016/j.renene.2017.05.022.
[10] R. Davis, J. Markham, C. Kinchin, N. Grundl, E.C.D. Tan, D. Humbird. Process Design and Economics for the Production of Algal Biomass: Algal Biomass Production in Open Pond Systems and Processing Through Dewatering for Downstream Conversion, National Renewable Energy Lab. (NREL), Golden, CO (United States), 2016. https://doi.org/10.2172/1239893.
[11] A. Bonomi, O. Cavalett, M.P. Cunha, M.A. Lima. Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization, Springer International Publishing, Switzerland, 2016. https://www.springer.com/la/book/9783319260433.
[12] P. Silva Ortiz, D. Flórez-Orrego, S. Oliveira Junior, R. Maciel Filho, F. Marechal. Exergetic, environmental and economic assessment of sugarcane first-generation biorefineries, JPT. (2019).
[13] P. Silva Ortiz, R. Maciel, J. Posada. Mass and Heat Integration in Ethanol Production Mills for Enhanced Process Efficiency and Exergy-Based Renewability Performance, Processes. 7(10) (2019) 670. https://doi.org/10.3390/pr7100670.
[14] P. Silva Ortiz, S. Oliveira Junior. Compared exergy analysis of sugarcane bagasse sequential hydrolysis and fermentation and simultaneous saccharification and fermentation, International Journal of Exergy. 19 (2016) 459. https://doi.org/10.1504/IJEX.2016.075880.
[15] J. Szargut, D. Morris, F. Steward. Exergy analysis of thermal, chemical, and metallurgical processes., Hemisphere Publishing Corporation, New York, 1988.
[16] C. Xiao, Q. Liao, Q. Fu, Y. Huang, A. Xia, W. Shen, H. Chen, X. Zhu. Exergy analyses of biogas production from microalgae biomass via anaerobic digestion, Bioresource Technology. 289 (2019) 121709. https://doi.org/10.1016/j.biortech.2019.121709.
[17] B.C. Klein, M.F. Chagas, M.D.B. Watanabe, A. Bonomi, R. Maciel Filho. Low carbon biofuels and the New Brazilian National Biofuel Policy (RenovaBio): A case study for sugarcane mills and integrated sugarcane-microalgae biorefineries, Renewable and Sustainable Energy Reviews. 115 (2019) 109365. https://doi.org/10.1016/j.rser.2019.109365.
[18] M. Ochoa-Garcia, L. Tejeda-Lopez, K. Ojeda-Delgado, A. Gonzalez-Delgado, E. Sanchez-Tuiran. Process Simulation and Exergy Analysis of Microalgal Biodiesel Production using Chlorella vulgaris via ZnCl2 Pretreatment, SRS Journal. (n.d.). https://indjst.org/ (accessed July 19, 2020).