

UNIVERSIDADE ESTADUAL DE CAMPINAS

Faculdade de Engenharia Química

BRUNO COLLING KLEIN

ESTABLISHING SUGARCANE-MICROALGAE BIOREFINERIES

AVALIAÇÃO DE BIORREFINARIAS INTEGRADAS DE CANA-DE-AÇÚCAR E MICROALGAS

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Tese apresentada à Faculdade de Engenharia Química da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Engenharia Química.

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A Ata da defesa com as respectivas assinaturas dos membros da banca examinadora encontrase no processo de vida acadêmica do aluno.

To my son's generation: may you continue to find solutions to the issues created by your forebears.

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ABSTRACT

The search for industrial processes with higher sustainability performance has led to a change towards the utilization of renewable sources for energy generation in substitution of fossil fuels, with the intention of modifying the global energy matrix. Under this scope, the present work evaluated the techno-economic feasibility and the environmental impacts of the integration between large-scale microalgae facilities and sugarcane mills into a true biorefinery concept. Process integration was based on: (1) the utilization of CO₂ produced during ethanol fermentation and that contained in biogas for the photoautotrophic growth of microalgae; (2) the employment of vinasse as the carbon source for the heterotrophic growth of microalgae; and (3) the use of energy vectors from the sugarcane mill to enable the production and processing of the microalgae biomass, such as electric energy and process steam. Several configurations were assessed via modeling and simulation with the commercial software Aspen Plus® (AspenTech) and electronic spreadsheets with data obtained from the scientific literature. The assessment indicates that increasing the operation period of a sugarcane mill from 200 to 330 days represents an important step towards increasing the economic return of biorefineries in view of the lower capital expenditures involved. Regarding microalgae production, the high intensity in terms of inputs, such as electric energy and chemicals, must be tackled to improve the overall feasibility of such projects. The results point out to a positive impact due to the addition of AD of vinasse for biogas production (and sequential upgrading to biomethane) on the environmental performance of anhydrous ethanol production. Finally, the influence of the National Biofuel Program (RenovaBio) over sugarcane mills and over co-located sugarcane-microalgae biorefineries was assessed. In view of the low climate change impact associated to biofuels produced in integrated biorefineries (ethanol and biodiesel, according to the assessed scenario), combined microalgae-sugarcane plants will be able to mitigate a larger amount of CO_2 emissions than conventional sugarcane mills - and, therefore, will be able to increase the revenues through the commercialization of larger quantities of decarbonization credits in the Brazilian market.

Keywords: microalga; sugarcane; biorefinery; economic assessment; environmental assessment.

RESUMO

A busca por sustentabilidade em processos industriais tem levado a uma mudança visando à utilização de fontes renováveis para geração de energia em substituição aos combustíveis fósseis, de modo a modificar a matriz energética global. Dentro deste escopo, o presente trabalho avaliou a viabilidade técnico-econômica e os impactos ambientais resultantes da integração entre plantas de microalgas em larga escala e usinas de cana-de-açúcar em um verdadeiro conceito de biorrefinaria. A integração de processos foi baseada em: (1) utilização de CO₂ produzido durante a fermentação e de CO₂ contido em biogás para crescimento fotoautotrófico de microalgas; (2) emprego de vinhaça como fonte de carbono para o crescimento heterotrófico de microalgas; e (3) uso de vetores energéticos da usina de cana-deaçúcar para permitir a produção e o processamento da biomassa de microalgas, como energia elétrica e vapor de processo. Diversas configurações foram avaliadas através de modelagem e simulação com o software comercial Aspen Plus® (AspenTech) e com planilhas eletrônicas, utilizando dados obtidos da literatura científica. A avaliação indicou que o aumento do período de operação de uma usina de cana-de-açúcar de 200 para 330 dias representa um passo importante para aumentar o retorno financeiro de biorrefinarias dado os menores investimentos fixos envolvidos. Em relação à produção de microalgas, o alto consumo de insumos, como energia elétrica e químicos, deve ser enfrentado em escala piloto e industrial de modo a melhorar a viabilidade de tais projetos. Os resultados também apontam para o impacto positivo da incorporação da biodigestão de vinhaça para produção de biogás (e sua purificação a biometano) sobre o desempenho ambiental da produção de etanol. Finalmente, a influência da atual Política Nacional de Biocombustíveis (RenovaBio) sobre usinas de canade-açúcar e biorrefinarias integradas foi avaliada. Dado o baixo impacto em aquecimento global dos biocombustíveis produzidos nas biorrefinarias integradas (bioetanol e biodiesel, de acordo com o cenário), plantas combinadas de microalgas e cana-de-açúcar serão capazes de mitigar mais emissões de CO₂ que usinas convencionais - e, dessa forma, poderão aumentar a sua receita através da comercialização de uma maior quantidade de créditos de descarbonização no mercado brasileiro.

Palavras-chave: microalga; cana-de-açúcar; biorrefinaria; avaliação econômica; avaliação ambiental.

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ABBREVIATIONS

1G: first-generation 1G2G: integrated first- and second-generation 2G: second-generation AD: anaerobic digestion AFEX: ammonia fiber expansion bioPE: biobased polyethylene BOD: biochemical oxygen demand: CAPEX: capital expenditure **CBio:** Decarbonization Credit CHP: Cogeneration of Heat and Power COD: chemical oxygen demand COP: coefficient of performance COP21: 21st Conference of Parties CTBE: Brazilian Bioethanol Science and Technology Laboratory DAF: dissolved air flotation DAP: diammonium phosphate EE: electric energy GHG: greenhouse gases HEFA: hydroprocessing of esters and fatty acids HTM: high-test molasses IPCA: consumer prices index (Índice Nacional de Preços ao Consumidor) IRR: internal rate of return LCA: Life Cycle Assessment LCM: lignocellulosic material LED: light-emitting diode LUC: land-use change LHV: lower heating value MAP: monoammonium phosphate MARR: minimum acceptable rate of return MSP: minimum selling price MTC: million tonnes of sugarcane per year NCC: nanocrystalline cellulose

NDC: Nationally Determined Contribution

NFC: nanofibrillated cellulose

NPV/I: net present value over investment ratio

NPV: net present value

OPEX: operational expenses:

PAR: photosynthetically active radiation

PBR: photobioreactor

PE: polyethylene

PHAs: polyhydroxyalkanoates

PHB: poly-3-hydroxybutyrate

PLA: poly-lactic acid

PNPB: National Program of Biodiesel Production and Use

Proálcool: National Alcohol Fuel Program

PSA: pressure swing adsorption

PVC: polyvinyl chloride

RenovaBio: National Biofuel Program

SAT: See Algae Technology

UASB: upflow anaerobic sludge blanket

UNFCCC: United Nations Framework Convention on Climate Change

VOL: volumetric organic load

VSB: Virtual Sugarcane Biorefinery

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CHAPTER 1 INTRODUCTION AND GOALS

1.1 Introduction

In the medium term, the reduction in the global dependence on fossil-based fuels passes by the production of large amounts of biomass for the synthesis of biofuels. Ethanol and biodiesel are currently the biofuels with the largest production volumes at 98.6 and 30.8 billion L in 2016, respectively, (REN21, 2017) and positive environmental impacts on the displacement of fossil fuels (Cavalett et al., 2012; Collet et al., 2011; Kim and Dale, 2005). This substitution, in fact, needs to occur in order to attend the increasing requirements to reduce greenhouse gases (GHG) emissions and other environmental impacts. Novel biofuels with very low sustainability impacts will be needed to constitute part of the global energy matrix in addition to more established, conventional biofuels, such as first-generation (1G) ethanol and biodiesel.

Moreover, Brazil is a biomass-driven economy. The country is known worldwide for being home to large agricultural areas of various types: grains, coffee, fruits, and energy crops. Due to such a prolific scenario, food *vs.* fuel debates common to other regions of the globe with lower biomass production, such as Europe, seldom occur in the Brazilian society. With this panorama, it is imperative that the country seizes the opportunity for diversification of its biofuels industry, in view of the ever-growing pressure on slashing fossil carbon emissions.

The potential of solely employing conventional energy crops, like sugarcane, corn, soybean, palm, and rapeseed, for the production of ethanol and biodiesel is somehow limited due to the difficulty in further increasing carbohydrate and lipid productivities of such species and to the large projected increase in global consumption of liquid fuels, usually obtained from fossil sources, in future years (Mohr et al., 2015). Another fact drawing attention towards alternative sources of carbohydrates and lipids is the concern with land use change combined with food production issues (Doshi et al., 2016). The possibility of using microalgae, a nonconventional biomass source, for the production of biofuels and other bioproducts is currently being considered an interesting option for the near future (Kligerman and Bouwer, 2015) due to positive sustainability impacts resulting from the technology (Lardon et al., 2009; Sander and Murthy, 2010; Yang et al., 2011).

In spite of the existence of technology for the production of microalgal biomass in industrial scale, more efforts in Research and Development are needed for achieving low biofuel production costs. Being highly intensive in nearly all aspects (fixed investment, operational expenses, and material and energy inputs), the overall costs of biofuels production could be reduced through process integration with established plants. In Brazil, sugarcane is one of the biomasses with the largest applications for both food and fuel, with a yearly national production of over 650 million tonnes per harvest and processing in hundreds of facilities (CONAB, 2017). Sugarcane mills, therefore, stand out as one of the best options for hosting microalgae biorefineries and supporting their development. In view of this panorama, the main research object of this Thesis revolves around the establishment of co-located biorefineries of such type in Brazil, with the sugarcane mill as the host plant and the microalgae facility as the unit which may highly benefit through process integration. Technoeconomic and environmental assessments were carried out using the Virtual Sugarcane Biorefinery (VSB), developed by the Brazilian Bioethanol Science and Technology Laboratory (CTBE), in order to qualitatively and quantitatively analyze different process configurations.

1.2 Goals

The main goals - divided into primary and secondary - of this Thesis are as follows:

Primary goals

- To determine the possibility and feasibility of integration between a sugarcaneprocessing facility and a microalgae production plant, thus expanding the biorefinery concept.

Secondary goals

- To assess the most promising cultivation system for microalgae production in Brazil (namely open or closed photobioreactors);

- To analyze the use of CO₂ from ethanol fermentation and contained in biogas for the growth of microalgae through photosynthesis;

- To evaluate the economic and environmental feasibility of heterotrophic cultivation of microalgae using sugarcane vinasse as the carbon source;

- To evaluate the potential of employing microalgae biodiesel and biomethane as substitutes for fossil diesel in sugarcane agricultural operations;

- To determine the economic impact of the new National Biofuel Policy (RenovaBio Program) on integrated biorefineries through the selling of low-carbon biofuels, namely anhydrous ethanol and microalgae biodiesel.

1.3 Thesis structure

The present document is divided into seven main Chapters.

Chapter 1 (*Introduction*) presents a brief introduction to the researched subject, as well as the primary and secondary goals expected for the development of this project.

Chapter 2 (*Product Portfolio Diversification in Sugarcane Mills*) provides an overview of the existing integrated sugarcane biorefineries in Brazil and of the potential of expanding the number of products obtained from sugarcane biomass.

Chapter 3 (*Integration of Microalgae Production with Industrial Biofuel Facilities: A Critical Review*) contains a critical exploration of the state of the art of process integration between sugarcane mills and other facilities, especially microalgae plants. The content roughly corresponds to that published in Renewable & Sustainable Energy Reviews in February 2018.

Chapter 4 (*Microalgae Production in Next-Generation Integrated Sugarcane Biorefineries: Fermentation-Derived CO*₂ and Vinasse as Carbon Sources for Algal Growth) provides scenarios and the full techno-economic and environmental assessment on the co-location between sugarcane biorefineries and microalgae facilities using mainly fermentation-derived CO₂ and sugarcane vinasse as the carbon sources.

Chapter 5 (*Microalgae Production in Next-Generation Integrated Sugarcane Biorefineries: Biogas-Derived CO*₂ *as an Additional Carbon Source for Algal Growth*), on the other hand, presents a similar analysis, although with the addition of anaerobic digestion (AD) of vinasse for the production of biogas and the subsequent upgrading to biomethane using microalgae cultivations.

Chapter 6 (*Influence of the new National Biofuel Program (RenovaBio) on Sugarcane-Microalgae Biorefineries*) carries out a quantitative assessment of the benefits that could be brought to the Brazilian biofuels industry by the RenovaBio Program through a new market of decarbonization credits.

Chapter 7 (*Conclusion*) revisits the main findings of the work and proposes several topics to be addressed in the future by other research projects.

Finally, Annex A.1 presents an article written in Portuguese (*Microalgas e Cana-De-Açúcar: Uma Parceria em Potencial*) for the diffusion of the theme among the general public. The paper has been published in Revista STAB, well-known among the Brazilian sugarenergy sector. Annexes A.2 and A.3 bear auxiliary tables with parameters employed in the assessment of scenarios in Chapters 4 and 5.

CHAPTER 2 PRODUCT PORTFOLIO DIVERSIFICATION IN SUGARCANE MILLS

2.1 Introduction

Process integration is an interesting option for cost reduction and improving the economic feasibility of new processes. This can be also the case of sugarcane mills, which are able to provide high amounts of both material and energy inputs for emerging technologies. Brazil has a prolific sugar-energy sector, with hundreds of sugarcane mills that could possibly act as sources of carbon, energy, and water to annexed plants. While many studies analyze the integration of new technologies to sugarcane biorefineries as greenfield plants (Cardona and Sánchez, 2007; Carvalheiro et al., 2008; Klein et al., 2017; Machado et al., 2016; Moncada et al., 2013; Santos et al., 2016; Silva et al., 2017a), the assessment and establishment of some brownfield integrated plants widely helps to detect process bottlenecks and better understand the required levels of integration prior to the design of a full-scale, greenfield biorefinery. Brownfield biorefinery design aims at finding practical solutions for an economic sector short of innovation alternatives and may also bring advances in the learning curve that can be useful for economically competitive designs. An expansion in the number of products that a sugarcane mill is able to supply to the market may add to the overall financial security of the plant, as well as providing an opportunity for such facilities to jump into previously unexplored markets. This further supports the thesis that brownfield biorefineries should be favored also as a means of improving the financial performance of such units.

2.2 Brazilian sugarcane mills

Brazil is the second largest producer of ethanol in the world with a current production of nearly 28 million m³ of ethanol per year (CONAB, 2017). The country's long-standing experience with ethanol for automotive purposes started in the first two decades of the 20th century. From the 1930s onwards, the mandatory use of gasoline blended with at least 5% anhydrous ethanol was introduced. Until 1975, the ethanol content in the commercialized gasoline varied through the decades, corresponding to an average of 7.5% during the period (BNDES, 2008). In the same year, the first oil choc led the Brazilian government to create an incentive program called Proálcool, aimed at reducing the country's energy dependency on foreign sources. Proálcool's first phase (1975-1979) focused at increasing the production of anhydrous ethanol for blending with fossil gasoline. From 1979 onwards, the program's second phase prioritized the synthesis of hydrated ethanol for adapted or ethanol-specific engines (BNDES, 2008; Laurini, 2017). The appearance (and market success) of flex-fuel vehicles in 2003, which allowed customers to choose between either gasoline or hydrated ethanol in view of price and performance, reignited the internal consumption of ethanol, thus shaping the current panorama in the country.

Brazilian sugarcane mills usually operate according to three distinct configurations: autonomous distilleries, which produce exclusively ethanol; sugar factories, producing only sugar; and sugar factories with annexed distilleries, which are able to produce a variable mix of sugar and ethanol. The vast majority of mills in Brazil are of the last type. The chosen production mix is normally guided by market conditions, especially the international sugar price. Even though, if a mill has a supply deal with distributors of C grade gasoline (a mixture of gasoline and 27% of anhydrous ethanol), the production established in contract must be followed.

In spite of distinct arrangements, sugarcane processing for sugar and ethanol production follows a relatively defined set of processes. After reception and cleaning of sugarcane stalks, sugar extraction is carried out in mills, thus generating bagasse and sugarcane juice. Juice treatment operations usually include liming (addition of Ca(OH)₂), settling, and filtration. In autonomous distilleries, the carbon source for fermentation is solely comprised of concentrated and treated sugarcane juice; in annexed plants, the fermentation broth is a mixture of concentrated treated juice and molasses (the final residue of sugar production, which contains sugars like glucose and sucrose and other proteins, salts and minerals found in sugarcane). The production of ethanol through fermentation with Saccharomyces cerevisiae strains yields large amounts of CO₂ - stoichiometrically, 1 mol of CO₂ per mol of ethanol produced. After fermentation, a centrifuge separates wine from the yeast, the latter being usually treated with H₂SO₄ and diluted with water prior to recycling to the fermenter. In the distillation area, ethanol is purified in columns until the ethanol-azeotrope is reached, with about 95% v/v ethanol. Ethanol is either sold in its hydrous form, as a fuel for Otto cycle engines, or as an anhydrous compound to be employed as a gasoline additive (mandatory mixing of anhydrous ethanol in gasoline is of 27% since March 2015) (Brazil, 2015). The production of anhydrous ethanol is carried out through the dehydration of hydrous ethanol in extractive or azeotropic distillation columns or with molecular sieves. For sugar production, sugarcane juice is concentrated until a solids content of about 65% is reached (65 °Brix in the terminology most commonly referred to in the industry). The concentrated juice (syrup)

The industrial production of sugar and ethanol requires electric energy (EE) and thermal energy, the latter supplied in the form of process steam. Steam is raised on-site through the burning of sugarcane bagasse (and eventually straw) in boilers. High-pressure steam is expanded to the pressure levels demanded by the process in turbines connected to turbogenerators, thus generating EE in this operation. Mills connected to the grid by transmission lines may sell the surplus EE either through established supply contracts or on the spot market. As the sales of energy become an interesting business for sugarcane mills after the regulation of sales of bioelectricity in Brazil (CPFL, 2016), several units intend to expand power output capabilities. Two main approaches can be explored with this purpose. Novel technologies for sugarcane lignocellulosic material (LCM) combustion, such as fluidized bed boilers, may be employed to raise steam at higher pressures than boilers with older technology - 65 or 90 bar in comparison to the more common, older 22 bar boilers (Miguel et al., 2017). High-efficiency turbo-generators may also be considered for the expansion of power output. Another currently under-exploited possibility is the recovery of sugarcane straw from the field for combustion in boilers. Straw is usually left in the field to form a protective cover to the soil and to cycle nutrients, thus retaining water and preventing nutrient lixiviation (Leal et al., 2013). Since straw alone corresponds to about a third of the total energy present in sugarcane (Cavalett et al., 2016), a portion could be removed and brought to the industrial unit, where it could be burned after undergoing proper cleaning operations. Several studies show that removal rates of up to 70% could significantly improve EE generation, with possible beneficial impacts on soil conditioning according to its type and edafo-climatic conditions (Cardoso et al., 2013; Cardoso et al., 2015). Both options require significant investment by mill owners, but the long-term return from additional EE commercialization compensates the effort. On the other hand, a future increase in ethanol production may come in the form of second-generation (2G) ethanol, in which sugarcane LCM is saccharified in a series of steps and fermented to enhance production of the biofuel. This is further explored in Section 2.4.

Sugarcane mills commonly operate during sugarcane harvest period (from March to November in the Central and Southeastern regions of Brazil). The inherent seasonality of sugarcane mill operation due to the natural sugarcane planting and harvesting cycle is often surprising to investors wishing to invest in this sector in Brazil. However, some strategies may enable mills to generate different outputs throughout the year, extending operation during sugarcane off-season. This period is often reserved for equipment maintenance and preparation for the next season. Strategies for ethanol and/or sugar production during sugarcane off-season period may include the utilization of other biomasses such as sweet sorghum, corn, or energy cane, for example (Eckert et al., 2018; Junqueira et al., 2017). Straw recovery from the field is also an option to transform a season-operating mill into a year-round mill through EE generation during the off-season. A second approach to ethanol production during the off-season is the storage of inverted syrup (a necessary procedure when storing concentrated sugarcane syrup for diminishing the degradation of sugars) or molasses for posterior processing.

Another factor that may directly impact the choice or the capability of a given sugarcane mill to host an annexed plant is its sugarcane crushing capacity. Depending on the size of the facility, the minimum requirements for integrating other industrial units may not be present, thus reducing or completely hindering the possibility of adding other processes to it. Figure 2.1 presents the breakdown of sugarcane crushing capacity of Brazilian sugarcane mills. Around 55% of mills in Brazil process less than 2 million tonnes of sugarcane per year (MTC), being considered small facilities.



Figure 2.1 – Breakdown of sugarcane crushing capacity of Brazilian mills.

2.3 Current types of portfolio diversification in sugarcane mills

In addition to ethanol, sugar, and EE, several other products can be extracted or synthesized from sugarcane biomass, as depicted in Figure 2.2. Existing sugarcane mills already benefit from this fact to expand their product range by exploring different streams of the industrial process. Current product options are generated through relatively unsophisticated technologies, which usually have lower capital expenditure (CAPEX) and are responsible for a small fraction of the biorefinery income. In some special cases, the technical feasibility of the integrated plant is directly linked to the availability of inputs throughout the year. The main existing examples of current product portfolio diversification in Brazilian sugarcane mills are presented hereafter, while their locations are shown in Figure 2.3.



Figure 2.2 – Selected routes for product portfolio diversification in sugarcane mills.



Figure 2.3 – Location of sugarcane mills with current product portfolio diversification.

2.3.1 Anaerobic digestion (AD)

AD refers to the degradation of complex organic matter into simpler molecules by a series of chemical reactions performed by different classes of microorganisms (Moraes et al., 2015). Several substrates can be used as carbon source for the process, either solid ones (municipal solid waste) or liquid wastewaters (domestic and industrial effluents). In Brazil, one specific wastewater remains largely untapped for this purpose: sugarcane vinasse. Vinasse is a liquid effluent generated in the ethanol production process. For each liter of ethanol, between 6 and 14 liters of vinasse are produced (Dias et al., 2015), making the destination of this residue an important issue for the economic and environmental sustainability of ethanol utilization as a fuel. The most common destination in Brazil is recycling to the field in a process named fertirrigation, in which nutrients such as potassium are cycled back to the agricultural phase of sugarcane production. Although this is the simplest option in dealing with such an abundant wastewater, the full potential of vinasse can be harnessed through AD. Current exploitation of AD in sugarcane mills in Brazil is limited to a handful of cases, with several digesters built and operated in a rather experimental fashion (Moraes et al., 2015).

Biogas produced in this way is fed in existing sugarcane LCM boilers to increase both electric and thermal energy production (Moraes et al., 2014), which is one of the most straightforward options for biogas utilization along with the combustion in internal combustion engines. Some companies are also betting on the potential of co-digesting sugarcane straw and bagasse with vinasse and other types of industrial wastewater. According to researchers in the field, the production and use of biogas in these ways would lead to higher overall conversion efficiencies than through the direct combustion of sugarcane LCM in conventional, low-efficiency boilers (GeoEnergética, personal communication, June 2016). One clear disadvantage of this approach includes the long hydraulic retention times involved with the AD of solids, especially those with high recalcitrance such as sugarcane LCM: while vinasse is usually digested in 24 h, solids may undergo digestion for several days or weeks (Costa et al., 2014; Janke et al., 2016).

Another option is to upgrade biogas through the removal of CO_2 and other impurities (such as H_2S) to generate a stream with a minimum CH_4 content of 96.5% v/v (Makaruk et al., 2010), named biomethane. The simplest destination to this product is commercialization through injection in the natural gas grid, although this alternative is quite restricted for

sugarcane mills in view of the limited grid span available in Brazil (Junqueira et al., 2016). A second possibility is to use biomethane in internal combustion engines for the replacement of fossil diesel in agricultural operations of sugarcane production, encompassing machinery for planting, harvesting, and transport, thus leading to more competitive sugarcane production costs and to a reduction in GHG emissions associated to ethanol production. The only sugarcane mill in Brazil with this type of technology is Usina Iracema (Iracemápolis, SP, Brazil), which employs an 80-m³ digester for biogas production and a Paques biogas upgrading system for further use in the truck fleet of the mill.

2.3.2 Industrial salts

During fermentation for ethanol production, large quantities of carbon dioxide are produced. From the stoichiometric reaction for fermentation, it is possible to observe that for each mole of ethanol generated, one mole of carbon dioxide is also generated. The specific consumption of sugar for each product is of 0.511 g sugar/g ethanol and 0.488 g sugar/g CO₂, which means that almost 50% of the sugars are lost to CO₂ production. This indicates that the recuperation and subsequent use of CO₂ can be an attractive alternative for sugarcane mills looking for an increase in revenues.

One possible application for the recovered CO₂ is the production of industrial salts like calcium carbonate (CaCO₃) and sodium bicarbonate (NaHCO₃), as well as ammonium chloride (NH₄Cl) as a coproduct. This alternative is already being employed by a company named RAUDI, which produces different salts (ammonium bicarbonate, calcium carbonate, sodium bicarbonate) using CO₂ generated during alcoholic fermentation. The company established a partnership with an agricultural cooperative of sugarcane planters named COOPCANA, located in São Carlos do Ivaí (PR, Brazil). The plant has a production capacity of 80 tonnes of sodium bicarbonate per day, obtaining up to 128 kilograms of sodium bicarbonate per tonne of sugarcane processed for ethanol production. The salt production factory is integrated with the sugarcane mill for both feedstock (CO₂) and energy (steam). Once CO₂ arrives at RAUDI, it passes through a solution of water and sodium carbonate. A reaction occurs between CO₂ and NaCO₃ and crystals of NaHCO₃ precipitate. The crystals are separated by centrifugation and subsequently dried using the steam provided by the sugarcane mill, while water is recycled to the process (Pacheco and Silva, 2008).

2.3.3 Dry yeast

Apart from ethanol and CO_2 , the fermentation of sugarcane juice by *Saccharomyces cerevisiae* produces a third indirect product: additional yeast biomass from cell multiplication during the process. Such type of stream can contain up to 42% in protein depending on the yeast strain (Butolo, 2002), thus consisting in an interesting option for both food and feed products.

One of the main examples of an integrated Brazilian biorefinery for the production of dry yeast can be found in Quatá (SP, Brazil), at the homonymous mill. The annexed plant supplies process steam, EE, and sugarcane juice to a joint unit for yeast propagation and recovery. The commercialization of 31 thousand tonnes of dry yeast and derived products in the 2015/2016 harvest season represented around 19% of the revenues of the Zilor Group, which controls the Quatá mill (NovaCana, 2017).

2.3.4 Food and feed products

Three mills from the Biosev Group produce around 85 thousand tonnes of animal feed per year from sugarcane bagasse, molasses, and dry yeast (Biosev, 2014). Since this composition has a lower price than conventional feed products in the market, the mills are able to establish a sort of agriculture-livestock integration system, in which both sides can perceive benefits.

Different pathways can also be employed for the production of animal feed from sugarcane-derived materials. One of the leading technologies is the ammonia fiber expansion (AFEX) pre-treatment, which consists in increasing the amount of fermentable sugars in the biomass to enhance its digestibility properties (Dale et al., 2010).

2.3.5 Biodiesel

Olivério et al. (2014) describe an integrated sugarcane-vegetable oil unit producing ethanol, sugar, EE, and biodiesel in Barra do Bugres (MT, Brazil). The biodiesel plant operates since late 2006 annexed to a sugarcane mill established in 1983, thus showing that the retrofitting of existing distilleries is not only possible but already performed. The integration occurs in both agricultural and industrial levels. The authors, through a preliminary evaluation, estimate that the capital cost of an independent, non-integrated biodiesel plant in Brazil is 22% higher than that of an integrated unit, which benefits mainly from reduced investment due to shared buildings, loading and unloading facilities, utilities sector, and wastewater treatment. Operating costs of biodiesel production also tend to be lower in view of the utilization of ethanol produced in the sugarcane mill for the transesterification reaction. In addition, the environmental advantages of such biorefinery configuration were already demonstrated, mainly due to reduced GHG emissions and more favorable energy balance of ethanol production (Souza and Seabra, 2013).

2.3.6 Farnesene

The American company Amyris produces farnesene (branded Biofene) in integration with a Brazilian sugarcane mill in Brotas (SP, Brazil). Farnesene is a 15-carbon terpene which has seen an increasing number of applications in the cosmetics and renewable jet fuel markets. Amyris' proprietary sugars-to-hydrocarbons technology for the production of farnesene- and farnesane-like compounds employs sugarcane juice as the carbon source. The integration strategy provides sugarcane juice directly from the crushing section of the distillery, thus reducing logistics costs involved in feedstock procurement. The plant was set to undergo expansion in 2016 in order to meet rising market demand through 2020 (Amyris, 2016).

2.4 Future options for portfolio diversification

Among the many possibilities of products for production in Brazilian sugarcane mills, biofuels are among the first to come to mind. However, such routes still depend on significant advances for the resolution of process bottlenecks. For instance, commercial 2G ethanol production from sugarcane LCM passes primarily through establishing an efficient pretreatment step. The large-scale technology is not yet commercially established since plants deployed in the country and abroad have been continuously affected by several operational problems (Dale, 2018). Brazilian pilot plants, however, plan to expand production capacities in spite of also facing operational issues (NovaCana, 2016). Another example is butanol, which could be produced through sugarcane juice fermentation (Mariano et al., 2013a), pentose liquor fermentation (Mariano et al., 2013b), *via* condensation reactions of ethanol

produced in 1G (Dias et al., 2014) or in integrated first- and second-generation (1G2G) (Pereira et al., 2014) sugarcane biorefineries. The economic feasibility of industrial butanol systems, either for the chemical or the biofuel market, also passes through the optimization of virtually all process steps, especially those associated with butanol synthesis.

The process alternatives further discussed here are either available in the market or could be easily adapted to use the outputs of a sugarcane mill, therefore not requiring a considerable technological leap for deployment. The main technologies identified, with short to medium time-to-market periods either due to a smaller deployment scale or readiness level, are further discussed over the next pages. The options are also depicted in Figure 2.2.

2.4.1 Production of fertilizers

Sugarcane processing into finished products generates several types of effluents besides vinasse. These include filter cake (a solid residue obtained during the treatment of sugarcane juice composed of vegetal fibers), soluble solids (organic acids and proteins), and boiler ashes from sugarcane LCM burning. A Brazilian company, Dedini, envisioned a project that could not only find a destination for these residues but also reduced the expenses with fertilizers and generated revenues with the commercialization of a new product. The solution, named BIOFOM, is a biofertilizer made of boiler ashes, filter cake, concentrated vinasse, and mineral additives (N, P, and K). The potential for reduction in expenses with BIOFOM can achieve 70% when compared to the use of mineral fertilizers - even when the sugarcane mill is close to the crop, investments in trucks and distribution systems showed a reduction of at least 67% in comparison to a mill without the production of BIOFOM (Olivério et al., 2010).

2.4.2 Hydrogen (H_2)

 H_2 is a fundamental input for several processes, ranging from the upgrading of hydrocarbons found in petroleum to hydrogenation of vegetable oils. Production of H_2 in industrial scale is often carried out in large, centralized natural gas steam reforming plants, which may supply the gas by truck to fairly distant consumers (up to 500 km from the producer). In spite of the involved transportation costs and associated environmental impacts, H_2 from steam reforming of natural gas is still highly cost-competitive. One alternative to this business model is to decentralize H_2 synthesis to plants with lower capacities, which may lose

competitiveness due to equipment size but would have shorter distances to clients. Sugarcane mills are able to become H_2 suppliers through production with water electrolysis or catalytic ethanol steam reforming. Both techniques would lead to significant reductions in the environmental impacts of H_2 production since the main inputs for their operation are derived from sugarcane biomass: electric energy from bagasse (and, possibly, straw) combustion for water electrolysis and ethanol from sugarcane juice for steam reforming. An assessment of the sustainability (economic, environmental, and social) impacts of such alternatives, though, should still be carried out. Besides, the Brazilian gas market is known to be controlled by a handful of players, a fact that must be taken into consideration when evaluating the best investment alternative in real mills (Klein et al., 2018).

2.4.3 Cellulose- and lignin-derived products

Sugarcane biorefineries produce colossal amounts of holocellulose in the form of sugarcane bagasse and straw. Although the conventional utilization involves combustion in boilers to produce energy, a fraction of such material could be diverted to other applications with higher added value. Two examples can be found in nanofibrillated cellulose (NFC) and nanocrystalline cellulose (NCC). NFC and NCC have very different applications (Khalil et al., 2014; Santucci, 2016) and, therefore, market prices vary significantly.

The isolation of lignin-derived products has been of increasing interest to the paper and pulp industry, especially. Kraft pulping, the most-used route worldwide (Khalil et al., 2012), yields a stream with a high content of lignin derivatives, named black liquor, while generating cellulosic fibers for transformation into paper and other products. In a similar way to what happens to sugarcane LCM in mills, the black liquor is burned to recycle essential chemicals to the pulping step (as well as to generate energy to the process). The most straightforward product in terms of number of processing steps from black liquor is kraft lignin. In spite of this characteristic, the development of this technological route has been difficult due to the lack of raw material with constant quality from different sources (Gellerstedt, 2016). Since lignin is a heteropolymer with a variable composition according to the biomass, the profile of compounds found in the black liquor can also highly fluctuate. In theory, sugarcane bagasse and straw are able to supply the same lignin-derived products than those originated from softwood in paper mills. Alternatively, sugarcane bagasse and straw can undergo different conversion processes for specific chemical products. Pulping using the sulfite process is able to provide lignosulfonates as a byproduct, which can, in turn, be used as a valuable raw material for the synthesis of vanillin (Fache et al., 2016). Direct routes from sugarcane LCM to finished commercial products are also object of current studies (Santos et al., 2016; Sherpa et al., 2017).

2.4.4 Organic acids

The recent years have seen a boom in the development of biobased solutions in substitution to fossil-based products, especially organic acids. Among the top value-added chemicals from biomass index elaborated by Bozell and Petersen (2004), four out of ten candidates on the list are organic acids. Organic acids are generally produced from renewable sources through fermentation of sugars. Some common examples of organic acids already produced from renewable sources include citric acid and lactic acid - more recently, succinic acid has also joined the list (Klein et al., 2017).

The vast majority of citric acid is obtained through microbiological processes; both submerse and surface fermentations (Max et al., 2010). Citric acid is most commonly produced in industrial scale through submerse fermentation using *Aspergillus niger*. Molasses, a by-product of sugar production, can be used as a carbon source for citric acid production, both from beet and sugarcane. However, sugarcane molasses contains traces of metals such as manganese, calcium, and iron, which have a negative effect especially for submersed cultures. For this reason, a pre-treatment must be performed on the substrate before the fermentation (Grewal and Kalra, 1995). A plant for citric acid production was built in Uberlândia (MG, Brazil) by Cargill in the early 2000's and later expanded in 2014 (NovaCana, 2014). Brazil imported around 17,000 tonnes of citric acid in 2017 (MDIC, 2018), which shows that a potential local market for this product already exists.

Lactic acid is a compound with large application in the food, pharmaceutical, and cosmetic industries, with a relatively recent spike of interest from the chemical sector due to the possibility of producing poly-lactic acid (PLA), a biodegradable plastic which can displace fossil-based competitors (Wang et al., 2015). Although the main industrial routes worldwide use sucrose as the raw material for fermentation with different micro-organisms, the production from glucose and xylose from sugarcane LCM breakdown has also been investigated (Mandegari et al., 2017).
2.4.5 Bioplastics

Bioplastics production is another possibility for portfolio diversification in sugarcane mills. Some examples include monomer-based bioplastics, such as polyethylene (PE), polyhydroxyalkanoates (PHAs) and PLA (Brodin et al., 2017).

PE is most commonly manufactured from petrochemical-sourced ethylene, but bioPE (using ethylene from renewable sources) is already commercially available. Braskem, a Brazilian company, produces bioPE on a commercial scale since 2010. The plant is located in Triunfo (RS, Brazil) and has a capacity of producing 200,000 tonnes of PE per year (Coutinho et al., 2013). The raw material for Braskem's BioPE is ethanol from sugarcane: the alcohol undergoes dehydration and further conversion to ethylene, which is submitted to conventional polymerization processes for the production of the polymer (Morschbacker, 2009).

Poly-3-hydroxybutyrate (PHB), of the PHAs class, is a biodegradable polymer and can be obtained from renewable sources using bacterial fermentation (Bonomi et al., 2016). One advantage of this biopolymer is that it displays some characteristics from fossil-based polymers, such as low gas permeability and high crystallinity (Bonomi et al., 2016). The commercial production of PHB and other PHAs is not yet significant, and this is most likely due to the production costs still being too elevated (Brodin et al., 2017). Currently, Usina da Pedra mill (Serrana, SP, Brazil) has a demonstration plant for production of PHB with a production capacity of 50 tonnes of PHB per year. This plant was constructed as a partnership between CTC (Center of Sugarcane Technology) and the mill in 1995 for an initial capacity of five tonnes per year, further expanded to the current production in 2003 (Mantelatto, 2011).

2.4.6 Microalgae

Microalgae are unicellular microorganisms which perform photosynthesis and present high biomass productivity under the right cultivation conditions (Brennan and Owende, 2010). As discussed in Section 2.2, sugarcane juice fermentation to ethanol produces large quantities of CO_2 as a byproduct, which could be used as a clean, high-purity carbon source for microalgae growth. Other streams with high CO_2 content, such as boiler flue gases or ADderived biogas, could also be eventually employed by microalgae for carbon uptake. The produced microalgal biomass could then be processed into several different products, ranging from biofuels to biopolymers, pigments, and active ingredients for pharmaceutical products (Brennan and Owende, 2010). Apart from carbon, microalgae processes could also benefit from other inputs from the sugarcane mill (especially low-cost electric energy) for leveraging of the technology. A more detailed review of the state of the art of this possibility is carried out in Chapter 3.

2.5 Preliminary conclusions

For the determination of integration possibilities in brownfield biorefineries, a thorough analysis of possible hosting sugarcane mills must be undertaken, case by case. The determination of the best options for integration in sugarcane mills passes through estimating both the economic and environmental performances of the industrial possibilities. For this, a flexible assessment tool is required. CTBE created and continually develops the VSB, a comprehensive assessment framework to evaluate, from a sustainability standpoint, different biorefinery alternatives. This tool integrates all the stages of the biomass chain: agricultural production, transport, industrial conversion, use, and final disposal of the products. In portfolio diversification in sugarcane mills, comparing technical and sustainability (economic and environmental) impacts, optimizing concepts and process configurations considering the whole production chain, and benchmarking the development stage of new technologies is fundamental in finding the best options for the sector.

CHAPTER 3 INTEGRATION OF MICROALGAE PRODUCTION WITH INDUSTRIAL BIOFUEL FACILITIES: A CRITICAL REVIEW

3.1 Introduction

Microalgae and cyanobacteria are a group of unicellular and filamentous microorganisms which performs photosynthesis as the primary route for assimilating carbon. They may develop as individual cells or in small colonies, being found in freshwater and marine environments (Kumar et al., 2010). There are, potentially, several reasons for microalgae to become largely employed by the industry with the aim of producing biofuels: (1) microalgae present high theoretical lipid and carbohydrate productivities, by far exceeding those of conventional energy crops like soybean and sugarcane, respectively; (2) these microorganisms can thrive in different aqueous media, notably with saline, brackish, and other non-potable water sources; (3) associated production of high-value compounds, such as proteins and pigments; (4) composition profile of the strain can be regulated according to the compound of interest through the modulation of process variables (Brennan and Owende, 2010; Singh and Dhar, 2011). Table 3.1 presents the composition profiles of selected microalgae species in terms of carbohydrates, lipids, and protein, which are highly variable depending on the strain and on cultivation conditions.

| Microalgae species | Lipids | Carbohydrates | Protein | Ash |
|---------------------------------|--------------------|---------------|---------|----------------|
| Chlorella vulgaris | | | | |
| Sydney et al. (2010) | 8-12 | 15-18 | 38-44 | 12-14 |
| Chen et al. (2015) | 15-50 | 20-51 | 6-55 | _ ^a |
| Isochrysis galbana | | | | |
| Férnandez-Reiriz et al. (1989) | 26-36 | 15-48 | 13-40 | _a |
| Botryococcus braunii | | | | |
| Sydney et al. (2010) | 31-35 | 2-3 | 37-43 | 7-8 |
| Ashokkumar and Rengasamy (2012) | 16-20 ^b | 31-35 | 16-19 | - |
| Spirulina platensis | | | | |
| Sydney et al. (2010) | 9-13 | 10-12 | 40-44 | 6-8 |
| Chen et al. (2015) | 13 | 30 | 48 | _ ^a |
| Dunaliella tertiolecta | | | | |
| Sydney et al. (2010) | 10-13 | 13-15 | 26-32 | 30-36 |
| Chen et al. (2015) | 3 | 22 | 61 | _ ^a |

Table 3.1 – Biochemical profiles of selected microalgae species (compositions in %, m/m).

^a Data from Chen et al. (2015) and Férnandez-Reiriz et al. (1989) are ash-free

^b Additional production of exopolysaccharides (hydrocarbons) of 10-14% (m/m)

Historically, industrial microalgae production focused on small consumer markets, namely pigments and dried whole microalgae for human consumption or animal feed (Borowitzka, 2015). Typical designs of industrial microalgae facilities are often based on stand-alone or minimally-integrated configurations, in which raw materials, energy supply, and product distribution are managed independently. Studies aiming to assess the potential of microalgae processes in large scale (Davis et al., 2011; Delrue et al., 2012; Gebreslassie et al., 2013; Molina Grima et al., 2003; Norsker et al., 2011) usually consider isolated units acquiring all or most part of the main inputs (water, nutrients, carbon sources) at prices found in the open market, which greatly increase operational expenses. In the incipiency of microalgae utilization as raw material for biofuels production, cost reduction in several possible sections of microalgae production should be carried out to make the process economically feasible, hence, competitive. Since biofuels production from microalgal biomass will require the expansion of microalgae units in both number and scale, their integration to other established facilities emerges as a real opportunity to leverage the worldwide deployment of microalgae projects and to outperform stand-alone microalgae units.

Only recently the production of microalgae has been thought of as an integrated concept, either by recovering various compounds from the microalgal biomass or by employing raw materials supplied by adjacent industrial units. The utilization of industrial effluents from different sources is an interesting option to tackle economic and environmental issues in a single step (Christenson and Sims, 2011). Recently, the importance of algal biomass in capturing CO_2 and creating value from it in future scenarios for the mitigation of GHG emissions has also been highlighted (Raslavičius et al., 2018).

The generation of liquid and gaseous effluents by chemical plants is an integral part of the processing of raw materials into finished products. In such typical sites, waste streams undergo several treatment techniques before being disposed of in the environment. One alternative to conventional end-of-pipe effluent treatments, the employment of heat and mass integration strategies with other processes represents a real opportunity for a suitable, low-cost effluent management. Some types of effluents - CO_2 in gaseous streams and liquid effluents with organic and inorganic content - are appropriate for use in microalgae cultivation as sources of carbon and other nutrients, as further discussed in this Chapter. Different aspects can be pointed out as direct advantages of process integration with industrial facilities: minimization of water, process steam, and energy requirements, reduction of effluent sent to treatment, and reduction of contaminating charges disposed of in the environment.

Microalgae processes may also benefit from thermal and electric energy supplied by established plants when an integrated design approach is considered. In this way, the integration opportunity offered by sugarcane mills is unique due to the available material and energy vectors: carbon, inorganic nutrients, water, process steam, and electric energy. The sugar-energy sector in Brazil, in constant development since the 70's, combines these features with the availability of low land prices and high solar insolation, besides water availability, to generate an ideal panorama for the deployment of microalgae plants in the country. Also, the establishment of a biorefinery concept between ethanol distilleries and microalgae production adds solidity and environmental benefits to the economic viability of the joint project, as ethanol production is highly affected by raw material prices (Balat and Balat, 2009).

Although the technology of microalgae production in industrial scale is widely soughtafter for meeting the rising biofuel demand, it is still at an early stage (Lam and Lee, 2012; Passell et al., 2013) and more research in the field is needed. In the case of sole biofuel production (namely ethanol, biodiesel, and oil-derived fuels), the use of conventional microalgae production technologies involves high investments and results in high biofuel production costs, as shown in Table 3.2. Ultimately, production costs and minimum selling prices are highly dependent on the scale of reactor deployment, since the biomass production step is cost-intensive. Besides, Table 3.2 shows that the techno-economic analysis of theoretical microalgae cultivation and processing plants are often based on the sole utilization of concentrated and compressed CO₂ from nearby flue gas sources and, still, the results are widely variable according to the processing technology. This Chapter expects to show the numerous approaches of integrating microalgae facilities into other more consolidated plants, from which the former may benefit in terms of technical practicality, environmental, and economic performance. In view of such fact, the potential of process integration to assist the development of microalgae production and processing technologies in the early stages of their industrial deployment is examined. The main inputs for industrial production of microalgal biomass - carbon and nutrient sources, water, energy, and land availability, are initially discussed. Special focus is given to Brazilian sugarcane mills acting as a backbone to larger and more complex biorefineries by exploring the current status of existing examples of integration between mills and non-microalgae related industrial plants. Additional arguments are put forward to assert that Brazilian sugarcane mills stand out as one of the best options for hosting microalgae biorefineries and supporting their development. The main goal is to lay solid foundations for the deployment of low-carbon emission, integrated biorefineries for the production of microalgal biofuels by showing different configuration possibilities.

| Compound | Obtention method | Reactor type | Integration level | MSP (US\$/gal) | Base year | Reference |
|---|--|------------------------------|--|------------------------|-----------|--------------------------------|
| Green diesel | Hydrotreatment | Open pond | CO ₂ from power plant flue gas | 9.84 | 2007 | Davis et al. (2011) |
| Green diesel | Hydrotreatment | Closed PBR | CO ₂ from power plant flue gas | 20.53 | 2007 | Davis et al. (2011) |
| Green diesel | Hydrotreatment | Open pond with plastic liner | CO ₂ from power plant flue gas Heat integration between CHP unit and solvent recovery | 19.60 | 2007 | Milbrandt et al. (2013) |
| Green diesel | Hydrotreatment | Open pond and PBR | CO ₂ from flue gas Wastewater at disposal | 9.82-16.95ª | 2011 | Delrue et al. (2012) |
| Biodiesel | Transesterification | Open pond | CO ₂ from flue gas Wastewater at disposal | 6.28-9.87ª | 2011 | Delrue et al. (2012) |
| Biodiesel | Simultaneous oil extraction and transesterification with methanol | Open pond | CO ₂ from flue gas | 1.60-3.72 ^b | 2012 | Nagarajan et al. (2013) |
| Algal lipids | Extraction with hexane | Open pond with plastic liner | CO ₂ from flue gas | 21.11 | 2013 | Ramos Tercero et al. (2014) |
| Algal lipids | Extraction | Open pond | - | 12.33 | 2013 | Richardson and Johnson (2014) |
| Biocrude | Hydrotreatment + solvent extraction | Open pond | - | 109.12 ^b | 2013 | Richardson et al. (2014) |
| Biocrude | Hydrotreatment + solvent extraction | Closed PBR | - | 76.98 ^a | 2013 | Richardson et al. (2014) |
| $a \in to US$ conversion (2011): 0.748$ | | | | | | |

Table 3.2 – Minimum selling price for microalgae-derived products.

 $e^{a} \in \text{to US}$ conversion (2011): 0.748

^b Production cost

CHP: Cogeneration of Heat and Power MSP: minimum product selling price PBR: photobioreactor

3.2 Large-scale microalgal biomass production

In the current scenario, large-scale microalgal biomass production for biofuel obtention generally involves higher costs and higher technical challenges than land crops (Alam et al., 2012), since strict cultivation conditions must be provided to obtain favorable microalgae growth rates and biomass processing is performed using sophisticated techniques. In addition, industrial microalgae cultivation is known for the consumption of copious amounts of carbon, water and nutrients, notably nitrogen (N) and phosphorous (P), which are supplied by conventional plant fertilizers or specially-developed formulae designed to suit the requirements of each microalgae species. Figure 3.1 shows an overview of a typical unit for the obtention of microalgal biomass-derived products. Main operations include microalgae cultivation, followed by biomass harvest, drying, extraction of compounds, and final processing into consumer goods. This broad outline, however, corresponds to microalgae production as thought of nowadays, employing conventional systems. Many studies aim at the simplification of microalgae processing through combining multiple unit operations into single steps or using novel, recently-developed techniques in order to improve the economic feasibility of the process: direct or in situ transesterification (Park et al., 2015) or hydrothermal liquefaction (Tian et al., 2014) of undried biomass, thus avoiding the need for an energy-intensive drying step; biomass harvest using nonconventional techniques alternative to chemical flocculation, such as electric-based systems (Barros et al., 2015) and micro/ultrafiltration (Sun et al., 2013); microalgal cell disruption in water suspensions with Pulsed Electric Field and Supersonic Flow Fluid Processing techniques (Vanthoor-Koopmans et al., 2013); cultivation and biomass pre-harvest in a single membrane bioreactor (Bilad et al., 2014; Luo et al., 2017); microalgae growth in biofilms to avoid dewatering (Johnson and Wen, 2010); among others. The detailing of such alternatives is not in the scope of this Chapter.



Figure 3.1 – Steps commonly involved in microalgal biomass production and processing into biofuels and bioproducts.

3.2.1 Cultivation

Microalgae are able to grow by using different metabolic regimes, namely the autotrophic, heterotrophic, and mixotrophic metabolisms. The autotrophic metabolism occurs through photosynthesis, a process that allows carbon assimilation from CO_2 using light energy. Equation 1 displays the overall reaction for the photosynthetic growth of microorganisms.

$$nCO_2 + nH_2O \xrightarrow{light} (CH_2O)_n + nO_2 \tag{1}$$

Heterotrophic growth of microalgae occurs through the uptake of low molar mass organic compounds dissolved in the culture medium, mainly carbohydrates (pentoses and hexoses), acetic acid, acetate, glycerol and other organic acids. The third type, mixotrophic growth, incorporates characteristics of the previous metabolic regimes: the microalgae absorb CO₂ when in the presence of light, shifting to the uptake of organic compounds in the medium under dark conditions and *vice versa*. Microalgae may also be cultivated in consortia with bacteria, which is beneficial for enhancing biomass productivities of both classes of microorganisms due to the exchange of organic compounds between them (Medipally et al., 2015). The parameters and issues involved in the discussed metabolic regimes guide the development of the present work.

In the industry, microalgae cultivation can be performed in open reactors, closed reactors, or in a combination thereof. The option for one or other alternative is strongly influenced by several factors, such as the microalgae species in question, desired metabolic regime, temperature, and final compound of interest (Brennan and Owende, 2010). There is still much debate over the best system for large-scale microalgal biomass production, since both present inherent advantages and downsides. The construction of open reactors is often less expensive than that of closed systems. Raceways, the most widespread design of open reactors, are relatively simple to build and employ little material. Many of the intrinsic disadvantages presented by open systems are due to the direct contact of the culture medium with the environment, e.g., contamination of the cultivation with other microalgae or microorganisms (possibly leading to culture crash), high water evaporation, and high CO_2 loss, which ultimately result in low microalgae concentration in the suspension. Closed reactors, by definition, are able to isolate the cultivation from the external environment. This

characteristic highly reduces the possibility of contamination and loss of water from the culture medium, which, in turn, contributes to easier process control and to the obtention of suspensions with high microalgae concentration. Nevertheless, these reactors are of expensive construction and maintenance due to their intricate design and nature of the employed materials, namely glass and steel, with few non-capital-intensive materials available, such as transparent polyvinyl chloride (PVC). Common models of closed reactors include horizontal and vertical tubes and flat-plate reactors. In addition to the aforementioned points, land occupation by each reactor alternative is an important issue to be considered in the choice of the most suitable option. Closed reactors show higher volume/area ratios than open reactors, i.e. they are able to enclose a higher volume of culture medium in a given space, thus presenting higher areal microalgae productivity. While open systems are attractive in terms of low capital investment, the high area requirement might hamper its deployment in countries or regions with little area availability or when competing with the arable land of nearby crops. Consideration also has to be given to the design of closed reactors in analogy with those used in chemical industries with special emphasis on the air-lift type (Hosseini et al., 2015), one of the most prominent alternatives for proper microalgae growth. Hybrid systems, incorporating elements of both open and closed systems, are employed in specific cases. Raceways or ponds covered with transparent plastic films to allow light penetration (Kumar et al., 2015; Li et al., 2013) may prove to be a more interesting and cheaper alternative than conventional closed reactors, despite having the downside of occupying the same land area as an open system. Another design option includes membrane photobioreactors (PBRs), which combine cultivation and harvest modules in a single piece of equipment and are able to reach microalgae concentrations up to 3.5 times higher than in closed PBRs (Luo et al., 2017), or porous substrate biofilm reactor (Podola et al., 2017). Finally, it is a consensus that achieving industrial-scale production of biofuels from microalgae passes through the reduction in energy consumption of reactors (Xu et al., 2018).

3.2.2 Harvest

Microalgal biomass separation from an aqueous suspension is often required for the isolation and extraction of compounds. This step, also called harvest, employs different solid-liquid separation operation units. The choice of the appropriate technique is affected by microalgae characteristics (cell diameter and cell concentration in the suspension), by the added value of the main compound of interest of the biorefinery (Brennan and Owende,

2010), by the possibility of adjusting the final biomass water content (Mata et al., 2010), and by the final processing technique (Shelef et al., 1984). Since microalgal biomass harvest can represent up to 30% of the total cost of biomass production in industrial scale (Brennan and Owende, 2010), the definition of the best operation units is fundamental for the economic feasibility of the biorefinery and in the design of the downstream process (Milledge and Heaven, 2013). In general, microalgae harvest is performed in two sequential steps: initial separation and thickening. Initial separation of biomass operates with concentration factors of up to 800 to attain a suspension with solid content as high as 7%, usually performed through flocculation of microalgae with salts of aluminum and/or iron, flotation with microbubbles of air, or gravitational sedimentation (Barros et al., 2015). Other low-cost, biobased flocculants such as chitosan (Xu et al., 2013), plant seeds (Hamid et al., 2014), and filamentous fungi (Alam et al., 2016), can be employed to improve economic and environmental impacts of the process. The thickening of the biomass slurry from the pre-concentration employs techniques with higher energy consumption, particularly conventional, micro, or ultrafiltration and centrifugation. Further detailing of harvest options can be found in the literature (Pragya et al., 2013).

3.2.3 Drying

Due to its perishable nature, the microalgal biomass must be promptly processed through drying after harvest to avoid spoilage. Sun drying of microalgae is the method with the lowest cost, although with downsides such as long operation period for appropriate drying, considerable loss of material, and high dependency on weather conditions. This type of technique is suitable when the final product does not require any other processing, i.e. *in natura* microalgal biomass. Spray drying is particularly adopted in the recovery of high added-value compounds due to relatively high operational costs (Molina Grima et al., 2003). Freeze-drying of microalgae, while largely employed in laboratory scale, is a dehydration method with limited application in large-scale units as a result of elevated operational costs. Still, few pilot/research units use the system (Acién et al., 2012).

Drying of microalgae prior to conversion into biofuels, such as biodiesel, is a controversial subject due to the amount of energy consumed by this operation. Besides affecting the energy balance of the process (Xu et al., 2011), the sustainability of biodiesel production may be significantly altered (Azadi et al., 2014). In order to solve this issue,

alternatives that bypass this operation are currently subject of study, mainly *in situ* transesterification of wet biomass (Salam et al., 2016).

3.2.4 Processing

When bulk microalgal biomass is not the desired final product, it must undergo further processing for the obtention of one or more cellular fractions. The most straightforward option is to perform cell lysis to release internal compounds: lipids and pigments, contained in the cytoplasm (Kay and Barton, 1991), and carbohydrates, stored in the cell wall (Harun and Danquah, 2011). Common techniques include physical methods such as high-pressure homogenizers, ultrasonication, hydrothermal liquefaction, microwaving, and autoclaving, and chemical methods, such as lysis with acids, enzymes, alkalis or salts (Doucha and Lívanský, 2008; Halim et al., 2012; Ho et al., 2013; Kröger and Müller-Langer, 2012; Lee et al., 2010; Lee et al., 2012; Pragya et al., 2013; Samarasinghe et al., 2012; Wang et al., 2016a). As shown in Figure 3.1, after cell disruption, the resulting biomass fractions may be subjected to a vast number of operations for the isolation or synthesis of a given compound, as synthesized by Amin (2009) and Zhu (2015). On first examination, lipids, carbohydrates, proteins, and pigments extracted from microalgal biomass are suitable to undergo the same modifications as their counterparts obtained from energy crops: transesterification (Ahmad et al., 2011; Arenas et al., 2017; Chisti, 2007; Dickinson et al., 2017; Tasić et al., 2016; Williams and Laurens, 2010) or hydroprocessing (HEFA) (Robota et al., 2013) of lipids and fermentation of carbohydrates (Harun and Danquah, 2010; Sirajunnisa and Surendhiran, 2016). Whole microalgal biomass can be subjected to direct conversion via pyrolysis or hydrothermal liquefaction (Chiaramonti et al., 2017) and AD (Ward et al., 2014).

3.3 Critical aspects of large-scale microalgae production

Industrial microalgae units require large amounts of raw material for biomass production and processing: carbon for microalgae growth, energy for powering equipment, and land for the construction of the facility. Such elements are fundamental for the establishment of a microalgae biorefinery and, therefore, it is crucial that intelligent logistic networks for their supply to the industrial unit are elaborated. In view of this, we strongly believe that a robust, economically-viable, sustainable microalgae plant should benefit from the integration with other established industrial units, which would largely simplify the supply chain of the needed inputs.

3.3.1 Carbon source

3.3.1.1 CO₂

The photosynthetic growth of microalgae employing CO₂ and sunlight is currently the approach of choice for microalgae production in large scale. Hence, the supply of CO₂ as the main carbon source for microalgae cultivations is of utmost importance for process optimization. Through photosynthesis, microalgae are capable of fixing carbon contained in many sources: atmospheric CO₂, CO₂ in flue gases, and CO₂ fixed in the form of watersoluble carbonates (Duarte et al., 2017; Kumar et al., 2010). At current atmospheric CO₂ levels of 404 ppm (NOAA, 2016), the aeration of microalgae cultivations solely with atmospheric air is not sufficient for the development of high-density microalgae cultures. Thus, it is imperative to supplement CO₂ to the culture medium for attractive growth rates to develop, especially when aiming at the production of biofuels from microalgae at industrial scale. Different authors (Anjos et al., 2013; Bhola et al., 2011; Mattos et al., 2012) report that cultivations aerated with gas streams supplemented with intermediate CO₂ concentrations (between 4 and 7% v/v) tend to present higher biomass productivity, although the adaptation of *Chlorella vulgaris* cultivations to 100% CO₂ feed is also possible (Acién et al., 2016; Concas et al., 2012).

Flue gases from boilers are interesting carbon sources for microalgae growth due to certain reasons: besides presenting suitable CO₂ concentrations (between 10% and 20% v/v) and being available at virtually no cost, such emissions are typically found in nearly every industry producing utilities through the burning of biomass or fossil fuels. Large-scale facilities are likely to be serious candidates for supplying CO₂ to microalgae cultivations. Examples of stationary CO₂ sources include sugarcane and corn ethanol plants, fossil fuelbased or biomass-based power plants, steel and cement industries, petroleum refineries, and fertilizer producers.

3.3.1.2 Organic molecules

Microalgae growth through heterotrophic or mixotrophic routes is currently the subject of extensive research (Lowrey et al., 2015; Mohan et al., 2015). Despite using carbon sources that are often more expensive than the readily-available CO₂, the cultivation of microalgae with organic molecules can be justified due to much higher growth rates found when in comparison to photosynthesis (Brennan and Owende, 2010).

Microalgae can assimilate many compounds associated with industrial activity. Glycerol, the main byproduct of biodiesel production from vegetable oils, is an effluent particularly abundant in Brazil and of difficult final disposal. Recent studies (Cabanelas et al., 2013; Leite et al., 2015) present the possibility of employing this effluent for microalgae cultivation. Also in the Brazilian scenario, streams within sugarcane processing contain interesting compounds for the development of microalgae cultivations: xylose obtained from sugarcane bagasse pre-treatment (Leite et al., 2015), carbohydrates produced during sugarcane bagasse hydrolysis (Mu et al., 2015), glucose and sucrose found in sugarcane juice (Cheirsilp and Torpee, 2012), and nutrients found in vinasse, a residue of ethanol production - further explored in Section 3.5.2. Other molecules, such as acetate, butyrate, and lactate ions from fermentative processes (Turon et al., 2014) and methanol (Bhatnagar et al., 2011), can also be employed to this end.

3.3.2 Macro and micronutrients

Besides carbon, the growth of microalgae requires several types of nutrients, divided into macronutrients and micronutrients. Elements consumed in relatively high amounts - N, P, sulfur (S), and potassium (K), are named macronutrients. Their supply to the cultivation consists of a bulky raw material input and could represent an important share of the operational costs of an industrial microalgae unit. Ultimately, providing controlled amounts of macronutrients to the culture medium can directly interfere in the microalgae growth, cell dimensions and composition in terms of carbohydrates, lipids, and proteins, as well as fatty acid profile (Converti et al., 2009; De Winter et al., 2014; Vanucci et al., 2012). On the contrary, micronutrients are part of the microalgal composition in a smaller degree than macronutrients. Elements such as Fe, Mg, Zn, Mn, Co, Cu, and Cd are employed by microalgae to perform specific functions within the cell - Fe, for instance, is responsible for electron transport during photosynthesis, N₂ fixation, and detoxification of reactive oxygen species (Zeng et al., 2011). Synthetic culture media are often of high cost, thus with application limited to laboratory scale. It is of general agreement that both urban and industrial wastewaters can play an important role in supplying nutrients to microalgae growth in larger scales. Numerous effluents are suitable to be used in this way, namely from the dairy industry (Hena et al., 2015; Ummalyma and Sukumaran, 2014), wineries (Mateo and Maicas, 2015), breweries (Mata et al., 2014), municipal wastewater treatment plants (Dong et al., 2014; Kiran et al., 2014), ethanol distilleries (Barrocal et al., 2010; Kadioğlu and Algur, 1992; Marques et al., 2013), and dark fermentation (Turon et al., 2016), among others (Chiu et al., 2015; Wu et al., 2014). The possibility of scaling up microalgae cultivation with wastewaters has been discussed by Quiroz Arita et al. (2015), being a quite reasonable approach in terms of operational costs and environmental care.

3.3.3 Water use

Water availability for culture medium composition in industrial cultivations becomes an important point to be considered, if not a full restriction for plant design. Microalgae production is known to be a high water-demanding process (Tu et al., 2016), mainly because microalgae concentrations obtained in the cultivation step are relatively low. Estimations point to the consumption of 1000 kg of water per kg of produced microalgal biomass (Murphy and Allen, 2011), although this figure can highly vary according to the concentration of microalgae in the reactor and to the steps involved in the downstream process (Subhadra and Edwards, 2011).

Among all possible forms of water loss in microalgae cultivation and processing, evaporation from the reactor should be taken into account when designing a biorefinery. This water loss depends on the reactor type, local air humidity, annual insolation, and wind speed, among other factors. In open PBRs, water evaporation may account for significant losses of the culture medium, which requires large amounts of water for reposition. Closed reactors lose less than half of the water normally evaporated in open systems (Davis et al., 2011).

In order to reduce water (and nutrient) make-up, culture medium recycle is essential for an economically interesting and environmentally conscious operation of industrial microalgae units (Chia et al., 2018). Among many process design variables, the choice of the appropriate biomass harvest method is fundamental to achieve good water quality for recycling. Metal-based flocculation (with Al or Fe) tend to increase the content of salts in the spent culture medium, making it inappropriate for recycling without performing a substantial purge of the stream. Alternative systems, such as a change in the medium pH (Liu et al., 2014) or use of bio-flocculants (Alam et al., 2016; Hamid et al., 2014; Xu et al., 2013), are able to perform biomass harvest without compromising water quality. The presence of residual organic matter, extra-cellular compounds, excess nutrients, and particulate matter in the recycled spent medium is often harmful to the cultivation (Biller et al., 2012) and should, therefore, be avoided. Besides, studies show that water recycling is not only beneficial towards the reduction of pressure on freshwater reservoirs but also favors the overall energy balance of the cultivation. It is estimated that, in the case of a 3000-m³ raceway pond where 1500 m³ of culture medium are harvested per day, the recycling of 90% of this volume to the cultivation from 96% to 13% of the energy produced as biodiesel from microalgal lipids when compared to a scenario without water recycling (Murphy and Allen, 2011).

The use of seawater as culture medium is also a tempting alternative since a great portion of microalgae species is found in saline media and the abundance of this resource is obvious. Studies have concluded, though, that employing seawater may not be a viable alternative for microalgae cultivation due to the high operational expenses involved in the treatment of spent medium before disposal in the environment and the increased freshwater requirement for the dilution of high-salinity recycled culture medium (Pate et al., 2011).

The utilization of urban and industrial effluents as culture media for microalgae growth is currently being vented as a possibility to reduce the dependence of microalgae production from freshwater sources, as well as supplying carbon and nutrients to the culture medium. In addition, microalgae cultivation with effluents can be viewed as a treatment method for residual wastewaters (Razzak et al., 2013). This type of alternative environmental treatment has the benefit of reducing the overall pollutant load of the wastewater (Cuellar-Bermudez et al., 2016; Gonçalves et al., 2017; Umamaheswari and Shanthakumaret al., 2016), including toxic compounds such as heavy metals (Wang et al., 2016b; Zeraatkar et al., 2016), before its final disposal and generating income through biomass production and commercialization. Ultimately, the combination of microalgae processes with wastewater treatment turns an environmental passive into an economic active (Patel et al., 2017).

3.3.4 Land availability and local geographic conditions

One of the main advantages of microalgal biomass production in substitution to conventional energy crops is the use of lands with low agricultural usability, such as deserts,

eroded soils, and with relatively high slopes. The availability of these types of land is naturally much higher than arable land in any given country. This fact, along with the correct climatic conditions, is critical for the establishment of an industrial microalgae unit. The main geography-related factors that influence microalgae cultivation are air humidity, wind speed, average temperatures, annual thermal range, solar irradiance, and cloud shading (Farooq et al., 2015). These elements affect many vital parameters for the dimensioning of microalgae production units: water evaporation from PBRs, local water precipitation, and microalgal growth rate. Different studies address the establishment of microalgae units in different countries, taking into account local geographic and climatic conditions (Coleman et al., 2014; Ghorbani et al., 2014; Li et al., 2015; Prasad et al., 2014; Scaife et al., 2015; Venteris et al., 2014). When considering process integration between a microalgae unit and another industrial facility, an important point to examine is whether to choose the microalgae species as a function of the place for the venture or the opposite: choosing a region with specific climatic conditions for the growth of a given microalgae species. This appears to be a very casedependent question that must be tackled individually. Among other points, the chosen site for such facilities is directly influenced by the availability of nearby water supply sources and disposal points.

3.4 Brazilian sugarcane mills: Potential for integration

Brazil boasts one of the most successful large-scale biofuel production programs in the world. In 1975, as a response to the 1973 oil crisis, massive government investments in the National Alcohol Fuel Program (Proálcool) promoted and boosted the use of sugarcane ethanol as a vehicular fuel in substitution to fossil fuels, mainly gasoline (Corrêa do Lago et al., 2012; Moreira, 2000). With the reduction of global oil prices and the consequent increasing maturity of the Brazilian market over the following decade, the government's financial support on the sector was slowly reduced and distilleries expanded their product portfolio with the production of sugar (Amorim et al., 2011) and EE.

Sugarcane processing in Brazil is currently performed *via* three different types of facilities: sugar mills, which produce only sugar; autonomous ethanol distilleries, providing either hydrated or anhydrous ethanol; and sugar mills with annexed distilleries, capable of producing a customizable mix of both sugar and ethanol. Depending on the design of the Cogeneration of Heat and Power (CHP) unit and the technological package of the mill, electricity may also appear as a valuable coproduct in all plant types. In the 2016-2017

harvest, more than 400 of such facilities (from which the great majority is of annexed plants) crushed nearly 658 million tonnes of sugarcane, yielding 38.7 million tonnes of sugar and 27.8 million m³ of ethanol (CONAB, 2017). Recent movements towards second-generation (2G) ethanol production point to an increase in the production of the biofuel in the near future without resorting to an equivalent expansion of crushing capacity in the mills (Junqueira et al., 2017).

Crushing in sugarcane mills operates during the sugarcane harvest period in Brazil, which varies according to the region: from April to November in the larger production zones of the Central-South and from September to March in the Northeast. Harvest season totals from 4000 to 4800 h, with the remainder of the year being considered off-season. Operation during the off-season is not a common practice in the sector, although a few mills store sugarcane LCM during the season or purchase different biomasses (Ghose, 2011) for year-round electric energy production in the CHP unit. In addition, some alternatives are currently being evaluated to extend plant operation period with other types of crops besides sugarcane - further discussed in Section 3.5.

Sugarcane crops and crushing facilities are concentrated in specific geographic regions in Brazil, as depicted in Figure 3.2. The main sugarcane exploitation cluster in the country takes place in the Central and Southeastern portions of Brazil, especially in the State of São Paulo. New frontiers of sugarcane cultivation now encompass States in the Central-West part of Brazil, namely Goiás and Mato Grosso do Sul. These regions account for nearly 87% of the total crushed sugarcane during 2016-2017 (CONAB, 2017). Another favorable area for sugarcane growth stays in the coastal Northeastern region of the country, where high solar incidence and adequate land enable the establishment of the crops.

The integration between sugarcane mills and other industrial units is already performed in Brazil in specific cases. Depending on the type of the industrial process, integrated plants may benefit from the joint management of feedstock supply and other raw materials; the obtention of intermediate product streams, finished products, or surplus energy from the sugarcane mill; and the sharing of administrative buildings, research facilities, agricultural resources, and process equipment. These and other advantages of integrating industrial units to sugarcane facilities in Brazil are well-known and have garnered several studies in the scientific literature in the last years for the estimation of economic and environmental impacts. Several possibilities were previously addressed in Chapter 2, which presents cases of procurement of low-cost feedstock and energy from sugarcane mills for



smaller plants in integrated biorefineries. Among such options, microalgae appear as one interesting prospect, further detailed in Section 3.5.

Figure 3.2 – Location of sugarcane mills and annual average photosynthetically active radiation (PAR) in Brazil. Created with data from CONAB (2016a) and INPE (2016), respectively.

3.5 Sugarcane-microalgae biorefineries in Brazil

The possibility of annexing microalgal biomass production to existing sugarcane mills is being currently vented in the industrial environment and scientific community. A

number of studies on the matter have considered the prospect. Two papers analyzed this type of biorefinery in the USA context: production of microalgal biomass integrated to a corn-toethanol facility in Iowa (Rosenberg et al., 2011) and to a sugar mill using sugarcane as feedstock in Louisiana (Lohrey and Kochergin, 2012). Through process simulation, a similar analysis was conducted in assessing the possibility of co-locating microalgae cultivation to a sugarcane mill producing sugar and ethanol in Colombia (Moncada et al., 2014). More recently, different studies focused on the environmental benefits of integrating microalgae production and sugarcane processing in the Brazilian context (Chagas et al., 2016; Maranduba et al., 2016; Maranduba et al., 2015; Souza et al., 2015). Microalgal biodiesel produced in integrated sugarcane biorefineries can be used to replace fossil diesel in the agricultural stage of sugarcane production. With this approach, overall GHG emissions associated with ethanol production are reduced by around 30% when using microalgae to capture half of the CO₂ produced in ethanol fermentation (Chagas et al., 2016). Concerning real sugarcane-microalgae biorefineries in Brazil, two main examples stand out. The SB joint venture between Bunge and TerraVia (previously Solazyme) for the production of up to 100 thousand tonnes of microalgal oil per year initiated in 2014 in Orindiúva (SP, Brazil), annexed to the local Bunge sugarcane mill (Bunge, 2016). In 2012, the Austrian company See Algae Technology (SAT) announced the establishment of its proprietary microalgae production in Vitória de Santo Antão (PE, Brazil) in partnership with Brazilian group JB (BiodieselBR, 2012). Unfortunately, the outcome of this agreement currently points to the dissolution of the partnership.

Due to the maturity of the sector in Brazil and to the need of diversification in the product portfolio of mills, the current sugar-energy industry configuration in Brazil constitutes a unique juncture for the implementation of integrated microalgae processes. The several grounds on which this assertion is based are further addressed in the present Chapter, namely the availability of CO_2 and vinasse for microalgae growth, the possibility of using nearby land areas for the establishment of the industrial unit, and the joint operation of facilities in terms of electric energy and steam utilization.

Figure 3.2 presents the annual average incidence of photosynthetically active radiation (PAR) in Brazil, which corresponds to wavelengths between 400 and 700 nm. The availability of this specific radiation type is vital to determine the possibility of establishing cultures of photosynthetic organisms (such as plants, cyanobacteria, and microalgae) and allows the estimation of associated theoretical biomass productivities. The largest amounts of PAR incidence are found in the Northeastern region of Brazil throughout spring and summer

(September to March), although significant irradiation levels also occur in the Central-West and South regions during spring and summer, respectively. In an overall analysis, most of the Brazilian territory presents year-round high solar incidence, with a large portion of the country averaging values above 2.0 kWh/m².day of PAR solar radiation (Pereira et al., 2006). Assuming an average daily insolation period of around 8 h and that 1 J is delivered by 4.6 umol photons in the range of PAR (Ting and Giacomelli, 1987), most of the Brazilian territory is irradiated by over than 1150 µmol photons/m².s. This photon flux, however, is found perpendicular to the surface. In open reactors, the effective light intensity is lower due to attenuation of the radiation by microalgae cells in the suspension and by water. A correction factor is also used for tilted reactors, in order to compensate for the inclination angle of the equipment (Pruvost et al., 2015). Photoinhibition is a serious problem affecting microalgae development, with a considerable number of studies addressing this issue. The degree to which microalgae are affected by extreme solar irradiances is highly dependent on the considered species. For instance, Bhola et al. found an optimal range of performance located between 150 and 350 µmol photons/m².s for a Chlorella vulgaris strain, with photoinhibition occurring at irradiances higher than 369 µmol photons/m².s (Bhola et al., 2011).

When comparing the maps presented in Figure 3.2, it can be seen that sugarcane mills in Brazil are located in areas with high solar insolation. This is expected since mills are often installed close to sugarcane crops aiming at the reduction of sugarcane production cost by shortening transport distances. Naturally, the establishment of sugarcane-microalgae biorefineries passes by the construction of microalgae reactors and all associated infrastructure adjacent to the existing mill. This directly incurs in the displacement of sugarcane culture to free space for the annexed unit, which may also result in higher land costs and induce slightly higher sugarcane production costs due to longer transport distances.

Figure 3.3 summarizes the main available resources in the sugar-energy industry that could be directly used in the microalgae cultivation and *vice versa*:

(1) CO_2 released by yeasts during ethanol fermentation or produced through sugarcane LCM combustion in boilers for heat and energy generation are adequate to compose the gaseous feed used in the photoautotrophic growth of microalgae, which rely on the gas for photosynthesis realization;

(2) vinasse produced in ethanol distillation can be employed as a culture medium for the growth of heterotrophic or mixotrophic microalgae; (3) excess electricity generated in the sugarcane facility can be promptly used in the various steps of microalgae growth and processing;

(4) when integrated to a 2G ethanol plant, carbohydrates extracted from microalgal biomass may undergo fermentation along with sugarcane juice and molasses by yeasts capable of assimilating both pentoses and hexoses or in independent vessels.

Year-round operation of the integrated microalgae unit is thought to be crucial for the economic viability of the process as a whole. The high CAPEX for the establishment of the plant could be overcome by a nearly-continuous operation, through maximization of product output and dilution of capital costs. Sugarcane mills, however, are normally designed for part-year operation and may require specific modifications - of structure, equipment or operating mode, when hosting a microalgae unit. Operation extension beyond sugarcane harvest is especially interesting for the supply of raw materials and electric energy for the microalgae plant throughout the year. In this way, certain options are possible: harvest extension with sweet sorghum (Jonker et al., 2015), off-season with fermentation of stored high-test molasses (HTM), and crushing of energy cane (high-fiber variety of sugarcane) during the off-season (Milanez et al., 2015).



Figure 3.3 – Raw materials and energy vectors available from a typical Brazilian sugarcane mill for employing in a microalgae-producing facility. Based on Lohrey and Kochergin (2012) and expanded.

The integration options are further detailed in the next sections. For exercise purposes, it is considered that the inclusion of microalgae units annexed to sugarcane mills in Brazil would be initially directed to the production of biodiesel and ethanol, in view of the Brazilian expertise in both areas. Simulation outputs of an optimized autonomous 1G distillery crushing 4 MTC per year - retrieved from simulations carried out with the VSB framework (Junqueira et al., 2016; Morais et al., 2016), are used as the basis for microalgae potential estimation for the remainder of the Chapter. Figure 3.4 shows a simplified flowsheet of the year-round sugarcane mill.



Figure 3.4 – Conceptualized sugarcane mill for year-round operation, encompassing sugarcane season and off-season.

During the season (200 days), the conceptualized facility operates its crushing, ethanol fermentation, and CHP sections; during the off-season (130 days), the distillery produces ethanol from stored HTM and burns stockpiled LCM. Such off-season configuration was determined in order to provide a constant, year-round output of vinasse and surplus electricity, two components that may be used as inputs for microalgae cultivations. It is worthwhile noting that this distillery employs a considerable fraction of straw, i.e. 50% of sugarcane straw that would be left in the field, to greatly improve its capacity of generation of surplus electric energy. When compared to the existing Brazilian sugarcane mills, the amount of produced electric energy is significantly higher. General parameters of optimized distilleries can be found in publications using the VSB framework (Junqueira et al., 2016; Morais et al., 2012a).

3.5.1 CO₂ from sugarcane mills

During the processing of sugarcane into ethanol, sugar, and electric energy, sugarcane mills generate a considerable amount of gaseous effluents containing CO_2 . Such emissions, in spite of being biogenic, occur in two main points of the process: complete combustion of sugarcane LCM in boilers and ethanol fermentation. Equation 2 shows a simplified combustion reaction of biomass, while Equation 3 displays the fermentation of glucose into ethanol, both producing CO_2 as an end product.

$$C_x H_Y O_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 \to x C O_2 + \frac{y}{2} H_2 O$$
 (2)

$$C_6 H_{12} O_6 \to 2 C_2 H_5 OH + 2 C O_2$$
 (3)

The most abundant emission originates in the CHP unit of a sugarcane mill. The complete combustion of sugarcane LCM generates a gaseous effluent with similar composition to other industrial flue gases, containing an average 14% v/v CO₂. The stream leaves the boiler at high temperatures (over 130 °C, depending on the thermal cycle efficiency) and contains particulate matter, thus needing to be cooled down and cleaned before injection in microalgae cultivations (Giostri et al., 2016; Malek et al., 2017). Sugarcane LCM burning in boilers may generate carbon monoxide (CO), hydrocarbons, and nitrogen oxides (NOx) (Teixeira and Lora, 2004). Although some microalgae species are tolerant to high concentrations of NO_x and SO_x (Ho et al., 2011), the growth of other species is inhibited by their presence (Cheah et al., 2015). Thus, the removal of such contaminants from boiler flue gases is required depending on the microalgae species in question. Taking for basis the distillery described in Section 3.5, the CHP unit alone could provide nearly 1.3 million tonnes of CO₂ per year, roughly 175 tonnes/h and 139 tonnes/h of CO₂ during season and off-season, respectively. Another CO₂-rich stream is obtained in ethanol fermentation vessels since CO₂ is the main byproduct of glucose conversion to ethanol. Here, CO_2 content in the effluent is close to purity, averaging 98% v/v, as fermentation gases are usually scrubbed with water before being released in the atmosphere to minimize ethanol losses through dragging. The suitability of such concentrated CO₂ stream to feed microalgae cultivations has already been demonstrated by Concas et al. (2012). Considering the same 4-MTC autonomous distillery analyzed in this section, ethanol fermentation could provide nearly 34 tonnes/h of CO₂ throughout the year, totaling over 266 thousand tonnes of CO_2 per year. Table 3.3 presents several integration possibilities between microalgae units and the autonomous distillery herein described. The shown scenarios associate different CO_2 sources available in the distillery and consider various limiting factors for each integration outline, which will be further detailed. Since biodiesel is the most straightforward product derived from microalgal biomass (Rashid et al., 2014), the obtention of this biofuel is the main focus of the analysis in Table 3.3.

Assuming that microalgae growth is only limited by CO₂ availability and using the parameters summarized in Table 3.4, exploiting the full potential of the distillery (i.e. consuming all CO₂ produced in the boiler, fermentation vessels and, anaerobic digester, in a combination of scenarios 1, 3, and 6) would yield 600 thousand tonnes/year of dry microalgal biomass in nearly 7,300 ha of reactors - an equivalent reactor radius around the distillery slightly higher than 4.8 km. For microalgae with 30% oil content, the estimated area for cultivations is small when compared to the land required for conventional crops to supply the same 180 thousand tonnes/year of oil: more than 437,000 ha for soybean and 32,000 ha for palm (Chisti, 2007). Obvious limitations for the deployment of reactors in such large scale can be pointed out. In this case, the main constraint would be storing CO₂ produced during nighttime to be used in microalgae photosynthetic growth during light hours, since the enormous gas volumes would make this task impractical. Even when considering only fermentation-derived CO₂, overnight storage of CO₂ would require 12 thousand m³ of tanks with pressurization of the gas at 20 bar (scenario 3). Therefore, the most realistic solution consists in employing exclusively daytime-produced CO₂, while venting in the atmosphere nighttime emissions, as considered in scenarios 2 and 4. Still, a substantial quantity of CO₂ is available from both sources, reaching up to 637 thousand tonnes of CO₂ per year for daytime boiler emissions and 133 thousand tonnes of CO₂ per year from daytime fermentation. It is interesting to note that scenarios 1 and 2 are designed for the uptake of the amount of CO₂ produced during the off-season; in this way, there is no idle capacity of the microalgae plant in year-round operation, since season emissions are higher than those in the off-season.

| CO ₂ source | Bagasse and | straw boiler | Fermentation vessels | | Biogas | |
|---|-------------------------|-------------------------|-------------------------|-------------------------|----------------|-------------------------|
| CO_2 fraction in the stream (%, v/v) | 12 | % | 95% | | 23% | |
| Pure CO ₂ flow - Season (tonne/h) | 175 | 5.2 | 33.6 | | | 1.1 |
| Pure CO ₂ flow - Off-season (tonne/h) | 138 | 3.8 | 33.6 | | 1.1 | |
| Scenario | 1^{a} | 2 ^b | 3° | 4 ^d | 5 ^e | 6 ^f |
| Configuration | Maximum CO ₂ | Daytime CO ₂ | Maximum CO ₂ | Daytime CO ₂ | Target: diesel | Maximum CO ₂ |
| Integration | | | | | | |
| Employed CO ₂ flow (tonne/h) | 277.5 | 138.8 | 67.3 | 33.6 | 26.2 | 2.2 |
| Overnight CO ₂ storage (thousand m ³ , at 20 bar) | 51.2 | - | 12.4 | - | - | 1.7 |
| Microalgae reactor area (ha) | 5,823 | 2,912 | 1,412 | 706 | 550 | 45 |
| Equivalent reactor area radius (km) | 4.31 | 3.04 | 2.12 | 1.50 | 1.32 | 0.38 |
| Microalgal biomass production (ktonne/year) | 480 | 240 | 116 | 58 | 45 | 3.7 |
| Biodiesel production (million L/year) | 161 | 80 | 39 | 19 | 15 | 1.2 |
| Ethanol production (million L/year) | 62 | 31 | 15 | 8 | 6 | 0.5 |
| Electric power consumption (MW) | 14.3 | 7.2 | 3.5 | 1.7 | 1.4 | 0.1 |
| Sugarcane harvest diesel substitution (%) | 1,058% | 529% | 257% | 128% | 100% | 8% |
| Total mill CO ₂ capture (%) | 56.8% | 28.4% | 13.8% | 6.9% | 5.4% | 0.4% |

Table 3.3 – Possibilities and potential of different integrated sugarcane-microalgae biorefineries configurations.

^a Microalgae cultivation during daytime with both daytime-produced and nighttime-stored CO₂ from bagasse and straw burning in the CHP unit.

^b Microalgae cultivation during daytime with daytime-produced CO₂ from bagasse and straw burning in the CHP unit.

^c Microalgae cultivation during daytime with both daytime-produced and nighttime-stored CO₂ from ethanol fermentation.

^d Microalgae cultivation during daytime with daytime-produced CO₂ from ethanol fermentation.

^e Microalgae cultivation during daytime with daytime-produced CO₂ from ethanol fermentation in order to supply the mill's sugarcane harvest diesel consumption.

^f Microalgae cultivation during daytime with both daytime-produced and nighttime-stored CO₂ from AD of vinasse.

| Parameter | Value | Reference | |
|---|--|--|--|
| Microalgae CO ₂ uptake | 80% | Brown (1996) ^a | |
| Microalgae CO ₂ requirement | 1.83 kg CO ₂ /kg microalgae | Chisti (2007) | |
| Areal productivity | 250 kg/ha.day | Quinn et al. (2014) ^b | |
| Photoperiod | 12 h | Assumption | |
| Microalgae oil content | 30% | Assumption | |
| Electric energy consumption | | | |
| Microalgae cultivation | 38 kWh/ha.day | Quinn et al. (2014) ^c | |
| Microalgae lipid extraction | 0.018 kWh/kg microalgae | Quinn et al. (2014) ^d | |
| Lipids transesterification ^a | 82.5 kWh/tonne biodiesel | Pleanjai and Gheewala (2009) ^e | |
| Lipids transesterification yield | 0.98 kg esters/kg lipids | Cheng (2009) ^f | |
| Carbohydrate fermentation yield | 0.51 kg ethanol/kg carbohydrates | nol/kg s Theoretical yield | |

Table 3.4 – Main parameters for potential estimation of microalgal biomass production.

^a Conservative CO_2 capture efficiency for large open ponds operated under optimum conditions.

^b Productivity of a three-stage bioreactor system for growing *Nannochloropsis salina* and increasing its lipid content.

^c Energy approximately 25% lower than that required for traditional paddlewheel raceway ponds.

^d Solvent extraction with hexane.

^e Considered as similar to that of palm oil transesterification with methanol.

^f Methanol transesterification.

In order to rationalize energy use, the obvious choice is to use higher-purity CO_2 emissions for microalgae cultivation, so that less energy is spent in concentrating CO_2 and in compressing gas streams. Given that the agricultural operations, i.e. the harvest of 4 MTC and the recovery of 50% of sugarcane straw from the field, consume roughly 3.8 L of diesel per tonne of sugarcane (according to VSB estimates), an interesting option is to design a biorefinery which substitutes 100% of the fossil diesel by biodiesel. Scenario 5 shows this possibility, which employs 544 ha of microalgae reactors for the production of 15.2 million L of diesel per year.

Moreover, additional electric energy could be generated through AD or direct combustion of defatted microalgal biomass, which are not envisaged in this study. However, taking the aforementioned distillery as the basis, a constant surplus power of 82 MW would be available for microalgae production and processing, which covers the preliminary consumption estimates of the main operations with microalgae in any scenario. In a theoretical brownfield sugarcane-microalgae biorefinery, the needed amount of electric energy demanded by the microalgae process could be supplied by current Brazilian sugarcane mills, in which surplus electric energy is significantly lower than in optimized, strawrecovering mills.

Microalgal debris after oil extraction can, alternatively, be further processed to yield other valued coproducts: ethanol through fermentation of microalgal carbohydrates (Brennan and Owende, 2010; Mata et al., 2010), either separately or along with sugarcane juice, thus profiting from the existing distillery infrastructure; high-protein microalgae meal (Becker, 2007; Harun et al., 2010); pigments (Gong and Bassi, 2016), and others.

3.5.2 Vinasse from sugarcane mills

Vinasse, also called stillage, is a byproduct obtained in large volumes during ethanol distillation ensuing carbohydrate-rich feedstock fermentation. Following yeast removal from the fermentation broth, wine with low ethanol concentration (8.5 °GL) is sent to a series of distillation columns in which its purity increases stepwise until reaching a concentration (94.4 °GL) close to the maximum defined by the water-ethanol azeotrope (96 °GL). As a result, a voluminous effluent stream is generated in the process, containing byproducts of the fermentation and non-volatile compounds found in sugarcane, such as K, N, and P (Moraes et al., 2015). According to VSB estimates, both autonomous ethanol distilleries and sugar mills with annexed distilleries generate around 8.6 m³ of vinasse per m³ of ethanol. Considering the 2016/2017 national ethanol production of nearly 28 million m³ (CONAB, 2017), total vinasse generation in the country can amount to 240 million m³ per harvest season. In Brazil, vinasse produced in sugarcane mills is often recirculated to sugarcane crops as a means to cycle nutrients in a process called fertirrigation. Application rates in the field are defined by K concentration in the effluent, which yields spread volumes in the range of 60 to 300 m³ of the effluent per ha (Santa Cruz, 2011; Van Raij et al., 1997). Since K delivered via fertirrigation completely supplies the demand of the sugarcane crop for the nutrient, the purchased mineral fertilizer is mainly constituted by N and P (Van Raij et al., 1997). In the case of vinasses with high K amounts, allowed application rates are lower in order to avoid excessive buildup of the nutrient in the soil. In turn, this leads to the need of spreading vinasse in increasingly higher distances from the mill, which is seldom economically feasible beyond a given radius (Chagas et al., 2015). Consequently, sugarcane mills often tend to apply higher vinasse rates than would be normally needed to supply K requirement of the crop, in spite of the previously cited environmental concerns.

Although a practice permitted by local laws in Brazil, fertirrigation with *in natura* vinasse is considered to be the simplest way to deal with this abundant effluent (Moraes et al., 2014). The uncontrolled practice of fertirrigation is also subject of thorough criticism for contaminating of superficial and subterraneous waters and buildup of salts in the soil, with risk of salinization, and loss of soil fertility (Fuess and Garcia, 2014a; Lekakis et al., 2011; Santa Cruz, 2011). Furthermore, due to the forecast increase in ethanol production in Brazil in the coming years (Guerra et al., 2015) and assuming the generation of 6-14 m³ of vinasse per m³ of ethanol (Dias et al., 2015), the growth of the generated amount of vinasse in the country calls for new technological solutions in order to deal with such plentiful wastewater. Microalgae cultivations can potentially benefit from the availability of vinasse in several ways, as depicted in Figure 3.5.



Figure 3.5 – Processing alternatives for harnessing the full potential of using vinasse as an input for microalgae cultivation.

The most straightforward option for vinasse use in microalgae cultivations is its direct employment as the totality or part of the culture medium. The presence of nutrients and organic carbon in the effluent may enhance microalgae growth rates under proper cultivation conditions (Mattos and Bastos, 2016; Silva et al., 2017b). Considering both photoautotrophic and mixotrophic metabolic regimes, the dark brownish color of sugarcane vinasse due to the presence of melanoidins is a possible obstacle to the photosynthetic growth of microalgae when employed as full culture medium. Therefore, color removal from the effluent prior to the cultivation is imperative. Treatments with this purpose include coagulation with polymers (Ferral-Pérez, 2016), application of microorganisms (Bharagava and Chandra, 2010; Pant and Adholeya, 2007; Sánchez-Galván et al., 2015) and oxides (Arimi et al., 2015), and advanced oxidation processes (Ioannou et al., 2015), which may result in increased costs for the production of the culture medium alone.

Conversely, studies show the possibility of employing sugarcane vinasse as a small fraction of the culture medium because growth inhibition may occur in the presence of high concentrations of toxic compounds above certain levels (Marques et al., 2013). As an example, when employing mixed residuary waters from ethanol and citric acid productions, concentrations of up to 10% can be employed without hindering microalgae growth: even with a more dark-colored medium, the emergence of the mixotrophic metabolic regime increases biomass production in comparison to purely autotrophic cultivations (Valderrama et al., 2002). It is interesting to note, however, that this type of mixed vinasse is not an industrial reality in Brazil. The use of diluted vinasse as culture medium is not a desirable feature for industrial-scale microalgae cultivation setups and should, therefore, be avoided by researchers. Instead, the direct utilization of raw vinasse as both culture medium and nutrient source should be the prioritized solution. Regarding the heterotrophic growth of microalgae, in natura vinasse displays high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), which are directly linked to the amount of organic molecules in the effluent. Such compounds can be used as carbon source in microalgae cultivation to some extent. A rough estimate can be drawn from the results presented in Mattos and Bastos (2016), in which the green algae Desmodesmus sp. is heterotrophically grown in culture medium containing 100% sugarcane vinasse. In this study, around 4 g/L of microalgal biomass are obtained after 30 h of cultivation in vinasse with initial COD of 27.5 g/L. Assuming that the average COD of sugarcane vinasse is of 30 g/L (Moraes et al., 2015), more than 1.8 million tonnes/year of dry microalgal biomass could be theoretically produced from the total vinasse in Brazil by taking into account these parameters. This value easily overshadows those shown in Table 3.3, which only considers CO_2 for microalgae growth. The deployment of such alternative in the industry still depends on minimizing or solving several issues, such as bioreactor design or culture medium sterilization to ensure low microbial contamination (Santana et al., 2017). Moreover, uptake of vinasse carbon in this way is limited to around 36% (Mattos and Bastos, 2016), which must still be optimized for large-scale applications.

Prior to use in microalgae cultivations, the full potential of vinasse can be harnessed by carrying out AD, which consists in the degradation of organic matter with biochemical reactions performed by different classes of microorganisms (Moraes et al., 2015). After the process, two main products are obtained: a gas mix, termed biogas, mainly composed of CH₄, CO₂, and H₂S; and a liquid mixture/sludge containing the remaining inorganic nutrients and unconverted organic matter. Besides removing COD from sugarcane vinasse prior to its disposal in the environment or its use in fertirrigation, application of AD in large scale offers the possibility of generating significant amounts of electric and thermal energy through biogas combustion (Fuess and Garcia, 2014b; Fuess and Garcia, 2015). In Brazil, despite the promising possibility of digesting vinasse for the diversification of the product portfolio of current sugarcane mills, this wastewater remains a largely untapped energy resource (Moraes et al., 2015). Starting with an upflow anaerobic sludge blanket (UASB) reactor constructed in a sugarcane mill in São Paulo State in the 1990s (Souza et al., 1992), an extensive adoption of other vinasse digesters in Brazil was hindered by several factors, such as the lack of a national biogas program (Salomon and Lora, 2009) and general funding (Nogueira et al., 2015).

Prior to utilization, raw biogas must undergo different levels of purification according to the desired application. H₂S is usually removed from biogas due to its high corrosion potential to storage tanks and prime movers (Ryckebosch et al., 2011). This operation can be carried out by existing large-scale solutions: chemical precipitation, adsorption, or biological techniques (Muñoz et al., 2015). Afterwards, biogas with low H₂S content is either burned for the generation of electric and thermal energy or sent to an additional purification step for the removal of CO₂ - called upgrading. This step, also performed with established industrial solutions such as pressure swing adsorption (PSA), membrane separation, or scrubbing with solvents (Muñoz et al., 2015) yields biogas with high CH₄ content (in excess of 95% v/v), often referred to as biomethane. Biomethane presents the advantage of being suitable for injection in the natural gas grid or for the replacement of conventional fuels in Diesel cycle engines (Weiland, 2010). Different studies (Junqueira et al., 2016; Morais et al., 2016) attest the economic feasibility and the environmental benefits of both alternatives in comparison to the more straightforward option of electric energy generation. A large-scale, real-life example of application of diesel replacement in Brazilian sugarcane mills started operation in mid-2016: Iracema mill (Iracemápolis, SP, Brazil) is currently performing AD of vinasse and upgrading of biogas to biomethane with Paques (Balk, The Netherlands) technology for substitution of diesel in trucks employed in sugarcane agricultural operations. The main goal of this configuration aims at lower sugarcane production costs and better associated environmental impacts due to a reduction in purchase and consumption of fossil diesel (Junqueira et al., 2016).

The possibility of biogas upgrading using PBRs with microalgae suspensions is currently present in the scientific literature (Muñoz et al., 2015; Tijani et al., 2015). Direct injection of biogas in microalgae cultivations for upgrading would mean the release of O_2 through photosynthetic consumption of CO₂ in the CH₄-rich stream leaving the reactors, thus requiring a two-step approach. Firstly, biogas is pumped through bubble columns, in order to dissolve CO₂ in the liquid while CH₄ leaves the equipment practically untouched (Meier et al., 2015; Posadas et al., 2017; Serejo et al., 2015). The recovered biogas presents much higher CH₄ content and heating value after CO₂ removal (Yan et al., 2014; Zhao et al., 2015). Then, the CO₂-rich liquid is supplied to the cultivations, where microalgae consume CO₂ (Morken et al., 2013; Sapci and Morken, 2014). This method of biogas upgrading can potentially compete with other industrial solutions for purification, such as the use of membranes for gas permeation. According to Moraes et al. (2014), sugar mills with annexed distilleries produce vinasse with COD of 33.6 kg/m³, while autonomous distilleries yield vinasse with COD of around 21.0 kg/m³. Assuming that the AD of vinasse removes 72% of the COD and yields 0.31 m³ of biogas/kg of removed COD, the same facility described in Section 3.5 could produce 2,600 m³/h of biogas from 390 m³/h of vinasse. Scenario 6 of Table 3.3 presents a projection on integration potential arising from biogas purification with microalgae, employing storage of nighttime production of biogas to be treated during illuminated hours. Considering biogas with 70% v/v CH₄ and 30% v/v CO₂ and that microalgae are able to fix CO_2 with the same efficacy considered in Table 3.4, an estimated 3.7 thousand tonnes of dry microalgal biomass/year could be produced. Biogas treated this way would present a significantly different composition: the purified 2,100 m³/h of biogas would be composed of an estimated 90% v/v CH₄, which is close to the target CH₄ level needed for injection in the natural gas grid (Moraes et al., 2015). In addition, using the digestate arising from the AD of vinasse as a culture medium for microalgae growth is an interesting option for the reduction of its toxicity towards microalgae (Marques et al., 2013). Besides generating a higher-grade biogas through this type of integration, the production and commercialization of microalgaederived products generate revenues to the biorefinery, while employing conventional biogas purification methods (sulfur removal, dehydration, membrane permeation) presents only operational costs to the plant.

Zhu et al. (2016) recommend an integrated scaled-up system for seizing the full potential of AD of a generic effluent: the digestate is used as the culture medium for microalgae growth, while raw biogas is also supplied for upgrading through the removal of CO_2 by microalgae. Besides, the production of microalgal biodiesel and biogas can be directed towards the production of thermal and electric energy, thus making the plant self-sufficient in terms of energy and possibly capable of exporting surplus electricity to the grid. Other authors propose equally integrated approaches to AD of vinasse and microalgae units.

Doušková et al. (2010) proposed a closed system for the full exploitation of ethanol distillery vinasse *via* AD: CO₂ contained in raw biogas was directly supplied to microalgae cultivations and N in the form of ammonia obtained after treatment of the fermenter digestate was fed to the PBRs. In both cases, the authors found that microalgal growth rate was not affected when compared to the base conditions - synthetic mixture of CO₂:air as the carbon source and urea as the N source, respectively.

Another alternative that has emerged in order to solve the difficulty in spreading high volumes of vinasse in the sugarcane crops is its concentration through evaporation, already adopted in several Brazilian sugarcane mills (Christofoletti et al., 2013). Prior to fertirrigation, the wastewater passes through multiple effects or falling film evaporators for volume reduction and solid content increase. While the resulting concentrated vinasse is a liquid fertilizer with better transportability conditions, the evaporated water is suitable to compose part of the microalgae culture medium after its condensation. As detailed in Section 3.3.3, water use in microalgae cultivations is of utmost importance and vinasse is an abundant water source in a simple analysis.

3.5.3 Surplus energy from sugarcane mills

Brazil is known worldwide for its diversified and sustainability-oriented energy matrix, in which biomass plays an essential role. Besides conventional energy-producing facilities, such as hydroelectric, coal, and natural gas power plants, some industrial sectors are self-sufficient in terms of electric energy generation and sell surplus electricity to the national grid, mainly pulp and paper mills and sugarcane mills (Teixeira and Lora, 2004).

Around 21% of the energy used in the industrial sector in Brazil comes from sugarcane LCM combustion (Vakkilainen et al., 2013). Other primary biomass sources, namely wood and charcoal, are mainly employed in the ceramics sector and iron/steelmaking, respectively. The exportation of electric energy from cogeneration in sugarcane mills is an important product helping to improve the profitability of such facilities (Grisi et al., 2012).

The main energetic requirement of microalgae facilities is electric energy, which is used in powering several types of equipment: impellers in open PBRs, pumps for the displacement of culture medium, microalgae suspensions, and make-up water, centrifuges for biomass separation, blowers for flotation systems, lipid extraction equipment, and conversion processes, varying greatly according to the chosen technological route (Boer et al., 2012). Process steam may play a role in supplying energy for certain microalgae conversion
technologies. Biodiesel production and ethanol distillation, for instance, consume around 300 kg of steam/tonne of biodiesel (Olivério et al., 2014) and 100-550 kg of steam/m³ of anhydrous ethanol depending on the use of either pervaporation or molecular sieves as the dehydration technology (Dias et al., 2015), respectively. In order to maintain the supply of thermal energy for microalgae cultivations inside the biorefinery, other energy vectors may be employed, such as heat integration between different equipment and microalgae cultivation. The influence of seasonal high and low temperatures requires the heating or cooling of culture medium according to each occasion, which could be carried out through integration with specific streams in sugarcane mills. An interesting feature that favors ethanol distilleries to host integrated biorefineries is the availability of various high-temperature process streams which could be used in supplying part of the energetic demand of an integrated process. For example, microalgae production could benefit from the energy contained in the vinasse stream, which leaves the distillation column at nearly 100 °C, to pre-heat fresh culture medium prior to sterilization in heterotrophic cultivations.

More complex paths include the co-location between microalgal biomass gasification and cycle-based power generation (Aziz et al., 2014): after cultivation, the microalgal water content is removed with a dryer integrated to gas turbines, which operate with syngas and whose flue gas is in turn used to enhance the photosynthetic growth of microalgae.

3.5.4 Land availability

Brazil is renowned for the great availability of unused land area as well as degraded pasture land, from which microalgae projects can benefit. Sugarcane crops, for instance, occupy less than 4% of the arable land in the country (Procana Brasil, 2015). Concerning the displacement of land for microalgae units, the Northeastern region of Brazil tends to present cheaper costs than the traditional South-Southeastern sugarcane region - although the latter is closer to the largest consumer markets in the country. A study from Adenle et al. (2013) deems all areas with average temperatures between 20 and 30 °C as favorable for microalgae growth, which corresponds roughly to all land comprised at latitudes between the 35th parallels. Through this perspective, all of the Brazilian territory is, in a first analysis, suitable for microalgae cultivation. However, as previously stated in Section 3.3.4, local atmospheric conditions highly influence the feasibility of outdoor production of microalgae (Farooq et al., 2015) and have a direct impact on the final location choice. Temperatures in Southern Brazil vary highly when comparing summer and winter periods. Intensive microalgae cultivations in

the region would require additional investment for both heating and cooling of the culture medium during temperature extremes, in a similar fashion to Northern Italy (Ramos Tercero et al., 2014). In this way, other portions of the country with more stable temperature patterns are preferable, namely the Southeast, Center-West, and Northeast regions. Another analysis on microalgal biofuels (Moody et al., 2014) pointed out nations such as Australia, Cambodia, Brazil, Egypt, India, Kenya, and Saudi Arabia as promising for microalgal lipid production due to land requirement and availability, solar irradiance, and annual average temperatures - without taking into account, however, the availability of freshwater sources. Among these countries, Brazil presents the clear advantage of disposing of large water resources, which are scarce and sought-after in desert and semi-arid regions. Water stress in such countries could spark "drinking water" *vs.* "water for fuel" controversies in the same way ethanol and biodiesel production from conventional crops (corn and oilseeds, respectively) trigger food *vs.* fuel debates.

Ultimately, the most suitable locations for microalgae cultivations in Brazil are virtually confounded with sugarcane production areas, since many climatic characteristics are shared by the cultures. Both thrive in regions with increased solar irradiance and moderate or high temperatures. Due to limitations of current machinery for sugarcane harvest (Pinheiro et al., 2010), land suitable for sugarcane cultivations often have low slopes, below 12% - a feature also interesting for the deployment of microalgae bioreactors. Finally, sugarcane fields are usually located near water bodies, from which water is drawn for crop irrigation (Scarpare, 2013). Due to the water-intensive nature of microalgal biomass production, this is also a valuable factor when considering the location of an industrial unit.

3.6 Hurdles to adoption of microalgae technology in Brazil

As shown in this Chapter, Brazil is a potential candidate for large-scale microalgae projects. Adenle et al. (2013) place Brazil among a group of countries which combine both favorable geographic conditions and might either develop or incorporate technology for microalgae production. Amid the several possible types of hurdles to the deployment of microalgae units, mainly technological, economic, environmental, and social (Oltra, 2011), the latter stands as one of the greatest to be overcome. In a recent study, Luthra et al. (2015) stressed the existence of multiple barriers for the adoption of sustainable technologies in India, in an analysis that can also be applied to the Brazilian context to some extent, namely

the lack of financing mechanisms, lack of governmental subsidies, and general resistance to change and adopt technologies for greater gains. Undoubtedly, for microalgae projects to thrive in Brazil, it is imperative that owners of sugarcane mills be open-minded towards new possibilities of product portfolio diversification, which could assist their own businesses in achieving higher economic stability. Besides, more financing for related projects is clearly needed from governments, funding agencies, and companies in the field (Brasil et al., 2017).

3.7 Preliminary conclusions

The utilization of microalgal biomass as the basis for future biorefineries is both logical and a promising concept for a gradual transition to a bio-based economy. Despite the presence of technical challenges on nearly every aspect of microalgae production for biofuels synthesis (i.e. process bottlenecks), a true boom of biotechnology joint ventures and corporate spin-offs issued from the huge increase in interest in this type of technology. Many of these companies still lack large-scale facilities, neither for cultivation nor for microalgae postprocessing. In view of the reasons shown in this Chapter, microalgae companies could benefit from the existing infrastructure of sugarcane mills in Brazil to assist in the establishment of pilot plants and industrial-scale units and stimulate the development of this technology for biomass production. As an initial step towards integrated sugarcane-microalgae biorefineries, the focus should be given to the utilization of CO₂ produced during ethanol fermentation and CO₂ contained in biogas obtained from AD of vinasse, in terms of practicality of integration instead of aiming at utilizing flue gas emissions - which would require extensive processing prior to injection in cultivations. Only after such demonstrations advance in the learning curve is that widespread, larger integrated microalgae projects could appear employing the more common, yet least practical, flue gas emissions as the carbon source.

Regardless of the chosen approach, several aspects of microalgae cultivation must still be proven in laboratory scale and through the deployment of new pilot plants worldwide. Scientific data concerning growth of different microalgae species, both wild and genetically modified ones, with *in natura* and digested vinasse are especially needed, as well as innovative configurations for biogas upgrading with microalgae cultivations and novel bioreactor designs for optimization of CO_2 uptake and microalgae concentration and productivity.

CHAPTER 4 MICROALGAE PRODUCTION IN NEXT-GENERATION INTEGRATED SUGARCANE BIOREFINERIES: FERMENTATION-DERIVED CO₂ AND VINASSE AS CARBON SOURCES FOR ALGAL GROWTH

4.1 Introduction

Sustainability is the object of much discussion nowadays, not only by scientists and policymakers but also by companies and the general public alike. Current actors in the field point at the possibility of establishing a circular economy aiming at the substitution of several fossil products by their biobased competitors, ranging from biofuels to chemical specialties. Microalgae biomass appears as a promising alternative for supplying such bioproducts, although with few industrial-scale facilities presently operating worldwide. Technologies for microalgae production are known to be costly both in terms of CAPEX and operational expenses (OPEX), demanding high quantities of EE, CO₂, and nutrients. This perception comes from the fact the industrial conversion of microalgal biomass into finished products is confounded with its cultivation, i.e. with the agricultural step of conventional energy crops.

However, the costs referring to inputs towards microalgae production and processing may be lowered through a strategy of co-location with other facilities which produce CO₂ as a byproduct or a waste stream. Many different CO₂ sources have been suggested as being suitable for utilization in autotrophic microalgae growth, primarily industrial emissions from steelmaking and cement production (Benhelal et al., 2013) and flue gases from stationary equipment (Pires et al., 2017). Several studies in the literature point at the reduction of both costs and environmental impacts from the production and processing of microalgae through its integration with mature technologies, such as in the case of sugarcane mills (Klein et al, 2018; Chagas, 2016; Maranduba, 2016; Maranduba, 2015; Souza, 2015; Moncada, 2014; Lohrey, 2012; Rosenber, 2011). The sugar-energy sector produces high quantities of biogenic, stationary CO₂ emissions, which could be employed as the carbon source for photoautotrophic microalgae growth. Two main CO₂-rich streams can be found in a traditional sugarcane mill: flue gases from bagasse and straw combustion in the CHP unit and ethanol fermentation offgas. While abundant and readily available for use, the required reactor area to absorb and consume with microalgae cultivations all the emitted CO₂ stands in the range of several thousand hectares, as shown in Table 3.2. This is virtually independent of the reactor type (raceways or closed PBRs) since both options present similar areal biomass productivities. Another interesting carbon source produced in large quantities by sugarcane mills is vinasse, a sub-product of ethanol purification that could be employed on the heterotrophic growth of microalgae (Mattos and Bastos, 2016). Besides, sugarcane mills also may offer a series of energy vectors to be used by adjacent microalgae plants, mainly in the form of EE and process steam. In an overall analysis, the sugar-energy sector is robust enough and sugarcane mills have an interesting industrial scale to host integrated biorefineries and help annexed technologies to gradually develop their learning curve until reaching market competitiveness.

In view of this potential, the study presented in this Chapter aims at assessing innovative configurations towards the deployment of large-scale sugarcane-microalgae biorefineries. The desired co-location level between plants lies beyond the supply of material and energy vectors from the sugarcane mill to the microalgae facility: an example is microalgal biodiesel produced in this way being consumed by the machinery employed in agricultural operations of sugarcane production - planting, harvesting, and transporting, for example (Cavalett et al., 2016). Little consideration has been given to the substitution of fossil diesel in integrated biorefineries in the scientific literature, being mainly restricted to the replacement of diesel by biomethane (Dias et al., 2016). For that reason, a full techno-economic and environmental assessment of co-located biorefineries for microalgal biodiesel production and substitution of fossil diesel is presented in this work. The chosen carbon sources to enable microalgae growth were ethanol fermentation-derived CO₂ and sugarcane vinasse. Sensitivity analyses were employed to point out the main variables impacting the economic feasibility of these novel biorefineries.

4.2 Material and methods

4.2.1 Process description

4.2.1.1 Sugarcane processing in ethanol distilleries

Among the possibilities of processing sugarcane into bioproducts, two configuration types stand out in Brazil in terms of plants: ethanol distilleries and distilleries with annexed sugar mills, producing, respectively, ethanol and both ethanol and sugar (Morais et al., 2016), although units producing exclusively sugar also exist, but to a smaller extent. Sugarcane mills produce large quantities of EE and heat in the CHP unit from the burning of bagasse and straw (whenever the recovery of the latter is carried out), which are supplied to the process to fulfill its energy requirements. Depending on the configuration and level of process optimization, the plants may be also capable of exporting surplus EE to the grid either through contracts established by regulated auctions or on the spot market. The main operations involved in sugarcane processing into anhydrous ethanol and EE in ethanol distilleries, namely sugarcane crushing, juice treatment, fermentation, ethanol purification, and heat and

4.2.1.2 Microalgae cultivation and downstream processing

Biodiesel production from microalgae is achieved through a series of steps, namely: microalgae cultivation, microalgae harvest, lipids extraction, and transesterification. Each of the processes is described in this section and the main associated parameters are presented in Annex A.2 (Table A.2.1).

4.2.1.2.1 Photoautotrophic growth with fermentation CO₂

The photosynthetic growth of microalgae was carried out with two different concepts: (1) covered raceways, an intermediate option between open raceways and closed PBRs, and (2) flat-panel closed PBRs. Covered raceways usually provide low final microalgae concentrations when compared to closed systems, while having relatively low initial investment; on the other hand, closed PBRs present higher CAPEX, although allowing better process control and higher cell densities (Brennan and Owende, 2010; Mata et al., 2010). Covered raceways are built as conventional open raceways, despite being covered by a semitransparent polypropylene, agricultural film. This largely helps in reducing the exposure of the culture medium to the environment and significantly restricts the amount of evaporated water, as well as contamination possibility (Lohrey and Kochergin, 2012). However, an additional side issue is created with greenhouse-like PBRs: the aging process of the film material, as well as the buildup of dust and dirt on top of it, leads to a natural decrease of its transmittance (Giacomelli and Roberts, 1993), thus entailing significant maintenance costs. Closed PBRs, on the other hand, were modeled as flat-panels, in which the microalgae suspension is circulated among the spacing of 5 to 8 cm existing between two square plates manufactured out of transparent material. Both systems operate with an average areal productivity of 250 kg/ha.day (flat-plate PBRs have a volume productivity of 1.25 kg/m³.day and an areal footprint of 200 m³/ha). Covered raceways and flat-panel PBRs achieve final microalgae concentrations of 0.5 and 4 kg/m³. Agitation of covered raceways is carried out with paddlewheels, while that of flat-panels is performed mainly through injection of the CO₂ stream and with recirculating pumps. A comprehensive list of parameters considered for open and close reactors are presented in Annex A.2 (Tables A.2.2 and A.2.3).

Besides carbon, other nutrients must be supplied to the cultivation to ensure proper microalgae development. The Redfield Ratio ($C_{106}H_{181}O_{45}N_{15}P$) was considered as representative of a generic microalgae strain for estimation of the required nutrients (Redfield, 1958). This simplified formula only takes into account macronutrients in microalgal biomass (ash-free), thus excluding micronutrients from the mass balance. In this way, a fertilizer combining urea and monoammonium phosphate (MAP) was supplied to microalgae cultivations in the proportion of 0.288 kg per kg of dry microalgal biomass. The amount represents a 20% excess of both N and P in comparison to the stoichiometric ratio, due to potential losses in view of competing organisms, volatilization to the atmosphere and downstream conversion (Ryan Davis, personal communication, 2017). The use of urea and MAP is roughly equivalent to that of urea and diammonium phosphate (DAP): the former combination results in an overall input consumption nearly 6% higher, although at a 4% lower total cost.

Microalgae cultivation must undergo thorough temperature control to ensure the best possible conditions for cell development (Ramos Tercero et al., 2014). Since the integrated biorefinery is considered to be located in the Southeastern part of Brazil, relatively high solar radiation incides year-round on the cultivation area and, therefore, cooling of the cultivation must be carried out throughout the year. For the determination of the required temperature reduction to be provided to culture medium, the method adapted from Domenicali (2013) was employed. Temperatures and solar radiation cycles for the city of Piracicaba (SP, Brazil) were retrieved from Climate Data (2017) and CRESESB Atlas (2000), respectively, and averaged for the four seasons. Since a temperature of 25 °C was chosen as best for microalgae growth, the calculations yielded estimates of 6.5 °C, 8.2 °C, 4.7 °C, and 0.7 °C to be removed from the cultivations during Spring, Summer, Autumn, and Winter, respectively. Heat removal is achieved through the combination of compression chillers (EE-driven) and absorption chillers, an interesting option for industrial plants which dispose of cogeneration systems. Absorption chillers here are considered to operate with waste heat from the process, either bleed steam from evaporators, condensed vapors, hot flue gases, and even high-temperature vinasse leaving the distillation train. In all scenarios, the required heat removal is supplied between 80% and 90% by absorption chillers and the remainder by compression chillers. Absorption and compression chillers are considered to have coefficients of performance (COP) of 0.7 and 7, respectively. The COP is defined as the ratio between the cooling provided by a given system (power output) and the total power consumption. Since absorption chillers use low-quality energy, their COP is naturally lower than that of compression chillers, which consume EE for operation. An arrangement of four identical compression chillers is used in the microalgae plant: the four of them are operational during Summer, with three functioning during Spring, and only two during Autumn. The absorption chiller operates yearround, being able to remove heat from the cultivations during all seasons without significantly requiring EE to operate. This configuration is especially appealing since it ensures low energy consumption, thus maximizing EE exports to the grid, and promoting the establishment of a biorefinery with high thermal efficiency. In plants with lower heat removal requirements (mainly with closed PBRs), the absorption chiller is considered to be capable of operating with variable load throughout the year. This minimizes EE consumption by compression chillers and slightly reduces the overall CAPEX of coolth generation units. Shell and tube heat exchangers are considered for heat removal from the culture medium with cold water generated in the chillers. Supplying of heat to the cultivations would be less frequent and could be achieved by using the same heat sources cited for the operation of the absorption chillers and the existing heat exchangers infrastructure.

4.2.1.2.2 Heterotrophic growth with vinasse

Data employed in the modeling of heterotrophic growth of microalgae using vinasse as the carbon source were largely based on information provided by Mattos and Bastos (2016). This reference is especially appealing for integrated biorefineries since it is one of the few that employs sugarcane vinasse as the full culture medium for microalgae growth (without pre-mixing with standard cultivation media). An inoculum of 1 kg/m³ was considered and, after 30 h, a final microalgae concentration of 4 kg/m³ is reached. Besides, 8 h are reserved for reactor loading with vinasse, 8 h for unloading of the microalgal suspension, and 2 h for reactor cleaning, yielding a total batch time of 48 h. Microalgae growth is carried out in vessels built in a similar fashion to ethanol fermentation reactors, while agitation is supplied by high-torque impellers. No sterilization or further nutrient addition is required for the heterotrophic growth of microalgae in sugarcane vinasse (Mattos and Bastos, 2016). More detailed parameters are shown in Annex 2 (Table A.2.4).

4.2.1.2.3 Harvest

After growth, microalgae biomass is harvested in a two-step process: initially, the culture medium is concentrated up to 1.5% dry biomass in settlers with AlCL₃-aided sedimentation; subsequently, a centrifuge further thickens the slurry up to 22% dry biomass. Since centrifugation for microalgal biomass separation usually presents high specific EE consumption, preliminary internal assessments investigated the possibility of employing a third, intermediate harvest step in order to reduce the volume of microalgae suspension sent to centrifuges. In this way, an operation of dissolved air flotation (DAF) was chosen as a means of pre-thickening the microalgae suspension prior to centrifugation. Results (not shown in this study) point towards an increase in both OPEX and CAPEX of the triple-step harvest strategy. Besides, the adaptation of centrifuges commonly employed in the sugar-energy sector tends to be a relatively low-cost solution to microalgae plants. Therefore, the simpler two-step layout of sedimentation followed by centrifugation was chosen for the remainder of the study.

When treating microalgae biomass from heterotrophic cultivations, the harvest was considered to be performed in a single step with centrifuges so as not to add chemicals (AlCl₃) to the spent vinasse, which can return to the sugarcane field for nutrient recycling.

4.2.1.2.4 Lipids extraction

Slurries containing 22% dry biomass are able to enter supercritical CO_2 extractors for the extraction of lipids, according to industrial suppliers. Supercritical CO_2 was chosen in order to eliminate the need for a microalgal biomass drying step and to ensure the commercialization of high-quality, solvent-free microalgae meal as a coproduct of the biorefinery. Another advantage consists in that CO_2 make-up to compensate eventual losses in the equipment can be obtained from the high-purity CO_2 stream issued from ethanol fermentation vessels, which operate year-round. However, no CO_2 make-up is considered in this analysis.

The processing of the slurry in a supercritical CO₂ extractor gives origin to two main streams: microalgae oil, which is sent to biodiesel production, and high-protein microalgae meal, a finished product with high market value.

4.2.1.2.5 Biodiesel production

Finally, the extracted lipids are transesterified with ethanol using homogeneous basic catalysis (NaOH) in a facility designed as conventional biodiesel plants in Brazil. The anhydrous ethanol make-up is obtained from the sugarcane mill, as well as process steam for heat supply. This final step yields two main streams: purified biodiesel and crude glycerin.

4.2.2 Process simulation

The analyses were carried out utilizing the VSB framework, which integrates a computer simulation platform with sustainability evaluation of different biorefinery alternatives through the combination of all steps of the biomass chain: agricultural production, transport, industrial conversion, use, and final disposal of the products (Bonomi et al., 2016). This comprehensive tool was initially aimed at solving issues of the sugarcane production chain but is adaptable to assess new biomasses and technological routes. Process simulation was performed using the Aspen Plus® software, version 8.6 (AspenTech, Bedford, MA, USA). Modelling of the ethanol distilleries was carried out through adapting pre-existing simulations of sugarcane mills in the VSB, as extensively described in previous publications (Dias et al., 2015; Morais et al., 2016). The microalgae plant was modeled and simulated jointly in the Aspen Plus® software and in electronic spreadsheets. All systems were considered to operate in steady-state.

Six scenarios were designed through a combination of the processes described in Section 4.2: two base scenarios and four integrated sugarcane-microalgae plants. Details of the processes are further described in Sections 4.2.2.1 and 4.2.2.2.

4.2.2.1 Base scenarios

Two base scenarios were conceived to provide a comparison basis to the integrated sugarcane-microalgae scenarios. Scenario BASE1 is a conventional ethanol distillery crushing 4 MTC per year and recovering 50% of the produced sugarcane straw from the field. This plant operates during 200 days per year, only during the sugarcane harvest season, as most of such facilities in Brazil. Figure 4.1a depicts this configuration.

On the other hand, scenario BASE2 was designed to generate constant outputs of anhydrous ethanol and EE from the CHP unit for 330 days, spanning both sugarcane harvest

season (200 days) and off-season (130 days). For this, the plant stores inverted sugarcane syrup and LCM (sugarcane bagasse and straw) for ethanol fermentation and firing of the CHP unit during the off-season, respectively. This process outline was primarily chosen in order to supply a constant flow of vinasse and fermentation CO_2 to microalgae growth in integrated biorefineries since cultivations should be kept operating throughout most part of the year due to the impracticality of process start-up in short periods of time. Another possible arrangement to avoid storing sugarcane LCM and syrup is through employing alternative feedstocks for off-season operation, such as sweet sorghum and corn (Dias et al., 2016) or energy cane (Junqueira et al 2017) - options which were not analyzed in this study. Figure 4.1b shows a simplified process diagram for scenario BASE2.



Figure 4.1– Process flow diagrams for base scenarios (a) BASE1 and (b) BASE2.

4.2.2.2 Integrated sugarcane-microalgae scenarios

As previously anticipated, microalgae production occurs in integration with sugarcane mills. Figure 4.2a presents the overall co-location strategy between ethanol distilleries and microalgae plants. In a general overview, several requirements towards microalgae production are obtained from the sugarcane mill: fermentation CO_2 and vinasse as carbon sources for the photoautotrophic and heterotrophic growth of microalgae, respectively; EE to power different types of equipment; and both process steam and anhydrous ethanol to carry out the transesterification of microalgal oil into biodiesel. As the main products of the biorefinery, anhydrous ethanol, surplus EE, microalgal meal, and glycerin can be cited. Microalgae-derived biodiesel is also produced, but does not correspond to an output of the biorefinery per se: since sugarcane agricultural operations consume large amounts of diesel (Cavalett et al., 2016), microalgal biodiesel production in the integrated plant was tailored to fully replace fossil diesel in such steps. Estimates point to the need of producing 17 million L of microalgae biodiesel in order to reach this target. In this way, the loop is closed and the agricultural phase of the sugarcane chain counts with lower fossil-based inputs. Besides, the production cost of both sugarcane stalks and straw are reduced in view of the dismissal of acquiring fossil diesel from the market.

Figures 4.2b and 4.2c show the layout of the microalgae facility of the four integrated scenarios: P1, P2, C1, and C2. The main goal of the designed scenarios was to assess the influence of different cultivation alternatives, namely covered raceways and flatpanel PBRs, either alone or in parallel with vessels operating in the heterotrophic regime, on the sustainability performance of the biorefinery. In scenarios P1 and P2, microalgae cultivations rely exclusively on daytime-produced CO_2 from ethanol fermentation as the carbon source; in scenarios C1 and C2, part of the microalgal biomass is produced through heterotrophic growth in vinasse and the remainder is obtained photoautotrophically. The highpurity CO_2 stream (over 98%, m/m) dismisses further processing prior to injection in microalgae reactors. In the same way, vinasse is only cooled down to room temperature before filling of the vessels. For further clarification, the integrated scenarios are summarized in Chart 4.1. More complex scenarios involving AD of vinasse are further assessed in Chapter 5.



Figure 4.2 – Process flow diagrams of integrated sugarcane-microalgae biorefineries. (a) Integration strategy between a sugarcane mill and a microalgae facility, with biodiesel used for the substitution of diesel in sugarcane agricultural operations (verticalized operation). (b) Layout of the microalgae facility in scenarios P1 and P2. (c) Layout of the microalgae facility in scenarios C1 and C2. EE not shown as an input to microalgae production since all steps shown require electricity to operate.

| Integrated scenario | Without heterotrophic growth | With heterotrophic growth |
|---------------------|------------------------------|---------------------------|
| Covered raceway | P1 | C1 |
| Closed PBR | P2 | C2 |

Chart 4.1 – Configuration overview of integrated scenarios.

4.2.3 Techno-economic assessment

A discounted cash flow for each scenario was created by taking into account the full CAPEX and OPEX of all involved units, as well as the revenues obtained from the commercialization of the bioproducts obtained in the biorefineries, and the parameters presented in Table 4.1. All plants are analyzed as greenfield projects, built in a 3-year timespan. Financial leverage was not considered in the economic assessment.

Table 4.1 – Main parameters considered for the establishment of discounted cash flows

| Parameter | Value |
|--|--|
| Minimum acceptable rate of return (MARR) | 12% |
| Working capital | 10% |
| Lifespan of the industrial plant | 25 years |
| | 3% (sugarcane mill) |
| Annual maintenance costs | 4% (microalgae plants, covered raceways) |
| | 5% (microalgae plants, closed PBRs) |
| Annual depreciation rate | 10% |
| Combined corporate taxes | 34% |
| R\$ to US\$ exchange rate, Dec/2016 | 3.35 |
| R\$ to € exchange rate, Dec/2016 | 3.53 |

The discounted cash flow allows the determination of several important economic indices, which include the Internal Rate of Return (IRR), the Net Present Value (NPV), the NPV over investment ratio (NPV/I), and the discounted payback. The NPV index compares the present value of the current cash inflows with that of cash inflows in a future period of time, taking into account the inflation rate and revenues. If the NPV of a project is calculated to be higher than zero, then the investment would add value to a company; otherwise, it would be negative and should be rejected. The IRR, on the other hand, can be defined as the discount

rate of a project with which the present value of the cash flow equals its initial investment. In other words, the IRR is the rate of return at which the NPV equals zero. Therefore, the higher the IRR, the better the investment option. The NPV/I index represents a normalized metric for the total discounted return over the lifespan of the project (Holland et al., 1976). Finally, the payback metric equals the time in which the investment in a given project is recovered and is normally given in years. The chosen methodology for estimating the production cost of anhydrous ethanol and biodiesel among scenarios was that of the economic allocation (Watanabe et al., 2016).

It is worthwhile to note that two types of results are presented for the economic assessment of the biorefineries: deterministic vs stochastic ones. The deterministic analysis employs static values for CAPEX, OPEX, and commercialization prices. Table 4.2 shows the estimated deterministic values for selling prices of biorefinery products.

| Dovomator | Val | I I:4 | |
|----------------------|----------|-------|-----|
| rarameter | R\$ US\$ | | Umt |
| Anhydrous ethanol | 1.70 | 0.51 | L |
| Microalgae meal | 1.76 | 0.53 | kg |
| Electric energy (EE) | 193.95 | 57.90 | MWh |
| Glycerin | 0.50 | 0.15 | kg |
| Biodiesel | 2.60 | 0.78 | L |

Table 4.2 – Main products prices employed in the economic assessment.

Selling prices of anhydrous ethanol, EE, and biodiesel (as well as for the majority of chemical inputs) were calculated using the following methodology. First, the available 10-year historic series in Brazil of several items were retrived from MDIC (2018). Monthly prices in US\$ were then converted to R\$ using the corresponding Month/year exchange rate, being further deflated to R\$₂₀₁₆ using the consumer prices index (IPCA, *Índice Nacional de Preços ao Consumidor*, equivalent to the Brazilian inflation rate). Finally, a single, average value is obtained from the 6-year moving average of the corrected prices. One limitation of such method is encountered when the exported or imported amount of a given good is unusually low, which tends to result in above-average prices for that period of time. The microalgae meal selling price was estimated taking soybean meal as the basis while correcting it through its overall protein content (microalgae and soybean meals present protein contents of 60% and 44%, respectively). Crude glycerin was considered to be sold at prices commonly

found in the Brazilian market when employing other raw materials (such as soybean oil) for biodiesel production. All prices and costs were updated to December/2016.

For obtaining stochastic results, uncertainty (or risk) analyses were carried out using Monte Carlo simulation in the @RISK software, version 6.3.1 (Palisade, Ithaca, NY, USA). Table 4.3 shows the main inputs of the analysis, in which both technical and economic parameters were varied. All variables follow triangular distributions, in which the highest probability corresponds to the mean value and, the lowest ones, to the extreme values.

Table 4.3 – Considered distributions of the main inputs and products of the biorefineries in uncertainty analyses. All variables follow triangular probability distributions.

| Parameter | Minimum | | Maximum |
|-----------------------------|---------|------|---------|
| Technical parameters | | | |
| Fertilizer consumption | 80% | 100% | 120% |
| Microalgae lipid content | 20% | 30% | 40% |
| Settling efficiency | 85% | 90% | 93% |
| Centrifugation efficiency | 90% | 95% | 98% |
| Lipid extraction efficiency | 95% | 98% | 99% |
| Operational level | 85% | 90% | 95% |
| Economic parameters | | | |
| Biomass price | 85% | 100% | 115% |
| Sugarcane mill CAPEX | 85% | 100% | 115% |
| Microalgae plant CAPEX | 80% | 100% | 130% |
| Anhydrous ethanol price | 82% | 100% | 118% |
| Electricity price | 70% | 100% | 130% |
| Microalgae meal price | 88% | 100% | 112% |

Technical parameters were considered to vary between optimistic and pessimistic values, but equally realistic on a biorefinery of large scale. For example, microalgae lipid content was varied from a minimum of 20% up to a maximum of 40%, with a mean (deterministic) value of 30%. The other parameters follow a similar reasoning. Sugarcane and straw prices were varied between $\pm 15\%$ of the base value due to fluctuations in the productivity between harvest seasons. Anhydrous ethanol price mainly stands in a ± 1

85%

100%

115%

Biodiesel price

standard deviation of the base value, which corresponds to around $\pm 18\%$ of R\$ 1.70/L (US\$ 0.51/L). EE price has a significantly higher variation ($\pm 30\%$) in view of the natural fluctuations in energy auctions in the country. Microalgae meal price varied between $\pm 12\%$ of the base price, representing a ± 1 standard deviation of soybean meal price in 2016. Biodiesel price was considered to vary in a range of $\pm 15\%$ around the deterministic value of R\$ 2.60/L (US\$ 0.78/L). Finally, the CAPEX of sugarcane mills was considered to vary between $\pm 15\%$ of the estimated values, while this range is higher for microalgae plants due to a higher uncertainty in investment determination.

The uncertainty analysis was carried out for three main economic indices: IRR, anhydrous ethanol production cost, and biodiesel production cost. The simulations were carried out with 5,000 iterations.

4.2.4 Environmental assessment

The Life Cycle Assessment methodology (LCA) was used for the quantitative assessment of environmental impacts. This method is described in the ISO 14000 series of standards (ISO, 2006a; ISO, 2006b) and is a widespread methodology for the environmental assessment of products and processes (Cavalett et al., 2012; Dias et al., 2012b; Hellweg e Milà i Canals, 2014; Macedo et al., 2008; Seabra et al., 2011). The LCA technique takes into account impacts in emissions and in the use of resources typically found in bioenergy systems.

The SimaPro software (PRé Consultants, 2016) was used as a supporting tool and the ecoinvent database v2.2 (Swiss Centre for Life Cycle Inventories, 2007) was employed to obtain the environmental profile of background product systems (e.g. diesel, fertilizers, pesticides, and other chemicals used as inputs in the processes). With the LCA methodology, the use of resources and emissions to soil, air, and water of the production chain as a whole are converted into different environmental impact categories using internationally-recognized environmental impact assessment methods. In this context, selected impacts categories from the ReCipe Midpoint method (Goedkoop et al., 2009) were used to compare the environmental impacts related to the production of anhydrous ethanol since this is the main product of all base scenarios and integrated biorefineries in terms of both volume and revenue.

Different environmental aspects can be covered with an LCA approach, ranging from climate change and depletion of fossil resources to freshwater eutrophication, water depletion, and land use aspects. The climate change impact category (also known as "carbon footprint", "global warming potential", or "GHG emissions") is measured in g CO₂eq. The characterization factor describing the radiative forcing of one mass-based unit of a given GHG relative to that of CO₂ over a time frame of 100 years is obtained from the 2007 Intergovernmental Panel on Climate Change (IPCC) method (IPCC, 2007). This method has global consensus on the relationship between GHG and the increase in global temperature.

The freshwater eutrophication category accounts for the emission of P (phosphorous) to water bodies, which may cause excessive biomass growth in aquatic ecosystems (Goedkoop et al., 2009). The measuring unit is g Peq (phosphorous-equivalent).

The agricultural land occupation impact category can be defined as the maintenance of an area in a particular state over a particular time period. It reflects the damage to ecosystems due to the effects of the occupation of land for agricultural production (Goedkoop et al., 2009). The impacts are measured in area time (m^2a) .

Water depletion refers to the extraction of water for consumption in both agricultural and industrial operations (Goedkoop et al., 2009), being measured in m³ of water.

The fossil depletion category considers the gradual decrease of quantity and quality of fossil resources. Since fossil resources become depleted and more costly, other resources need to be exploited. The characterization factors are based on the projected change in the supply mix between conventional and unconventional oil sources (Goedkoop et al., 2009). This impact category is measured in oil-equivalents (g oil eq).

Life cycle inventories used in this assessment were obtained from agricultural and industrial simulations for the definition of mass and energy balances. Since multiple products are obtained in each plant, it is necessary to split part of the environmental impacts to each one of them. In this study, an allocation procedure based on economic relationships was chosen, as detailed in Watanabe et al. (2016). As previously stated, since anhydrous ethanol is the product of choice for comparison among scenarios, the impacts allocated to it correspond to its share among all the revenues obtained from the commercialization of biorefinery products. Boundaries of the system include the stages of agricultural production, transport of biomass to industrial units, and industrial conversion (production phase). The transport of anhydrous ethanol to the market and its use in Otto-cycle engines belong to the use phase, the impacts of which are only accounted for when comparing them to the fossil type A gasoline.

As for the economic assessment, the environmental results are also presented for a deterministic evaluation (with static values) and for a stochastic one (with a variation range for each independent variable). The Monte Carlo simulations for risk analysis consider the following impacts from Table 4.3: anhydrous ethanol price, EE price, microalgae meal price, biodiesel price, microalgae lipid content, and fertilizer consumption. Besides, a simplified variation on the impact of producing one tonne of sugarcane was also employed, with a variation of $\pm 15\%$ in relation to the base value of the deterministic assessment. The simulations were carried out with 5,000 iterations. Stochastic results are only shown for the climate change impact category.

4.3 Results and discussion

4.3.1 Technical results

Table 4.4 summarizes the main technical results obtained after simulation of both base scenarios and integrated sugarcane-microalgae biorefineries.

All scenarios process equal amounts of sugarcane stalks and straw. For the production of roughly 17 million L of microalgae biodiesel/year, scenarios C1 and C2 consume less CO₂ from fermentation vessels than their equivalents P1 and P2 due to the consumption of sugarcane vinasse. On the other hand, the same scenarios require significant amounts of EE for the microalgae plant (over 200 GWh/year). Despite the reduction in the area occupied by photoautotrophic reactors, the utilization of large impellers in heterotrophic reactors increases the total quantity of consumed EE (further discussions over the next pages and around Figure 3.3). Scenarios C1 and C2 also consume less fertilizer than the P1 and P2 counterparts. This is important in terms of both economic and environmental performances due to the high cost and the well-known impacts involved in their production.

In terms of product output, scenarios BASE1 and BASE2 produce 347 million L of anhydrous ethanol/year, with integrated sugarcane-microalgae biorefineries commercializing a slightly lower volume (344 million L/year) in view of its partial consumption in the transesterification of microalgae oil. Scenario BASE1 exports nearly 742 GWh/y to the national grid, with scenario BASE2 being able to sell less EE to the grid (708 GWh/y) due to the production of inverted sugarcane syrup for off-season operation: process steam that would normally generate EE in condensation turbines in scenario BASE1 are diverted towards the evaporation of sugarcane juice in scenario BASE2). The EE sold to the grid is significantly

lower in the integrated biorefineries. Finally, the outputs concerning the production of microalgae are rigorously the same from scenario P1 to C2: 17 million L of microalgae biodiesel/year (fully sent to agricultural operations of sugarcane), 44 thousand tonnes of microalgae meal/year (with 60% protein content and 15% moisture content), and residual amounts of 1.8 thousand tonnes of glycerin/year from microalgae oil transesterification.

| D | | S | cenari | io | | |
|--|-------|-------|-----------|------|-----------|------|
| Parameter | BASE1 | BASE2 | P1 | P2 | C1 | C2 |
| Main inputs - Sugarcane processing | | | | | | |
| Sugarcane stalks (MTC/y) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 |
| Sugarcane straw (thousand tonnes/y) | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 |
| Inputs from sugarcane mill - Microalgae production | | | | | | |
| Fermentation CO ₂ (thousand tonnes/y) | - | - | 218 | 207 | 186 | 177 |
| Vinasse (million m^3/y) | - | - | - | - | 2.8 | 2.8 |
| Process steam (thousand tonnes/y) | - | - | 26 | 26 | 26 | 26 |
| Anhydrous ethanol (million L/y) | _ | - | 3.6 | 3.6 | 3.6 | 3.6 |
| Electric energy (GWh/y) | _ | - | 189 | 141 | 252 | 217 |
| External inputs - Microalgae production | | | | | | |
| Urea and MAP (thousand tonnes/y) | _ | - | 15 | 15 | 12 | 12 |
| AlCl ₃ (thousand tonnes/y) | - | - | 1.2 | 0.2 | 1.1 | 0.1 |
| NaOH (thousand tonnes/y) | - | - | 3.5 | 3.5 | 3.5 | 3.5 |
| HCl (thousand tonnes/y) | - | - | 0.2 | 0.2 | 0.2 | 0.2 |
| H_3PO_4 (thousand tonnes/y) | - | - | 0.03 | 0.03 | 0.03 | 0.03 |
| Outputs | | | | | | |
| Anhydrous ethanol (million L/y) | 347 | 347 | 344 | 344 | 344 | 344 |
| Electric energy to grid (GWh/y) | 742 | 708 | 516 | 582 | 563 | 485 |
| Biodiesel to sugarcane operations (million L/y) | _ | - | 17 | 17 | 17 | 17 |
| Microalgae meal (thousand tonnes/y) | - | - | 44 | 44 | 44 | 44 |
| Glycerin (thousand tonnes/y) | - | - | 1.8 | 1.8 | 1.8 | 1.8 |

Table 4.4 – Main inputs and outputs of base scenarios and integrated biorefineries.

Table 4.5 presents additional results concerning the dimension of the designed microalgae facilities. Scenarios C1 and C2, which employ vinasse for the growth of microalgae, require roughly 14% less area for the construction of covered raceways and closed PBRs. In these plants, 20% of the needed microalgae biomass for biodiesel production is supplied by heterotrophic reactors. Due to the large flow of vinasse issued from ethanol distillation columns (around 352 m³/h), and since all of it is directed towards microalgae growth, vessels of large proportions are employed. An arrangement of seven reactors with 2,800 m³ working volume each (19,600 m³ total volume) was defined in this case. Heterotrophic growth of microalgae with sugarcane vinasse yields an oil productivity that is two orders of magnitude higher than that of photoautotrophic growth (7,600 ton oil/ha.year *vs.* 22 ton oil/ha.year, respectively). With this hybrid arrangement of photoautotrophic and heterotrophic reactors, a significant portion of the microalgae biomass can be produced with a low area occupation and without external fertilizer input.

| D | | | | |
|--|----------|----------|----------|----------|
| Parameter | P1 | P2 | C1 | C2 |
| Required reactor area (ha) | 831.8 | 831.0 | 717.7 | 716.4 |
| Photoautotrophic area (ha) | 831.8 | 831.0 | 717.3 | 716.0 |
| Heterotrophic area (ha) | - | - | 0.4 | 0.4 |
| Microalgae from photoautotrophic reactors | 100% | 100% | 80% | 80% |
| Microalgae from heterotrophic reactors | - | - | 20% | 20% |
| CO ₂ consumption | | | | |
| Photoautotrophic reactors (thousand tonnes/y; % of fermentation CO ₂) | 218; 41% | 207; 39% | 175; 33% | 166; 31% |
| Inoculum for heterotrophic reactors (thousand tonnes/y; % of fermentation CO ₂) | -; - | -; - | 11; 2% | 11; 2% |

Table 4.5 – Required reactor area for integrated microalgae biorefineries and estimated CO₂ consumption from the sugarcane mill.

Figure 4.3 presents the breakdown of EE requirements in microalgae plants of scenarios P1 to C2. The EE demanded for mixing of microalgae cultivations in flat-panel PBRs is much higher than in covered raceways, therefore the variance among scenarios.

Mixing energy requirements in raceways are the object of much discussion nowadays, with figures in the scientific literature varying up to six-fold (Lohrey and Kochergin, 2012; Rogers et al, 2014). Besides, as previously mentioned, heterotrophic reactors consume large amounts of EE due to the employment of high-torque impellers. Nearly 81% and 45% of the cultivation EE are directed to heterotrophic reactors in scenarios C1 and C2, respectively. Concerning the temperature control strategy, the volume of culture medium needing to be cooled down is roughly eight times higher in covered raceways, as in scenarios P1 and C1. This is a direct result of the final microalgae concentration obtained in the reactors. Analogously, closed PBRs demand much less energy for cooling. Besides, below a determined threshold, only absorption chillers are required, thus dismissing the use of compression chillers. This helps explaining energy requirements of scenarios P2 and C2 for temperature control being virtually zero.



Figure 4.3 – Breakdown of EE consumption for microalgae production and processing in the integrated biorefineries. Values shown on top of the bars refer to the total EE consumption in GWh/y.

The harvesting step corresponds to a significant amount of energy consumption, between 38% and 45% in all integrated scenarios. There is a clear trade-off when centrifuges are employed to this end: in spite of having low CAPEX, the required EE is high. On the other hand, different harvest systems promote the opposite situation (high CAPEX and low EE consumption). Another major component in Figure 4.3 is lipid extraction, carried out with supercritical CO₂ extractors. There is practically no requirement for external inputs (such as

4.3.2 Economic results: deterministic assessment

The CAPEX breakdown of all scenarios is presented in Table 4.6. The distillery functioning as the basis for the biorefineries in scenarios P1 to C2 (i.e. scenario BASE2) presents a CAPEX of R\$ 921 million (US\$ 275 million), a reduction of more than 20% from the estimated CAPEX of a season-only distillery (scenario BASE1, R\$ 1,159 million or US\$ 346 million). In view of the year-round operation of the distillery, a reduction in the CAPEX of the unit is expected in comparison to season-only distilleries, since many areas have equipment with reduced sizes, such as fermentation and distillation/dehydration units. However, an increase in the investment with evaporators and large storage tanks is also found because concentrated sugarcane syrup is produced for utilization during the off-season. The total amount of required syrups (over 193 thousand m³) is stored in four large tanks. Besides, scenarios BASE1 and BASE2 present varying amounts of sugarcane LCM burned in the CHP unit during season and off-season to account for an even production of surplus EE to the grid year-round. This results in CHP units with different configurations in terms of boiler capacity and turbine arrangements, which impacts the economic assessment of the biorefineries.

In the microalgae facility, the main fixed investment refers to photoautotrophic reactors, corresponding to around 80% of the investment in scenarios P2 and C2. In spite of being more expensive than covered raceways, the use of flat-panel reactors allows a much leaner downstream process, such as in temperature control systems and microalgae biomass harvest. Lipid extraction and biodiesel production require the same CAPEX in all scenarios since the amount of processed biomass remains unchanged.

Heterotrophic reactors are responsible for 5% of the R\$ 532 million (US\$ 159 million) in scenario C1 and for 3% of the R\$ 753 million (US\$ 225 million) in scenario C2. These figures, as well as other numbers associated to operational costs related to vessels for heterotrophic growth of microalgae, may be further reduced since batch time can be shortened from 30 h to 15 h due to contamination issues regarding *in natura* vinasse (Bastos RG, personal communication, February 2018). Other authors (Silva et al., 2017b) employ even shorter batch times (10 h) for the heterotrophic growth of *Desmodesmus subspicatus* in sugarcane vinasse.

| Parameter | Scenario | | | | | | | |
|-----------------------------------|----------------|--------------|----------------|----------------|----------------|----------------|--|--|
| R\$ million (US\$ million) | BASE1 | BASE2 | P1 | P2 | C1 | C2 | | |
| 1G distillery | 1,159 (346) | 921 (275) | 921 (275) | 921 (275) | 921 (275) | 921 (275) | | |
| Microalgae facility | - | - | 575 (172) | 831 (248) | 532 (159) | 753 (225) | | |
| Cultivation | - | - | 351 (105) | 691 (206) | 327 (98) | 620 (185) | | |
| Temperature control | - | - | 71 (21) | 13 (4) | 61 (18) | 11 (3) | | |
| Harvest | - | - | 61 (18) | 12 (4) | 56 (17) | 15 (4) | | |
| Lipid extraction | - | - | 19 (6) | 19 (6) | 19 (6) | 19 (6) | | |
| Biodiesel production | - | - | 21 (6) | 21 (6) | 21 (6) | 21 (6) | | |
| Other equipment | - | - | 52 (16) | 76 (23) | 48 (14) | 68 (14) | | |
| TOTAL | 1,159 (346) | 921 (275) | 1,496 (447) | 1,753 (523) | 1,453 (434) | 1,675 (500) | | |

Table 4.6 – CAPEX breakdown of assessed scenarios.

Due to the verticalization of the production chain envisaged for the integrated scenarios, the use of microalgae biodiesel in agricultural operations reduces the production costs of both sugarcane stalks and straw. When fossil diesel is used, the calculated production costs of sugarcane stalks and straw are of R\$ 76.08/tonne (US\$ 22.71/tonne) and R\$ 121.37/tonne (US\$ 36.23/tonne), respectively. The local production of microalgae biodiesel in substitution to fossil diesel significantly affects the final cost of sugarcane cultivation, harvesting, and transportation. As a matter of comparison, Table 4.7 shows the reduction in the production cost of sugarcane stalks and straw in integrated scenarios in comparison to base scenarios.

Table 4.7 – Production costs of sugarcane stalks and straw in the assessed scenarios.

| De me en et en | Scen | ario |
|---|----------------|----------------|
| rarameter — | BASE1, BASE2 | P1, P2, C1, C2 |
| Sugarcane stalks - R\$/tonne (US\$/tonne) | 76.08 (22.71) | 65.87 (19.66) |
| Sugarcane straw* - R\$/tonne (US\$/tonne) | 121.37 (36.23) | 100.83 (30.10) |
| | | |

* dry basis

Table 4.8 presents the main components of the OPEX of both base and integrated scenarios.

Table 4.8 – OPEX breakdown of assessed scenarios.

| Parameter | Scenario | | | | | | | |
|------------------------------------|----------|--------|-----------|--------|-----------|-----------|--|--|
| R\$ million/y (US\$ million/y) | BASE1 | BASE2 | P1 | P2 | C1 | C2 | | |
| Sugarcane stalks | 304.3 | 304.3 | 263.5 | 263.5 | 263.5 | 263.5 | | |
| | (90.8) | (90.8) | (78.7) | (78.7) | (78.7) | (78.7) | | |
| Succession a statement | 22.3 | 22.3 | 18.5 | 18.5 | 18.5 | 18.5 | | |
| Sugarcane straw | (6.7) | (6.7) | (5.5) | (5.5) | (5.5) | (5.5) | | |
| Chemicals for successing | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 | | |
| Chemicals for sugarcane processing | (3.6) | (3.6) | (3.6) | (3.6) | (3.6) | (3.6) | | |

Inputs, microalgae facility - R\$ million/y (US\$ million/y)

| Urea and MAP | | 47.8 | 47.8 | 40.8 | 40.8 |
|--|---|--------|--------|--------|--------|
| | - | (14.3) | (14.3) | (12.2) | (12.2) |
| NaOH | | 5.1 | 5.1 | 5.1 | 5.1 |
| | - | (1.5) | (1.5) | (1.5) | (1.5) |
| 4101 | | 3.2 | 0.4 | 2.8 | 0.3 |
| AICI3 - | - | (1.0) | (0.1) | (0.8) | (0.1) |
| HCl and H ₃ PO ₄ | | 0.2 | 0.2 | 0.2 | 0.2 |
| | - | (0.1) | (0.1) | (0.1) | (0.1) |

| Other operational components - R\$ million/y (US\$ million/y) | | | | | | | | |
|---|------|------|------|------|------|--|--|--|
| Maintananaa | 34.8 | 27.6 | 50.6 | 69.2 | 48.9 | | | |

| Maintenance | 34.8 | 27.6 | 50.6 | 69.2 | 48.9 | 65.3 |
|-------------|--------|-------|--------|--------|--------|--------|
| Maintenance | (10.4) | (8.2) | (15.1) | (20.7) | (14.6) | (19.5) |
| Labor | 12.2 | 12.2 | 17.8 | 17.8 | 18.0 | 18.0 |
| | (3.6) | (3.6) | (5.3) | (5.3) | (5.4) | (5.4) |

The amount spent on the purchase of sugarcane and stalks leads to a reduction in the OPEX of integrated scenarios following the values presented in Table 4.7: the abatement amounts to nearly R\$ 42 million/year (US\$ 12.5 million/year). The consumption of fertilizers, the single most important item in the OPEX of such plants, accounts for about the same as the reduction in the production cost of sugarcane yielded by the removal of fossil diesel from sugarcane agricultural operations. On the other hand, the determined value of 0.288 kg fertilizer/kg microalgae tends to be in accordance with other studies, since the literature often reports figures around 0.3 kg fertilizer/kg of microalgae (Davis et al., 2016). In an overview, all integrated sugarcane-microalgae biorefineries are plants of large dimensions with high maintenance costs, leading to a significant yearly expense. The number of employees in each

scenario is presented as follows: 262 in BASE1 and BASE2, 382 in P1 and P2, and 388 in C1 and C2. The estimated workforce allows for three-shift operation.

The main economic results of this assessment are shown in Table 4.9. There is a clear trend of inherently lower economic performances for integrated scenarios due to an increase in both CAPEX and OPEX of the plants. Scenarios P2 and C2 have IRR lower than the MARR of 12%. On the other hand, scenarios P1 and C1 present IRR higher than the MARR, but still lower than the base sugarcane biorefinery. Batan et al. (2016) showed that the commercialization of the extraction debris as a high-protein meal is the best option for the maximization of revenues, while the option of selling this fraction as a co-firing supply leads to lower IRRs. This is additionally supported by the findings of Kern et al. (2017). According to the authors, the use of microalgae biomass for energy production through direct combustion or via an indirect biogas route is only interesting if the microalgae meal price suffers a 90% drop. In either way, Christiansen et al. (2012) have already determined that pioneer microalgae plants for biofuels production represent a risky venture with high uncertainties.

| Parameter | Scenario | | | | | | |
|-------------------------------------|----------|--------|-----------|--------|-----------|--------|--|
| | BASE1 | BASE2 | P1 | P2 | C1 | C2 | |
| IRR | 17.1% | 20.6% | 13.6% | 11.5% | 13.8% | 11.9% | |
| NPV - R\$ million (US\$ million) | 141 | 201 | 53 | -18 | 60 | -4 | |
| | (42) | (60) | (16) | (-5) | (18) | (-1) | |
| NPV/I | 0.41 | 0.73 | 0.12 | -0.03 | 0.14 | -0.01 | |
| Payback (years) | 5 | 4 | 6 | 7 | 6 | 7 | |
| Anhydrous ethanol production cost - | 1.27 | 1.19 | 1.42 | 1.51 | 1.41 | 1.49 | |
| R\$/L (US\$/L) | (0.38) | (0.36) | (0.42) | (0.45) | (0.42) | (0.44) | |
| Biomass | 0.76 | 0.76 | 0.69 | 0.68 | 0.70 | 0.69 | |
| | (0.23) | (0.23) | (0.21) | (0.20) | (0.21) | (0.21) | |
| Sugarcane mill capital cost | 0.38 | 0.30 | 0.27 | 0.27 | 0.28 | 0.27 | |
| | (0.11) | (0.09) | (0.08) | (0.08) | (0.08) | (0.08) | |
| Biorefinery maintenance | 0.08 | 0.06 | 0.11 | 0.14 | 0.10 | 0.14 | |
| | (0.02) | (0.02) | (0.03) | (0.04) | (0.03) | (0.04) | |
| Biorefinery labor | 0.03 | 0.03 | 0.04 | 0.04 | 0.04 | 0.04 | |
| | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | |

Table 4.9 – Main economic results of the assessed biorefineries and breakdown of anhydrous ethanol production cost.

Table 4.9 - Continued

| Parameter | Scenario | | | | | | |
|--------------------------------------|----------|--------|-----------|--------|-----------|--------|--|
| | BASE1 | BASE2 | P1 | P2 | C1 | C2 | |
| Chemicals for sugarcane processing | 0.03 | 0.03 | 0.02 | 0.02 | 0.03 | 0.03 | |
| | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | |
| Microalgae facility capital cost | - | - | 0.17 | 0.24 | 0.16 | 0.22 | |
| | | | (0.05) | (0.07) | (0.05) | (0.07) | |
| Microalgae facility operational cost | - | - | 0.12 | 0.11 | 0.10 | 0.10 | |
| | | | (0.04) | (0.03) | (0.03) | (0.03) | |
| | | | | | | | |
| Biodiesel production cost - | | | 2.17 | 2.31 | 2.16 | 2.28 | |
| R\$/L (US\$/L) | - | - | (0.65) | (0.69) | (0.64) | (0.68) | |
| Biomass | - | - | 1.05 | 1.04 | 1.07 | 1.06 | |
| | | | (0.31) | (0.31) | (0.32) | (0.32) | |
| Sugarcane mill capital cost | - | - | 0.40 | 0.46 | 0.40 | 0.45 | |
| | | | (0.12) | (0.14) | (0.12) | (0.13) | |
| Biorefinery maintenance | - | - | 0.16 | 0.22 | 0.16 | 0.21 | |
| | | | (0.05) | (0.07) | (0.05) | (0.06) | |
| Biorefinery labor | - | - | 0.06 | 0.06 | 0.06 | 0.06 | |
| | | | (0.02) | (0.02) | (0.02) | (0.02) | |
| Chemicals for sugarcane processing | - | - | 0.04 | 0.04 | 0.04 | 0.04 | |
| | | | (0.01) | (0.01) | (0.01) | (0.01) | |
| Microalgae facility capital cost | - | - | 0.28 | 0.32 | 0.27 | 0.31 | |
| | | | (0.08) | (0.10) | (0.08) | (0.09) | |
| Microalgae facility operational cost | - | - | 0.18 | 0.17 | 0.16 | 0.15 | |
| | | | (0.05) | (0.05) | (0.05) | (0.04) | |

For the determination of the production costs of both anhydrous ethanol and biodiesel, a new control volume was defined in this case, as shown in Figure 4.4, in order to have biodiesel as a full output of the integrated biorefinery. Since biodiesel commercialization is only possible in an "open" configuration, i.e. without substitution of fossil diesel by microalgal biodiesel. Up to this point, microalgae biodiesel has been considered as an internal stream of the verticalized venture, being fully used in the agricultural step of the biomass chain (Figure 4.2a). In this particular analysis, the full production costs of sugarcane stalks and straw were considered, since biodiesel is now commercialized instead of replacing diesel in sugarcane production. In relation to the production cost of anhydrous ethanol, a significant increase can be perceived in the integrated scenarios due to both capital and operational costs of the microalgae facility. Still, the determined costs remain between R\$ 1.42/L (US\$ 0.42/L)

and R\$ 1.51/L (US\$ 0.45/L), both lower than the considered selling price of R\$ 1.70/L (US\$ 0.51/L), as shown in Table 4.2. The best economic results among co-located biorefineries were obtained for scenario C1. Regarding microalgal biodiesel, the lowest production cost of R\$ 2.16/L (US\$ 0.64/L) was obtained in scenario C1. Sugarcane stalks and straw correspond to nearly half of the total cost, contributing to R\$ 1.07/L (US\$ 0.32/L). Combining both CAPEX and OPEX, the microalgae facility is responsible for a share of R\$ 0.44/L (US\$ 0.13/L), equivalent to 20% of the total production cost. Biodiesel production costs in all integrated biorefineries stand below the defined selling price of R\$ 2.60/L (Table 4.2). In all cases, the determined costs remain below those found by Brownbridge et al. (2014), of around £ 0.8-1.6/kg (or roughly R\$ 3.34-6.67/L); by Batan et al. (2016), of US\$ 3.46/L (or R\$ 13.40/L) for raw oil in a 38 million-L biofuel plant; or by Nagarajan et al. (2013), which stand between US\$ 1.60-3.72/L or roughly R\$ 5.36-12.46/L.



Figure 4.4 – Considered control volume for the assessment and comparison of both anhydrous ethanol and biodiesel production costs among integrated scenarios (non-verticalized operation).

4.3.3 Economic results: stochastic assessment

Figure 4.5 presents the results of the uncertainty analysis of the biorefineries in terms of IRR.



Figure 4.5 – Risk analysis results for IRR uncertainty of the assessed scenarios.

From the plot, scenarios BASE1 and BASE2 present a similar probability distribution, while co-located biorefineries P1, P2, C1, and C2 also display an analogous shape. Scenarios P1 and C1, specifically, have distributions that significantly overlap that of scenario BASE1. This means that, with the right conditions and tuning of process variables, integrated sugarcane-microalgae biorefineries could compete in economic terms with the current average Brazilian sugarcane mill. In sum, scenarios P1 and C1 have a chance of 73% and 76%, respectively, of presenting an IRR higher than the MARR of 12%. These probabilities decrease to 34% and 41% for scenarios P2 and C2, respectively.

Figure 4.6, on the other hand, presents the tornado plots for scenarios BASE1, P1, and C1. Tornado plots are a representation of the variables with the highest influence on a given response, in which the bars show the variation of the response within the extreme values of the variables.

Ethanol price fluctuations are the single factor that most impacts the IRR of any biorefinery since this product is responsible alone for more than 80% of the total revenue in base scenarios and around 75% for integrated biorefineries. Other two variables with high impact in all cases are the biomass price (both sugarcane stalks and straw) and the microalgae lipid content. The needed area of PBRs for biomass production is directly linked to this last parameter, thus justifying its great influence over the economic feasibility of the biorefinery. Increasing microalgae lipid from 30% to 40% could lead, alone, to IRRs of integrated biorefineries P1 and C1 to over 14%. Scenarios P2 and C2 behavior in a similar manner,

despite the influence of the microalgae plant CAPEX being higher in the risk analysis in view of the high investment required for closed microalgae reactors. Other factors, such as unpredictability in CAPEX estimation, and EE price, contribute to the uncertainty in the IRR to a lesser extent.

The tornado plots help to explain the broader shape of the IRR of base scenarios in comparison to co-located biorefineries: the economic performance of scenarios BASE1 and BASE2 rely much more on sugarcane stalks than either P1, P2, C1, or C2. This behavior arises from the fact that sugarcane biomass responds for a higher share of the OPEX in base scenarios than in the integrated biorefineries since the full biomass price is considered in the first case (Table 4.7).

Brownbridge et al. (2014) found similar probability distributions for the return on investment of microalgae plants. However, the authors determined that lipid content (also with a variation between 20% and 40% of the algal biomass) was the single most important factor affecting this response. In their work, the microalgae plant CAPEX played a smaller role, possibly in view of the also lower variation range ($\pm 10\%$) in comparison to this study.



Figure 4.6 – Tornado plots for IRR uncertainty analysis for scenarios (a) BASE1, (b) P1, and (c) C1.

The uncertainty analysis also affects the production costs of both anhydrous ethanol and biodiesel, as shown in Figures 4.7a and 4.7b, respectively. The results match those presented in Table 4.9 and follow the general behavior of the curves in Figure 4.5. Integrated biorefineries present a significant mutual overlap of possible anhydrous ethanol and biodiesel costs; on the other hand, scenarios P1 and C1 may appear as competitive alternatives in comparison to scenario BASE1.



Figure 4.7 – Risk analysis results for the production costs of (a) anhydrous ethanol and (b) biodiesel of the assessed scenarios.

4.3.4 Environmental results: deterministic assessment

The main results concerning the environmental assessment of the biorefineries in question are presented in Figure 4.8a. For a direct comparison between anhydrous ethanol and those of gasoline type A, the impact associated to the use phase of anhydrous ethanol (equivalent to roughly 1 g CO₂eq/MJ) is added to the impacts calculated for the production phase, as briefly mentioned in Section 4.2.4.



Figure 4.8 – Environmental impacts of anhydrous ethanol production: (a) assessed impact categories and (b) breakdown of GHG emissions.

The global warming potential of anhydrous ethanol produced in scenarios BASE1 and BASE2 are virtually the same, at 20.6 and 20.7 g CO₂eq/MJ, respectively. This represents a reduction of around 75% in comparison to fossil gasoline, which has a climate change impact of 83.7 g CO_2eq/MJ . When considering integrated biorefineries, the annexing of a microalgae facility helps to further improve the sustainability of anhydrous ethanol: in comparison to base scenarios, reductions in the order of 15% are obtained for scenarios P1 and C1 (with covered raceways) and of 17% for scenarios P2 and C2 (with flat-panel PBRs). This level of around 17 g CO₂eq/MJ of anhydrous ethanol is comparable to the current stage of 2G ethanol production from sugarcane biomass (Junqueira et al., 2017). It can be concluded, therefore, that the environmental benefits from the complete removal of diesel from sugarcane agricultural operations outperform those from the inclusion of conventional N and P fertilizers for microalgae biomass production. In all cases, Figure 4.8b presents a breakdown of climate change impacts of anhydrous ethanol production in all biorefineries. Sugarcane production (cultivation, harvest, and transport) accounts for most of the impact in all scenarios. In co-located biorefineries, a small component related to the cultivation and processing of microalgae appears, mainly due to the use of urea and MAP as fertilizer for algal growth. In sum, all scenarios showed a reduction of over 75% in GHG emissions compared to the fossil baseline, hence being classified as advanced biofuels according to the Renewable Fuel Standard of the United States Environmental Protection Agency (EPA, 2010).

Figure 4.8a also presents the impacts of biorefining in four other categories. Since all biorefineries employ fertilizers for the production of either sugarcane or microalgae, it is natural that the local impact from the buildup of N and P is higher in bioenergy systems than in fossil-based ones. The impacts in scenario P1 are the largest in view of the high consumption of fertilizers (equal to that of P2), but with a higher blowdown of spent culture medium than any other integrated biorefinery.

The agricultural land occupation of fossil gasoline is virtually equal to zero, whereas that of biorefineries is significant in view of the nature of the operation of biomass systems.

Concerning water depletion, the highest impacts can be observed for scenarios P1 and C1, in which covered raceways are employed for producing the totality or the majority of microalgal biomass. The impact is significantly lower in scenarios with closed PBRs (P2 and C2), being only from 14% to 18% higher than that of base scenarios.

Finally, the fossil depletion impact of gasoline type A is from 12 to 16 times higher than in sugarcane biorefineries. However, the use of fossil resources in integrated biorefineries is nonzero even with the removal of the direct use of conventional diesel in sugarcane machinery, mainly because fossil resources are indirectly used in the production of fertilizers and several other process inputs.

Another interesting assessment that can be carried out is comparing two biorefinery configurations among a single scenario: verticalized and non-verticalized industrial production with the agricultural phase (as in Figures 4.2a and 4.4, respectively). The main results are shown in Figure 4.9. The comparative behavior of all scenarios is similar: lower climate change and fossil depletion impacts in verticalized biorefineries. This arises mainly from the lower utilization of conventional diesel in sugarcane operations (and regardless of the higher allocation of impacts to anhydrous ethanol due to a larger participation in the revenues).



Figure 4.9 – Comparative environmental impacts of anhydrous ethanol production in verticalized and non-verticalized biorefineries.
4.3.5 Environmental results: stochastic assessment

The risk analysis for climate change impacts of the biorefineries in question is presented in Figure 4.10.



Figure 4.10 - Risk analysis results for the climate change impacts of anhydrous ethanol production of the assessed scenarios.

From the plot, scenarios BASE1 and BASE 2 follow the same pattern, as well as scenarios P1 and C1 (covered raceways) and P2 and C2 (closed PBRs) present nearly-confounded behaviors. Despite a better environmental performance of scenarios P2 and C2 in the deterministic assessment (Figure 4.8), the uncertainty assessment carried out shows that their probability curves overlap significantly with those of scenarios P1 and C1.

As for the economic assessment, a variation on impacts of sugarcane biomass production is largely influential on the result of the risk analysis, as attested by the tornado plots in Figure 4.11. The prices of the main products (anhydrous ethanol and EE) are also essential in the determination of GHG emissions of anhydrous ethanol through influencing the economic allocation of all scenarios. Microalgae-related parameters play a smaller role in defining the climate change impacts of all integrated sugarcane-microalgae biorefineries.



Figure 4.11 – Tornado plots for climate change impact uncertainty in scenarios (a) BASE1, (b) P1, and (c) C1.

4.4 Preliminary conclusions

This Chapter presented the techno-economic and environmental performances of integrated sugarcane-microalgae biorefineries benchmarked against standalone ethanol distilleries. Industrial microalgae cultivations often require high fixed investments, as well as massive inputs at high costs. The integration with sugarcane biorefineries helps in reducing those expenses while profiting from an overall reduction in environmental impacts. Scenario C1, in which both vinasse and fermentation-derived CO_2 are used as carbon sources for the production of microalgal biomass through different metabolic regimes, presented the best economic results among the integrated biorefineries assessed in Chapter 4 and equivalent environmental impacts.

The fine-tuning and optimization of the conditions involved in microalgae cultivation may lead to improved economic and environmental impacts associated with the processing of sugarcane into anhydrous ethanol and several other coproducts. The ultimate intention of assessments of such type is to better understand the current development level of existing technologies for microalgae production and to help in setting efficiency goals for applied researchers to achieve in experimental setups.

CHAPTER 5

MICROALGAE PRODUCTION IN NEXT-GENERATION INTEGRATED SUGARCANE BIOREFINERIES: BIOGAS-DERIVED CO₂ AS AN ADDITIONAL CARBON SOURCE FOR ALGAL GROWTH

5.1 Introduction

In addition to conventional CO₂ streams for microalgae growth such as boiler emissions and fermentation off-gas in sugarcane mills, another important carbon source may also be considered: biogas. This alternative biofuel has been gaining attention in modern sugarcane biorefineries for a simple reason: increasing revenues through the processing of waste streams into an important final product. The produced biogas can be purified (or upgraded) through desulphurization and CO₂ removal for the production of a stream with high CH₄ content (over 96.5% v/v), named biomethane. In sugarcane mills, the most straightforward option for obtaining biomethane is through the AD of vinasse. As presented in Section 3.5.2, vinasse remains a largely untapped source of carbon, which could be employed for both the cultivation of microalgae and the production of biogas/biomethane. In fact, both processes could be combined for the indirect upgrading of biogas: CO₂ contained in the biogas stream could be retained in the culture medium when passed in bubble columns, while microalgae could promote carbon uptake through photosynthesis. Table 5.1 presents a handful of studies with this possibility. Biogas upgrading with microalgae benefits from the advantage that several microalgae species have their growth kinetics practically unaffected by high concentrations of CH₄ in biogas (Meier et al., 2015). In last analysis, the biogas stream can be one promising link to establish pilot sugarcane-microalgae biorefineries, acting both as a material vector (CO₂) and an energy vector (CH₄ for power generation either in stationary equipment or in the vehicle fleet using Diesel engines).

In spite of the vast number of experimental studies attesting the technical feasibility of biogas upgrading through photoautotrophic microalgae cultivation and the possibility of establishing a co-located biorefinery of such type (Chen et al., 2018a), there is a lack of works in the scientific literature dealing with the technological assessment of such facilities in largescale plants. In this way, the present Chapter aims at pointing the path towards the deployment of integrated sugarcane-microalgae biorefineries in a practical way, as well as identifying process bottlenecks and technical difficulties. Thus, the utilization of microalgae cultivations for vinasse-derived biogas upgrading through CO₂ removal in different scenarios is assessed in terms of both economic and environmental impacts and compared to conventional biomethane production. The developed study was entirely carried out with mathematical modeling and computer simulation of the involved processes - sugarcane processing, AD of vinasse, and microalgae production. A true concept of biorefinery was established: apart from conventional sugarcane products, other compounds, such as microalgae meal and biodiesel, were also obtained and assessed in the analyses. Finally, the effects of several process parameters on the economic and environmental performances of the plants were also determined.

| CO ₂ removal from biogas | CH4 fraction in purified biogas (v/v) | Observations | Reference |
|-------------------------------------|---|--|-------------------------|
| 75-85% | 92.6% | Cultivation with the liquid fraction (digestate), 85% COD removal, 73% N and P removal, light- emitting diode (LED) lighting | Yan et al. (2014) |
| 80-100% | - | Cultivation with the liquid fraction (digested vinasse), 100% H ₂ S removal | Serejo et al. (2015) |
| 50-62% | 78-82% | Cultivation with the liquid fraction (digestate), 40-60% N and P removal, LED lighting | Zhao et al. (2015) |
| 95% | _ | O ₂ desorption in the PBR, CO ₂ absorption in the external column (indirect upgrading) | Meier et al. (2015) |

Table 5.1 – Selected studies concerning biogas upgrading with microalgae cultivations.

5.2 Material and methods

5.2.1 Process description

5.2.1.1 Sugarcane processing in ethanol distilleries

The main operations involved in sugarcane processing into anhydrous ethanol and EE are briefly discussed in Section 4.2.1.1. Further information on sugarcane conversion into finished products in Brazilian biorefineries can be found in Morais et al. (2016).

5.2.1.2 AD of vinasse, biogas purification, and liquid fertilizer production

Biogas is primarily produced through AD of vinasse in UASB reactors, considering parameters shown in Annex A.3 (Table A.3.1). NaHCO₃ is used in the proportion of 6 kg per m^3 of vinasse for pH adjustment purposes (Fuess, 2017). For this, NaOH is purchased and reacted with CO₂ issued from fermentation vessels for NaHCO₃ synthesis. Biogas produced in

AD reactors is considered to be composed of 76% CH₄, 23% CO₂, and 1% H₂S (v/v), and is dubbed raw biogas. Biogas storage in tanks requires the removal of H₂S in view of its corrosive potential (Ryckebosch et al., 2011). Therefore, sulfur removal in all scenarios is performed with a biological system (micro-aeration), 24 h per day, prior to storage in spherical tanks or sent to upgrading. The upgraded biogas (or biomethane) consists of biogas with high methane content (at least 96.5% v/v). There are several different established possibilities of biogas upgrading alternatives (Muñoz et al., 2015); in the present Chapter, this was performed either with a PSA unit or with microalgae cultivations. Biomethane produced after upgrading with microalgae cultivations is considered to have low O₂ and N₂ contents, an issue found in some experimental setups using raceways coupled with bubble columns (Meier et al., 2015; Putt et al., 2011; Serejo et al., 2015). H₂S content is negligible in both clean biogas and biomethane. Other parameters of biogas production and upgrading can be found in Annex A.3 (Table A.3.1).

A liquid, concentrated fertilizer can also be obtained from digested vinasse. For this, the digestate leaving AD reactors is concentrated in a multiple-effect evaporator by a factor of around 17. Afterwards, NH₃ is added to the concentrated digested vinasse in order to adjust the N:K₂O ratio required for sugarcane growth. The pH of the mixture is corrected by adding H₂SO₄. The final fertilizer, obtained in the liquid form with 25 % of solids (m/m), presents significantly improved transport properties over conventional, highly-diluted vinasse, and therefore can reach greater distances in the field. However, the use of N-based fertilizer in the fluid form leads to higher indirect emissions of N₂O (high global warming potential) in the field and lixiviation in the form of NO₃⁻ in comparison to conventional, solid NPK fertilizers.

5.2.1.3 Microalgae cultivation with biogas and downstream processing

Biodiesel production from microalgae is achieved through a series of steps, namely: microalgae cultivation, microalgae harvest, lipids extraction, and transesterification. The processes are described in Section 4.2.1.2 and the main associated parameters are presented in Annex A.2.

5.2.1.3.1 Photoautotrophic growth

The natural light-dark cycle of sunlight is often overlooked when estimates are made on the industrial potential of a given microalgae process or during the design of large-scale photoautotrophic microalgae units. When using microalgae cultivations as an upgrading solution, and such is the case in biogas purification through the photosynthetic removal of CO₂ with microalgae, process designers must take into account the photoperiod and still make sure that this technological option is able to handle all of the raw material in the same way as the replaced conventional technology. The capability of a PBR to efficiently upgrade biogas through the uptake of CO₂ is highly dependent on the photosynthetic activity of the microalgae cultivation (Muñoz et al., 2015). Therefore, three main approaches can be pictured: (1) supplying artificial light to all of the cultivation extension during night hours, as performed by Bahr et al. (2014) and Serejo et al. (2015); (2) storing biogas overnight for simultaneous upgrading during daylight hours of both stored and daytime-produced biogas; or (3) biogas upgrading during daylight hours and combustion of biogas during night hours. Although the first option may be picked in some special, low-to-medium scale processes (such as in the production of high value-added chemical specialties from microalgal biomass), large-scale deployment of artificial lighting consumes high amounts of EE and demands a relatively high capital investment. In this study, only alternative (2) was considered for scenario design. As stated in Section 5.1, in spite of microalgae being able to remove 100% of the H₂S contained in raw biogas (Serejo et al., 2015), H₂S is previously removed in separate biological reactors. In this way, microalgae cultivations are considered to be fed with biogas containing only CH₄ and CO₂. A schematic drawing of the upgrading system is shown in Figure 5.1.



Figure 5.1 – Simplified configuration of an indirect biogas upgrading system by microalgae. In this system, CO_2 is absorbed by the culture medium in a bubble column, yielding upgraded biogas (biomethane). The culture medium rich in carbonates is sent to the PBRs, where the carbon is consumed by microalgae (adapted from Xia et al., 2015).

When employing fermentation CO₂, microalgae growth was carried out with the broad considerations of Section 4.2.1.2.1.

5.2.1.3.2 Heterotrophic growth with vinasse

Since the AD step significantly reduces the amount of available carbon in vinasse, the heterotrophic growth of microalgae with digested vinasse was not taken into account. However, the use of *in natura* vinasse for microalgae biomass production is described in Section 4.2.1.2.2.

5.2.1.3.3 Harvest, lipid extraction, and biodiesel production

After biomass production, the harvest, lipid extraction, and biodiesel production steps follows the description in Sections 4.2.1.2.3, 4.2.1.2.4, and 4.2.1.2.5, respectively.

5.2.2 Process simulation

The analyses were carried out utilizing the VSB framework (Junqueira et al., 2016). The framework was adapted to model and simulate sugarcane biorefineries with and without AD of vinasse, microalgae production systems, and sugarcane agricultural operations. All systems operate in steady-state.

5.2.2.1 Base scenarios

The base scenarios BASE1 and BASE2 described in Section 4.2.2.1 and shown in Figure 4.1 were also employed as a comparison basis in this Chapter. The ethanol distillery of scenario BASE2 was designed to provide constant outputs of anhydrous ethanol and EE from the CHP unit for 330 days, spanning both sugarcane harvest season (200 days) and off-season (130 days), through the storage of inverted sugarcane syrup and LCM for ethanol fermentation and firing of the CHP unit during off-season, respectively. A third base scenario (including AD of vinasse), named BASE3, was created to assess the purification of biogas and production of biomethane through conventional methods - in this case, with a PSA column for CO₂ removal. Figure 5.2 shows a simple process flow diagram of this biorefinery configuration. Since best economic and environmental results come from the utilization of biomethane as a substitute for diesel in sugarcane agricultural operations (Moraes et al., 2016), this option was prioritized in all scenarios (in detriment to the generation of EE or injection in the natural gas grid, for example). Therefore, biomethane is utilized to replace fossil diesel up to a limit of 70% so that the engines remain operating in the Diesel cycle. Several authors (Fletcher, 2008; Ray et al., 2013) indicate that diesel substitution with biomethane in the range of 70-85% tends to be optimum, so engine operation remains unchanged. Higher substitution levels would alter the thermodynamic cycle from Diesel to Otto and lead to substantial investment in revamping the vehicle (addition of spark plugs).



Figure 5.2 – Process flow diagram for base scenario BASE3.

Scenario BASE3 was considered as the basis for the establishment of integrated sugarcane-microalgae biorefineries, further described in Section 5.2.2.2. This operational strategy was primarily chosen to supply a constant flow of vinasse to AD reactors and, consequently, of biogas to microalgae cultivations, once both microorganism cultures should be kept operating throughout most part of the year due to the impracticality of process start-up in short periods of time. Besides, this type of configuration provides constant supplies of vinasse, fermentation-derived CO₂, and anhydrous ethanol for microalgae cultivation and processing.

In scenario BASE3, 77% of the vinasse flow is directed to AD reactors; with the considered COD removal efficiency and the specific biogas production rate, this is the amount of vinasse required to supply biomethane for the substitution of 70% of the diesel consumed in sugarcane agricultural operations. The remaining 23% of *in natura* vinasse are combined with the digested vinasse issued from AD reactors and sent to the field in a process called fertirrigation. The main nutrient in vinasse, potassium, passes through the AD step practically unaffected, thus maintaining its fertilization power in fertirrigation of sugarcane crops.

5.2.2.2 Integrated sugarcane-microalgae scenarios

Four different scenarios were designed through a combination of the processes described in Sections 4.2.1 and 5.2.1. Figure 5.3a depicts the integration strategy between a sugarcane mill with AD of vinasse and an industrial microalgae facility. Again, in this Chapter, all scenarios have been designed in order to close the loop in terms of CO₂ emissions and diesel substitution in sugarcane agricultural operations - a verticalized biorefinery. Besides EE, process steam, and anhydrous ethanol for microalgae biomass production and processing, the distillery also supplies carbon for microalgae growth in three different sources: CO₂ contained in biogas, fermentation-derived CO₂, and vinasse. Two outputs of the biorefinery, namely biomethane and biodiesel, are employed to displace diesel in the agricultural production of sugarcane stalks and straw. Biomethane produced this way replaces 70% of the agricultural diesel, while microalgae biodiesel is responsible to substitute the remaining 30%.

Figure 5.3b illustrates the main operations for the production of microalgae biodiesel in the integrated biorefineries. Since the best economic results in Chapter 4 were obtained with the combination of photoautotrophic and heterotrophic growth of microalgae, this arrangement was chosen for all scenarios, from B1 to B4. Scenarios B1 and B2 employ covered raceways for the photoautotrophic growth of microalgae, while this is performed with flat-panel PBRs in scenarios B3 and B4. As stated in the previous section, vinasse is split as follows: 77% to AD reactors for biogas production and 23% to closed vessels for the heterotrophic growth of microalgae. Biogas produced during nighttime is stored in spherical tanks for it to be upgraded during daytime with microalgae cultivations. Besides, the mere existence of spherical tanks for biogas storage improves the overall operation security of the integrated plant since they are able to absorb operational variations, such as biogas production peaks or temporary shutdown of microalgae reactors. The scenarios are briefly summed up in Chart 5.1.



Figure 5.3 – Process flow diagrams of integrated sugarcane-microalgae biorefineries with AD of vinasse. (a) Integration strategy between a sugarcane mill and a microalgae facility, with biodiesel and biomethane used for the substitution of diesel in sugarcane agricultural operations (verticalized operation). (b) Layout of the microalgae facility in scenarios B1 to B4. EE not shown as an input for microalgae production since all steps shown require electricity to operate.

| Integrated scenarios | Without extra biodiesel | With extra biodiesel |
|----------------------|-------------------------|----------------------|
| Covered raceway | B1 | B2 |
| Closed PBR | B3 | B4 |

Chart 5.1 – Configuration overview of integrated scenarios with AD of vinasse.

In scenarios B1 and B3, the size of the microalgae plant is designed so as to provide exactly the amount of biodiesel to substitute the remaining 30% fossil diesel not displaced by biomethane. In these cases, part of the photoautotrophic reactors operates with the strategy shown in Figure 4.1 (with bubble columns for biogas upgrading), while other reactors use fermentation CO_2 . The amount of fermentation-derived CO_2 diverted to microalgae cultivations is calculated so scenarios B1 and B3 are able to produce around 5.1 million L of biodiesel/year. On the other hand, scenarios B2 and B4 were conceived to seize the full potential of CO_2 from ethanol fermentation: all of the CO_2 producing during daytime is employed in the cultivations, as well as the CO_2 contained in biogas. Here, the biorefineries are able to commercialize a significant amount of microalgae biodiesel to the market, besides anhydrous ethanol, EE, glycerin, and microalgae meal.

Among the four assessed scenarios, the one with the best economic performance was chosen for the inclusion of vinasse concentration and processing into a liquid fertilizer for sugarcane in the integrated biorefinery. Further details on the case study and its full techno-economic assessment are provided in Section 4.3.4.

5.2.3 Techno-economic and environmental assessments

The methodologies employed in the techno-economic and environmental assessments of scenarios BASE3, B1, B2, B3, and B4 are presented in Sections 4.2.3 and 4.2.4, respectively. The results obtained for scenarios BASE1 and BASE2 in Chapter 4 are often revisited in this Chapter for benchmarking purposes.

An additional variable was added for the uncertainty analyses of economic and environmental impacts of biorefineries employing AD of vinasse: use of NaOH for pH adjustment in digesters. A variation from 0% to 120% of the base value was considered, meaning either the dismissal for pH adjustment or the use of 20% more NaOH than that determined experimentally (Fuess, 2017). NaOH accounts for a significant share of the OPEX of the AD step and presents high climate change emission factors, so the minimization of its use is important in all possible ways.

5.3 Results and discussion

5.3.1 Technical results

The main technical results for base scenarios and integrated biorefineries are presented in Table 5.2. Among the three base scenarios, BASE1 and BASE2 are the same as those presented in Chapter 4.

Scenario BASE3 and all integrated sugarcane-microalgae biorefineries produce equal amounts of biogas (15.9 million Nm³/year), consuming large quantities of NaOH for the correction of vinasse pH prior to digestion in reactors. The totality of the biomethane (12.6 million Nm³/year) is used in the production of sugarcane stalks and straw. As detailed in Section 5.2.2.2, scenarios B2 and B4 produce much more microalgae biomass than scenarios B1 and B3, respectively, thus requiring higher amounts of inputs in an overall analysis: fermentation CO₂, process steam, anhydrous ethanol, fertilizers, and other chemicals. As a result, the volume of biodiesel sold in the market reaches 17.3 and 17.5 million L/year in scenarios B2 and B4, respectively. Additionally, the same scenarios are also able to commercialize more microalgae meal and glycerin.

Table 5.2 - Main inputs and outputs of base scenarios and integrated biorefineries.

| | Scenario | | | | | | | |
|---|----------|-------|-------|-----------|----------|-------|----------|--|
| Parameter | BASE1 | BASE2 | BASE3 | B1 | B2 | B3 | B4 | |
| Main inputs - Sugarcane processing | | | | | | | | |
| Sugarcane stalks (MTC/y) | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | 4.00 | |
| Sugarcane straw (thousand tonnes/y) | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | |
| NaOH for AD of vinasse (thousand tonnes/y) | - | - | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | |
| Inputs from sugarcane mill - Microalgae production | | | | | | | | |
| Fermentation CO ₂ (thousand tonnes/y) | - | - | - | 44 | 266 | 41 | 266 | |
| Vinasse (thousand m ³ /y) | - | - | - | 637 | 637 | 637 | 637 | |
| Biogas (million Nm ³ /y) | - | - | - | 16 | 16 | 16 | 16 | |
| Process steam (thousand tonnes/y) | - | - | - | 6.5 | 34 | 6.5 | 34 | |
| Anhydrous ethanol (million L/y) | - | - | - | 1.1 | 4.7 | 1.1 | 4.8 | |
| Electric energy (GWh/y) | - | - | - | 61 | 269 | 62 | 206 | |
| External inputs - Microalgae production | | | | | | | | |
| Urea and MAP (thousand tonnes/y) | - | - | - | 3.9 | 18.7 | 3.9 | 18.9 | |
| AlCl ₃ (thousand tonnes/y) | - | - | - | 0.3 | 1.6 | 0.04 | 0.2 | |
| NaOH (thousand tonnes/y) | _ | - | - | 1.0 | 4.6 | 1.0 | 4.7 | |
| HCl and H ₃ PO ₄ (thousand tonnes/y) | - | - | - | 0.07 | 0.33 | 0.07 | 0.33 | |
| Outputs | | | | | | | | |
| Anhydrous ethanol (million L/y) | 347 | 347 | 347 | 346 | 342 | 346 | 342 | |
| Electric energy to grid (GWh/y) | 742 | 708 | 704 | 643 | 436 | 643 | 499 | |
| Biodiesel to sugarcane operations/to market (million L/y) | - | - | - | 5.1/0 | 5.1/17.3 | 5.1/0 | 5.1/17.5 | |
| Biomethane to sugarcane operations (million Nm ³ /y) | _ | - | 13 | 13 | 13 | 13 | 13 | |
| Microalgae meal (thousand tonnes/y) | - | - | - | 13 | 58 | 13 | 59 | |
| Glycerin (thousand tonnes/y) | - | _ | - | 0.6 | 2.4 | 0.6 | 2.5 | |

Table 5.3 presents further information on the size of the microalgae plants in the integrated biorefineries. Scenarios B2 and B4 have their reactor area increased by almost fivefold in comparison to scenarios B1 and B3, respectively. If the 1000+ ha of microalgae reactors were disposed evenly around the sugarcane mill, this would be equivalent to a circle with a radius of over 1.8 km, which gives a glimpse into the size of such structures.

Since all scenarios consume roughly one quarter of the total vinasse issued from ethanol recovery columns, relatively small closed vessels are employed. In this way, seven reactors with a working volume of 650 m³ each were employed. The amount of microalgae biomass coming from heterotrophic reactors is the same in all integrated scenarios, although the proportion is higher in scenarios B1 and B3 due to a smaller production in photoautotrophic reactors than in scenarios B2 and B4. Still, all scenarios in this Chapter consume four times as less vinasse as in scenarios C1 and C2 (Chapter 4) for microalgae growth.

| Devenuetor | Scenario | | | | | |
|---|-----------|---------------|-----------|------------|--|--|
| rarameter | B1 | B2 | B3 | B4 | | |
| Required reactor area (ha) | 224.7 | 1072.4 | 223.8 | 1081.9 | | |
| Photoautotrophic area (ha) | 224.5 | 1072.2 | 223.6 | 1081.6 | | |
| Heterotrophic area (ha) | 0.2 | 0.2 | 0.2 | 0.2 | | |
| Microalgae from photoautotrophic reactors | 87% | 97% | 87% | 97% | | |
| Microalgae from heterotrophic reactors | 13% | 3% | 13% | 3% | | |
| % of PBRs with biogas-derived CO ₂ | 26% | 5% | 27% | 5% | | |
| % of PBRs with fermentation-derived CO ₂ | 74% | 95% | 73% | 95% | | |
| CO ₂ consumption | | | | | | |
| Photoautotrophic reactors (thousand tonnes/y; % of biogas CO ₂) | 14; 100% | 14; 100% | 14; 100% | 14; 100% | | |
| Photoautotrophic reactors (thousand tonnes/y; % of fermentation CO ₂) | 41; 7.7% | 263; 49.5% | 38; 7.2% | 263; 49.5% | | |
| Inoculum for heterotrophic reactors (thousand tonnes/y; % of fermentation CO ₂) | 3; 0.5% | 3; 0.5% | 3; 0.5% | 3; 0.5% | | |

Table 5.3 – Required reactor area for integrated microalgae biorefineries and estimated CO_2 consumption from the sugarcane mill.

Figure 5.4 shows the breakdown of EE consumption in microalgae plants of scenarios B1 to B4. An analogous reasoning to that presented in Section 4.3.1 can be employed in order to explain the total figures and the distribution per processing step. Scenario B2 stands out (negatively) in terms of energy consumption for temperature control in view of the large area covered with raceways, while both scenarios with flat-panel PBRs (B3 and B4) present very small EE requirements towards this end. All scenarios consume, proportionally, the same amount of EE for harvest through sedimentation and centrifugation.



Figure 5.4 – Breakdown of EE consumption for microalgae production and processing in the integrated biorefineries. Values shown on top of the bars refer to the total EE consumption in GWh/y.

5.3.2 Economic results: deterministic assessment

The breakdown of CAPEX of both base and integrated scenarios is presented in Table 5.4. Scenario BASE3 requires a fixed investment of R\$ 957 million (US\$ 286 million) corresponding to that of the distillery of scenario BASE2 with the addition of R\$ 22 million (US\$ 7 million) for the AD of vinasse and H₂S removal from biogas, as well as R\$ 13 million (US\$ 4 million) for biogas upgrading using PSA columns. The base investment for scenarios B1 to B4 represents R\$ 943 million (US\$ 281 million), which corresponds to the CAPEX of scenario BASE3 with the exclusion of the PSA upgrading system.

As in Chapter 4, the main investment in the microalgae plant refers to photoautotrophic reactors: 60% of the CAPEX in scenario B1 (covered raceways) and 83% in

scenario B4 (flat-panel PBRs). From the total amount, around R\$ 44 million (US\$ 13 million) in all scenarios are dedicated to the purchase of bubble columns for biogas upgrading with microalgae cultivations. Temperature control systems are significantly more expensive in scenarios B1 and B2 than in scenarios B3 and B4 due to the larger volumes of microalgae suspension processed in the first than in the latter.

| Parameter | Scenario | | | | | | |
|-----------------------------------|--------------------|-------|-------|-----------|-----------|-----------|-----------|
| R\$ million (US\$ million) | BASE1 | BASE2 | BASE3 | B1 | B2 | B3 | B4 |
| 1C distillant | 1,159 | 921 | 957 | 943 | 943 | 943 | 943 |
| 1G distillery | (346) | (275) | (286) | (281) | (281) | (281) | (281) |
| Mianalgaa fasility | | | | 233 | 793 | 296 | 1,133 |
| Microalgae facility | (70) | (237) | (88) | (338) | | | |
| Cultivation | | | | 149 | 507 | 238 | 952 |
| Cultivation | Cultivation | (44) | (151) | (71) | (284) | | |
| Tome out on out of | emperature control | 22 | 90 | 3 | 14 | | |
| Temperature control | | - | (7) | (27) | (1) | (4) | |
| Howcoot | | | | 17 | 77 | 5 | 16 |
| Harvest | - | - | - | (5) | (23) | (1) | (5) |
| I inid automation | | | | 6 | 25 | 6 | 25 |
| | - | - | - | (2) | (7) | (2) | (7) |
| Diadianal and dustion | | | | 17 | 22 | 17 | 22 |
| Biodiesel production | - | - | - | (5) | (7) | (5) | (7) |
| Other equipment | | | | 21 | 72 | 27 | 103 |
| Other equipment | - | - | - | (6) | (21) | (8) | (31) |
| ΤΟΤΑΙ | 1,159 | 921 | 957 | 1,176 | 1,736 | 1,239 | 2,076 |
| IUIAL | (346) | (275) | (286) | (351) | (518) | (370) | (620) |

Table 5.4 – CAPEX breakdwn of assessed scenarios.

As previously mentioned, the verticalization of the sugarcane step with the industrial facility reduces the production costs of both sugarcane stalks and straw. Table 5.5 presents the production costs for three categories of scenarios. Scenarios BASE1 and BASE2, which rely exclusively on fossil diesel for agricultural operations, present the full production costs of R\$ 76.08/tonne (US\$ 22.71/tonne) and R\$ 121.37/tonne (US\$ 36.23/tonne) for sugarcane stalks and straw, respectively. When biomethane replaces 70% of the diesel, such as in scenario BASE3, the production costs are reduced to R\$ 69.91/tonne of stalks (US\$ 20.87/tonne of stalks) and R\$ 111.99/tonne of straw (US\$ 33.43/tonne of straw),

respectively. Finally, in those scenarios with an annexed microalgae plant (B1 to B4), the final costs are of R\$ 66.35/tonne of stalks (US\$ 19.81/tonne of stalks) and R\$ 105.82/tonne of straw (US\$ 31.59/tonne of straw). These values are slightly higher than those presented in Table 4.7 for scenarios P1, P2, C1, and C2 as a reflex of minor modifications that Diesel engines must undergo in order to properly use biomethane as a fuel.

| Deveryster | | Scenarios | |
|--|--------------|-----------|-----------------------|
| Farameter | BASE1, BASE2 | BASE3 | B1, B2, B3, B4 |
| Succession a staller D¢/tampa (LIS¢/tampa) | 76.08 | 69.91 | 66.35 |
| Sugarcane stalks - R\$/tonne (US\$/tonne) | (22.71) | (20.87) | (19.81) |
| S | 121.37 | 111.99 | 105.82 |
| Sugarcane straw* - K\$/tonne (US\$/tonne) | (36.23) | (33.43) | (31.59) |
| * dry basis | | | |

Table 5.5 – Production costs of sugarcane stalks and straw in the assessed scenarios.

* dry basis

Table 5.6 provides a breakdown of the OPEX of all scenarios under scrutiny in this Chapter. Expenses with sugarcane and stalks are decreased in integrated scenarios following the values presented in Table 5.5. The reduction totals R\$ 25 million/year (US\$ 7 million/year) in scenario BASE3 and R\$ 39 million/year (US\$ 12 million/year) in the integrated biorefineries (in comparison to base scenarios BASE1 and BASE2). Scenarios with high microalgae biomass production (B2 and B4) spend more than R\$ 60 million/year with fertilizers alone, which more than outweighs the economy provided by the reduction in sugarcane production costs. In an overview, scenarios B1 and B3 present OPEX equivalent to those of BASE1 and BASE2 (around R\$ 380 million/year or US\$ 113 million/year), while scenarios B2 and B4 have a total OPEX at least R\$ 80 million/year (US\$ 24 million/year) higher than the considered base scenarios. The economics of microalgae cultivation may be improved with the use of wastewaters for the substitution of conventional fertilizers, even digestates from the AD itself (Zhu et al., 2016), or benefit from a reduction in the amount of fertilizer consumed.

| Parameter | Scenario | | | | | | | |
|--------------------------------|----------|--------|--------|--------|-----------|-----------|-----------|--|
| R\$ million/y (US\$ million/y) | BASE1 | BASE2 | BASE3 | B1 | B2 | B3 | B4 | |
| Sugaraana stallas | 304.3 | 304.3 | 279.7 | 265.4 | 265.4 | 265.4 | 265.4 | |
| Sugarcane starks | (90.8) | (90.8) | (83.5) | (79.2) | (79.2) | (79.2) | (79.2) | |
| Successon a stress | 22.3 | 22.3 | 20.5 | 19.4 | 19.4 | 19.4 | 19.4 | |
| Sugarcane straw | (6.7) | (6.7) | (6.1) | (5.8) | (5.8) | (5.8) | (5.8) | |
| NoOH for AD of vineses | | - | 8.9 | 8.9 | 8.9 | 8.9 | 8.9 | |
| NaOH IOI AD OI VIIIasse | - | | (2.7) | (2.7) | (2.7) | (2.7) | (2.7) | |
| Chemicals for sugarcane | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 | 11.9 | |
| processing | (3.6) | (3.6) | (3.6) | (3.6) | (3.6) | (3.6) | (3.6) | |

Table 5.6 – OPEX breakdown of assessed scenarios.

| Inputs, microalgae facility - R\$ million | /y | (US\$ | million/y) |
|---|----|-------|------------|
|---|----|-------|------------|

| Urea and MAP - | - | - | 12.7 (3.8) | 61.4 (18.3) | 12.7 (3.8) | 62.1 (18.5) |
|----------------------------------|---|---|----------------|----------------|----------------|----------------|
| NaOH - | _ | - | 1.5 (0.4) | 6.7 (2.0) | 1.5 (0.4) | 6.7 (2.0) |
| AlCl ₃ - | _ | - | 0.9 (0.3) | 4.1 (1.2) | 0.1 (0.03) | 0.5 (0.1) |
| HCl - | _ | - | 0.04 (0.01) | 0.19 (0.06) | 0.04 (0.01) | 0.19 (0.06) |
| H ₃ PO ₄ - | - | - | 0.02 (0.01) | 0.09 (0.03) | 0.02 (0.01) | 0.09 (0.03) |

Other operational components - R\$ million/y (US\$ million/y)

| _ | | • · | | - | | | |
|-------------|--------|-------|-------|--------|--------|--------|--------|
| Maintananaa | 34.8 | 27.6 | 28.7 | 37.6 | 60.0 | 43.1 | 85.0 |
| Maintenance | (10.4) | (8.2) | (8.6) | (11.2) | (17.9) | (12.9) | (25.4) |
| Labar | 12.2 | 12.2 | 12.2 | 14.2 | 19.8 | 14.2 | 19.8 |
| Labor | (3.6) | (3.6) | (3.6) | (4.2) | (5.9) | (4.2) | (5.9) |
| | | | | | | | |

Table 5.7 shows the main deterministic results of the economic assessment conducted. Scenario BASE3 presented the best overall IRR, at 20.7%. Among co-located biorefineries, scenario B1 presented an IRR of 17.5%, which is higher than that of the design of conventional ethanol distilleries currently operational in Brazil. Scenarios B2 and B4, which are dedicated to the production of large quantities of biodiesel, have IRR either close to or lower than the MARR of 12%.

In relation to production costs of anhydrous ethanol and biodiesel, a different control volume of the biorefineries was defined (Figure 5.5), since not all verticalized biorefineries have biodiesel as a product to the market (scenarios B1 and B3). This is similar to the procedure adopted in Section 4.3.2. With this configuration, the production costs of sugarcane stalks and straw with a 70% substitution of fossil diesel were considered for OPEX

determination in sugarcane-microalgae biorefineries (equivalent to that of scenario BASE3 in Table 5.5).

Scenario B1 presented an anhydrous ethanol production cost of R\$ 1.22/L (US\$ 0.36/L), which is lower than that of scenario BASE1 (R\$ 1.27/L or US\$ 0.38/L): the output of other coproducts, such as microalgae meal, helps in reducing the proportion of costs allocated to anhydrous ethanol in scenario B1. Scenario B1 also yielded the lowest biodiesel production cost, at R\$ 1.87/L (US\$ 0.56/L). The combined costs of the microalgae plant (both OPEX and CAPEX) tend to significantly increase the biodiesel production costs, especially in scenarios B2 and B4. Still, all integrated biorefineries were able to produce biodiesel at a lower cost than the stipulated selling price of R\$ 2.60/L (US\$ 0.78/L). Here, too, biodiesel production costs remain well below those found by Batan et al. (2016), Brownbridge et al. (2014), and Nagarajan et al. (2013).

| Deveryeter | Scenario | | | | | | | |
|---|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--|
| Parameter | BASE1 | BASE2 | BASE3 | B1 | B2 | B3 | B4 | |
| IRR | 17.1% | 20.6% | 20.7% | 17.5% | 12.3% | 16.6% | 10.1 % | |
| NPV - R\$ million (US\$ million) | 141 | 201 | 211 | 157 | 10 | 135 | -84 | |
| | (42) | (60) | (63) | (47) | (3) | (40) | (-25) | |
| NPV/I ratio | 0.41 | 0.73 | 0.74 | 0.45 | 0.02 | 0.36 | -0.14 | |
| Payback (years) | 5 | 4 | 4 | 5 | 6 | 5 | 8 | |
| Anhydrous ethanol production cost - R\$/L (US\$/L) | 1.27 (0.38) | 1.19 (0.36) | 1.16 (0.35) | 1.22 (0.36) | 1.44 (0.43) | 1.25 (0.37) | 1.55 (0.46) | |
| D. | 0.76 | 0.76 | 0.70 | 0.65 | 0.58 | 0.65 | 0.57 | |
| Biomass | (0.23) | (0.23) | (0.21) | (0.19) | (0.17) | (0.19) | (0.17) | |
| Sugaraana mill canital cost | 0.38 | 0.30 | 0.31 | 0.30 | 0.27 | 0.30 | 0.27 | |
| Sugarcane min capital cost | (0.11) | (0.09) | (0.09) | (0.09) | (0.08) | (0.09) | (0.08) | |
| Riorafinary maintananaa | 0.08 | 0.06 | 0.07 | 0.09 | 0.12 | 0.10 | 0.17 | |
| Biorennery maintenance | (0.02) | (0.02) | (0.02) | (0.03) | (0.04) | (0.03) | (0.05) | |
| Riorafinary Jahar | 0.03 | 0.03 | 0.03 | 0.03 | 0.04 | 0.03 | 0.04 | |
| Biorennery labor | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | |
| Chemicals for sugarcane | 0.03 | 0.03 | 0.03 | 0.03 | 0.02 | 0.03 | 0.02 | |
| processing | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) | |
| Microalgae facility capital cost | _ | - | - | 0.07 (0.02) | 0.23 (0.07) | 0.09 (0.03) | 0.32 (0.10) | |

Table 5.7 – Main economic results of the assessed biorefineries and breakdown of anhydrous ethanol production cost.

| Table 5.7 | – Continued |
|-----------|-------------|
| | |

| Parameter | Scenario | | | | | | |
|--------------------------------------|----------|-------|--------|-----------|-----------|-----------|-----------|
| | BASE1 | BASE2 | BASE3 | B1 | B2 | B3 | B4 |
| Microalgae facility operational cost | - | - | - | 0.03 | 0.15 | 0.03 | 0.14 |
| | | | | (0.01) | (0.04) | (0.01) | (0.04) |
| AD operational cost | - | - | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| | | | (0.01) | (0.01) | (0.01) | (0.01) | (0.01) |
| | | | | | | | |
| Biodiesel production cost – | _ | _ | _ | 1.87 | 2.20 | 1.91 | 2.38 |
| R\$/L (US\$/L) | - | - | - | (0.56) | (0.66) | (0.57) | (0.71) |
| Biomass | _ | _ | _ | 0.99 | 0.89 | 0.99 | 0.88 |
| | - | - | - | (0.30) | (0.27) | (0.30) | (0.26) |
| Sugarcane mill capital cost | _ | _ | _ | 0.46 | 0.42 | 0.46 | 0.41 |
| | _ | _ | _ | (0.14) | (0.13) | (0.14) | (0.12) |
| Biorefinery maintenance | - | - | _ | 0.13 | 0.19 | 0.15 | 0.26 |
| | | | | (0.04) | (0.06) | (0.04) | (0.08) |
| Biorefinery labor | - | - | _ | 0.05 | 0.06 | 0.05 | 0.06 |
| | | | | (0.01) | (0.02) | (0.01) | (0.02) |
| Chemicals for sugarcane | - | - | - | 0.04 | 0.04 | 0.04 | 0.04 |
| processing | | | | (0.01) | (0.01) | (0.01) | (0.01) |
| Microalgae facility capital cost | - | - | - | 0.11 | 0.35 | 0.14 | 0.49 |
| | | | | (0.03) | (0.10) | (0.04) | (0.15) |
| Microalgae facility operational | - | - | _ | 0.05 | 0.23 | 0.05 | 0.22 |
| cost | | | | (0.01) | (0.07) | (0.01) | (0.07) |
| AD operational cost | - | - | - | 0.03 | 0.03 | 0.03 | 0.03 |
| | | | | (0.01) | (0.01) | (0.01) | (0.01) |



Figure 5.5 – Considered control volume for the assessment and comparison of both anhydrous ethanol and biodiesel production costs among integrated scenarios (non-verticalized operation).

5.3.3 Economic results: stochastic assessment

Figure 5.6 shows the results of the risk analysis regarding the IRR of the biorefineries in question.



Figure 5.6 – Risk analysis results for IRR uncertainty of the assessed scenarios.

The results for BASE2 are nearly confounded with those of BASE3, which presented the best IRRs in the deterministic assessment. The risk analysis carried out attests that the economic return of scenarios BASE1, B1, and B3 are nearly equal - something that has been hinted at in the deterministic analysis in Section 5.3.2. On the other hand, scenarios B2 and B4 present a certain overlap of the distribution curves but lag the economic performances of either the base scenarios or the remaining integrated biorefineries. Scenario B2 has a 51% chance of presenting an IRR higher than the MARR of 12%, while this probability decreases to only 9% in scenario B4. The IRRs of all other scenarios have a probability of at least 98% of being above the MARR of 12%.

From the tornado plots in Figure 5.7, it can be observed that the variation of anhydrous ethanol selling price is the single factor that most influences the IRR of the biorefineries. Therefore, the less anhydrous ethanol is sold by a given biorefinery, the sharper its probability distribution in Figure 5.6. Other parameters that highly influence the economic performance of co-located biorefineries (as per Figures 5.7b and 5.7c for scenarios B1 and B2, respectively) include the sugarcane biomass price, the CAPEX of both sugarcane mill and microalgae plant, and the EE price. The impact of the uncertainty in the microalgae plant CAPEX is higher in scenario B2 since the facility is larger (and more expensive) than in scenario B1.



Figure 5.7 – Tornado plots for IRR uncertainty analysis for scenarios (a) BASE3, (b) B1, and (c) B2.

Figures 5.8a and 5.8b present the risk analysis for the production costs of both anhydrous ethanol and biodiesel. The behavior of the curves for both types of biofuels matches those determined for the IRR (Figure 5.6). In general, base scenarios and integrated scenarios B1 and B3 have overlapped probability distributions, while those for scenarios B2 and B4 usually stand out (with higher values) among all assessed alternatives.



Figure 5.8 – Risk analysis results for the production costs of (a) anhydrous ethanol and (b) biodiesel of the assessed scenarios.

5.3.4 Environmental results: deterministic assessment

The deterministic results of the environmental assessment of the scenarios are presented in Figure 5.9a, in which the impacts related to anhydrous ethanol production are compared to those of gasoline type A.



Figure 5.9 – Environmental impacts of anhydrous ethanol production: (a) assessed impact categories and (b) breakdown of GHG emissions.

Scenario BASE3 yields anhydrous ethanol with lower GHG emissions (17.9 g CO₂eq/MJ) than scenarios BASE1 and BASE2, both discussed in Section 4.3.4. This occurs in view of the substitution of 70% of the fossil diesel in sugarcane agricultural operations by biomethane and despite the use of large quantities of NaOH, which presents relatively high emission factors for the climate change category. This breakdown can be seen in Figure 5.9b: the reduction concerning sugarcane production impacts is significant from scenario BASE1 or BASE2 to BASE3, while the increase in impacts related to industrial inputs (such as NaOH). Concerning the four integrated biorefineries, all provided anhydrous ethanol with lower GHG emissions than the three base scenarios, a trend previously observed in Section 4.3.4. Lowest scores were achieved in scenario BASE3. Scenarios B1 and B3 rely on the lowest microalgae biomass productions since the amount of produced biodiesel is limited to suffice the substitution of the remaining 30% of diesel not displaced by biomethane. This is a direct consequence of overall lower fertilizer consumption by the co-located biorefinery.

Figure 5.9a also depicts the results of the environmental assessment of the biorefineries in terms of four other selected impact categories, which are in accordance with those already seen in Figure 4.8a. Scenario BASE3 presents a higher impact on freshwater eutrophication than scenarios BASE1 and BASE 2 in view of the utilization of NaOH for pH adjustment in AD of vinasse. The highest scores in this category were found in scenarios B2 and B4, which have, besides NaOH consumption in AD reactors, high requirement of N and P fertilizers for microalgae growth.

The agricultural land occupation of scenarios B2 and B4 are lower than their B1 and B3 counterparts, respectively, since they are able to produce more biofuels per area unit than any other of the analyzed biorefineries in Chapters 4 and 5. Regarding the water depletion category, the highest impact is observed for scenario B2, in which a high microalgae production is carried out in covered raceways. Finally, the fossil depletion impact of gasoline type A reaches values nearly 19 times higher than in integrated biorefineries B1 and B3.

The comparison between verticalized and non-verticalized was also carried out, as in Section 4.3.4. The main results are shown in Figure 5.10.



Figure 5.10 – Comparative environmental impacts of anhydrous ethanol production in verticalized and non-verticalized biorefineries.

The plot depicts the same comparative behavior between verticalized and nonverticalized biorefinery configurations as in Figure 4.9. Substituting fossil diesel with biodiesel yields lower climate change and fossil depletion impacts for anhydrous ethanol due to the lower associated impact of producing sugarcane (less fossil diesel consumption in sugarcane operations, and transport of biomass and other inputs).

5.3.5 Environmental results: stochastic assessment

Figure 5.11 presents the uncertainty analysis for climate change impacts of the assessed biorefineries.



Figure 5.11 - Risk analysis results for the climate change impacts of anhydrous ethanol production of the assessed scenarios.

From the plot, scenario BASE 3 presents a much lower climate change impact, with a distribution that overlaps with those of scenarios B2 and B4. All integrated scenarios, as well as scenario BASE3, present a nearly 100% probability of having a climate change impact lower than the deterministic value of 20.6 g CO₂eq/MJ of anhydrous ethanol in scenario BASE1.

The tornado plots in Figure 5.13 depict the impact of sugarcane biomass production on the environmental assessment. Another parameter that appears to be determinant in the analysis is the consumption of NaOH for pH adjustment in the AD of vinasse, since this chemical has high emission factors for the climate change category.



Figure 5.12 – Tornado plots for climate change impact uncertainty in scenarios (a) BASE3, (b) B3, and (c) B4.

5.3.6 Liquid fertilizer production: a case study

Among the four integrated scenarios, the configuration of scenario B1 presented the best results in terms of economic feasibility and environmental impacts. Therefore, a new scenario named B1-FERT was created to investigate the possibility of producing a liquid fertilizer from vinasse and to be benchmarked against scenario B1. In this new scenario, digested vinasse (from the AD) and spent vinasse (from heterotrophic microalgae growth) are combined and concentrated, then follow to the addition of NH₃ and H₂SO₄ for N:K₂O ratio adjustment and pH correction, respectively. The process is broadly outlined in Section 5.2.1.2 and Figure 5.13 presents the main integration strategy of liquid fertilizer production in scenario B1-FERT.



Figure 5.13 – Layout of the integrated facility for the production of liquid fertilizer from both digested and spent vinasse (scenario B1-FERT).

The main results of the assessment are presented in Figure 5.14 and benchmarked against those of scenario B1. CAPEX in scenario B1-FERT increased from R\$ 1,176 million (US\$ 351 million) to R\$ 1,187 million (US\$ 354 million). The R\$ 9 million (US\$ 3 million) difference appears after the addition of equipment related to fertilizer production (R\$ 22 million or US\$ 7 million), although with a slight reduction of R\$ 13 million (US\$ 4 million) in equipment required for the steam island. There is a naturally lower output of EE in scenario B1-FERT due to the use of significant quantities of process steam to heat the multiple-effect



(IRR and NPV/I ratio) are slightly lower in comparison to scenario B1.

Figure 5.14 – Comparative techno-economic results between scenarios B1 and B1-FERT in selected categories.

Figure 5.15a presents the comparative analysis of environmental impacts between scenarios B1 and B1-FERT. In all categories, scenario B1 outperforms its counterpart. This can be explained by the fact that the *in situ* production of a liquid fertilizer suffers from process inefficiencies that an optimized conventional route for fertilizer production does not have. In this way, more NH₃ and/or more H_2SO_4 than the stoichiometric amounts may be consumed in this configuration. This is confirmed by the breakdown of climate change impacts shown in Figure 5.15b, in which the increase in the share corresponding to industrial inputs outweighs the reduction in the impact of sugarcane production through the use of a liquid fertilizer. Therefore, this option does not appear to be a feasible alternative for biorefineries due to both economic and environmental reasons.



Figure 5.15 – Comparative environmental impacts of anhydrous ethanol production in scenarios B1 and B1-FERT: (a) assessed impact categories and (b) breakdown of GHG emissions.

Figure 5.16 presents a chart for the positioning of all assessed scenarios (Chapters 4 and 5) in terms of IRR and climate change impact of anhydrous ethanol production. The plot clearly shows integrated sugarcane-microalgae biorefineries lagging base scenarios in terms of economic performance. However, nearly all integrated biorefineries (scenarios P1, P2, C1, C2, and B1 to B4) produce anhydrous ethanol with low associated climate change impacts. With the imminent approval of the National Biofuel Policy (RenovaBio Program), biorefineries producing biofuels with low GHG emissions and efficiently will be able to generate extra revenues from the commercialization of credits in the Brazilian stock market. This initiative will help microalgae facilities, such as those presented here, in having higher economic performances and attracting further investments in the development of both pilot and industrial-scale plants. The possible benefits from the RenovaBio Program are further explored in Chapter 6.



Figure 5.16 – Combined results for economic (IRR) and environmental (GHG emissions) performance of scenarios assessed in Chapters 4 and 5.
5.3.8 Preliminary conclusions

The synergy between sugarcane biorefineries, AD of vinasse, and microalgae cultivations is clear with the assessment presented in this Chapter. The environmental assessment detailed herein helps to assert that the great advantage of producing both biomethane and microalgae biodiesel is the displacement of fossil diesel in sugarcane production and transport. This can be verified especially in scenario B1, which presented one of the lowest climate change impacts among all biorefineries of Chapters 4 and 5, while having the most positive IRR of all integrated sugarcane-microalgae plants (17.5%).

Further experiments with digested vinasse as the carbon source for microalgae growth could provide new insights towards the feasibility of this alternative in practical terms, with increased economic performance, and with an environmentally-friendly operation.

CHAPTER 6 INFLUENCE OF THE NEW BRAZILIAN NATIONAL BIOFUEL POLICY (RENOVABIO) ON INTEGRATED SUGARCANE-MICROALGAE BIOREFINERIES

6.1 Introduction

In 2012, the Brazilian transport sector was responsible for around 14% of the national CO₂ emissions (SEEG, 2014). This encompasses emissions by road cargo movement, individual and collective transportation, and other transportation modes (air, rail, and water), accounting for over 200 million tonnes of CO₂eq. The sector saw an annualized growth rate of nearly 4.5% per annum between 2002 and 2012 while maintaining a heavy dependence on fossil fuels (over 82%). With the goal of changing this panorama both in Brazil and worldwide, the 21st Conference of Parties (COP21) organized by the United Nations Framework Convention on Climate Change (UNFCCC) established an international agreement, called Paris Agreement, as a measure to limit the effects of global warming to a maximum of 2 °C by the end of the century. Under the Paris Agreement, each country sets individual targets for CO₂ mitigation in order to reach the global goals. The Brazilian proposal for its Nationally Determined Contribution (NDC) involves reducing GHG emissions by 37% and 43% by 2025 and 2030, respectively, in comparison to 2005 levels (MMA, 2018). The plan towards reaching those targets passes mainly through recovering extensive areas of native vegetation as well as through supplying large amounts of renewable electricity and biofuels.

The deployment of biofuel production in large scale is usually supported or subsidized by nationwide policies or incentive programs. In Brazil, one of the most emblematic examples is the Proálcool Program, deployed in 1975 and previously described in Section 3.5. Another important case refers to the National Program of Biodiesel Production and Use (PNPB), established in 2005 and created to reduce the country's dependence on diesel imports. For instance, Brazil currently consumes annually around 52 billion liters of diesel, of which 15% are imported (EPE, 2017). The PNPB prioritizes biodiesel production with high sustainability (economic, environmental, and social) character and from several feedstocks according to the availability in each Brazilian region (MME, 2017). The Program established a mandatory blend of biodiesel in fossil diesel, which represented 2% v/v in 2005. For commercial purposes, this blend is referred to as B2. With the increasing maturity of the Program, diesel commercialized in Brazil passed through several grades, such as B5 (2010-2013), B7 (2014-2017), and B8 (2017-onwards). After full deployment of the PNPB, the Brazilian production of biodiesel increased from 69 million liters in 2006 to over 3.8 billion liters in 2016 (EPE, 2017).

The newest effort by the Brazilian State comes in the form of Law 13.576/2017, which creates the National Biofuel Policy, publicly known as RenovaBio. Its ultimate goal is to stimulate the production of several types of biofuels, encompassing ethanol, biodiesel, biomethane (purified biogas), and renewable jet fuel (Senado Brasileiro, 2017), through the mechanism schematically shown in Figure 6.1. In summary, the RenovaBio Program will create a controlled market of Decarbonization Credits (CBios), emitted by either biofuels producers or importers. The amount of CBios which an entity may emit in the Brazilian stock market is directly linked to the reduction in GHG emissions associated with the production of a given biofuel in comparison to its fossil competitor. A tool to verify the environmental performance of biofuels producers, named RenovaCalc, is currently under development by multiple Brazilian institutions and will be made available in late 2018. The tool, which is heavily LCA-based, will aid companies both in identifying process bottlenecks and in paving the way for certification. The RenovaBio Program will also establish decarbonization targets to fuel distributors, who will be obliged to reduce their carbon footprint either through the purchase of low-impact biofuels or through acquiring CBios in the stock market. In the end of the chain, the money from this exchange is redirected to biofuels producers or importers.



Figure 6.1 – Mechanism of emission and trade of decarbonization credits (CBios) created by the RenovaBio Program.

Sugarcane mills, as well as integrated sugarcane-microalgae biorefineries, will hugely benefit from such mechanism, both in terms of increasing revenues of the industrial plant and of biofuel demand forecasting. The RenovaBio Program will further allow the expansion of the already consolidated sector of biofuels in Brazil, as well as the deployment of new technologies to increase the offer of renewable energy in the country. Through the assignment of an economic value to carbon emissions in a different fashion than in the still valid cap and trade system of carbon credits, the Program will provide an opportunity to increase the use of renewable energy in the Brazilian matrix. Its main goals include a greater predictability of biofuels demand over the next years, which will, in turn, greatly boost the capacity of companies and government alike of planning investments. Besides, an indirect effect of the RenovaBio Program will be the induction of higher Research and Development efforts aiming at higher biomass productivities and higher conversion efficiencies as a means of optimizing processes and reducing the overall climate change impact of the operation.

The biodiesel production chain in Brazil is largely based on soybean: in 2016, this oil crop responded for more than 75% of the raw material employed industrially (ABIOVE, 2017). The RenovaBio Program could also boost the diversification of the pool of raw materials for the supply of vegetable oil. Among possibilities, the use of high-quality oils from palm, sunflower, and rapeseed, which amounted to more than 150 thousand tonnes in the 2015/2016 harvest (CONAB, 2016b). Another plant crop potential of supplying vegetable oil in the medium term is macaw palm, a Central and South America native plant with high per hectare oil productivity. Microalgae oil is also a potential candidate to compose the Brazilian matrix of oils for conversion.

Another benefit of the RenovaBio Program could be the reduction in unused capacity of biodiesel plants, as the average operational level in Brazil remains below 35% nowadays. Since industrial units are capable of year-round operation, the ideal level for promoting their economic feasibility would be of at least 90%. This outcome, in combination with the procurement of CBios by producers, could potentially lead to a new era in the Brazilian biodiesel industry.

This Chapter aims at assessing quantitatively the benefits of the RenovaBio Program for each of the biorefineries presented in Chapters 4 and 5. Estimates for CO_2 mitigation by the considered biorefineries are presented, as well as the potential gains with CBios. Finally, the influence of this extra revenue from commercializing CBios is taken into account for the determination of the increase in the economic performance of biorefineries as a function of the price associated to this decarbonization credit.

6.2 Methodology

The determination of the total CO₂ mitigation by a given biorefinery was carried out through a direct comparison between the total emissions of biofuels produced by that plant (anhydrous ethanol and biodiesel, as in Equation 4) and that associated to the amount of equivalent fossil fuel (gasoline type A and diesel, as in Equation 5) dislocated by those biofuels. This procedure was determined in order to mirror the procedure that will be put into place through the use of the RenovaCalc. The amounts of fossil fuel that would be substituted by biofuels were estimated through simple relations between their lower heating values (LHVs), as shown in Equations 6 and 7. Table 6.1 presents the employed LHVs for the fuels in question. Finally, the total mitigation was calculated as in Equation 8.

$$Emissions_{biofuels} = Volume_{ethanol} * Impact_{ethanol} + Volume_{biodiesel} * Impact_{biodiesel}$$
(4)
$$Emissions = Volume = Volume = Volume = Volume = (4)$$

$$Emissions_{fossil} = Volume_{gasoline} * Impact_{gasoline} + Volume_{diesel} * Impact_{diesel}$$
(5)

$$Volume_{gasoline} = Volume_{ethanol} * \binom{LHV_{ethanol}}{LHV_{gasoline}}$$
(6)

$$Volume_{diesel} = Volume_{biodiesel} * \left(\frac{LHV_{biodiesel}}{LHV_{diesel}} \right)$$
(7)

$$\Delta_{emissions} = Emissions_{fossil} - Emissions_{biofuels} \tag{8}$$

Table 6.1 – Lower Heating Values (LHVs) of the fuels involved in the analysis.

| Fuel | Lower heating value (MJ/kg) | Reference |
|-------------------|-----------------------------|----------------------|
| Anhydrous ethanol | 28.215 | ANP (2015) |
| Gasoline type A | 43.472 | ANP (2015) |
| Biodiesel | 32.600 | Aspen Plus® estimate |
| Fossil diesel | 42.218 | ANP (2015) |

Climate change impacts for the production phase of both anhydrous ethanol and microalgal biodiesel were retrieved from Chapters 4 and 5. The impact associated with the use phase of anhydrous ethanol (equivalent to roughly 1 g CO_2eq/MJ) was then added to the previously calculated impacts. For biodiesel, however, due to the unavailability of the impact associated with its use phase, no additions were made to the calculated values. This has very little influence on the results for the estimate of the total decarbonization credits earned, since the majority of CO_2 mitigation comes from the substitution of gasoline type A by anhydrous ethanol. It is worthwhile to emphasize that all climate change impacts associated to the

production of anhydrous ethanol in Chapters 4 and 5 were determined through economic allocation between products of the biorefineries, although the method of choice within the RenovaCalc calculation framework will be energetic allocation. The impacts associated with gasoline type A and fossil diesel were of 86.4 and 87.4 g CO₂eq/MJ, respectively (Matsuura et al., 2017). These values already cover both the production and use phases of fossil fuels.

The influence of the RenovaBio Program on the economic performance of Brazilian biorefineries was then assessed through a sensitivity analysis using the CBio price as the independent variable. The studied range went from a minimum of R\$ 10/tonne CO₂eq (US\$) up to a maximum of R\$ 130/tonne CO₂eq. Such figures were based on all-time low and high prices for carbon credit trading in the international market of around US\$ 4/tonne CO₂eq and US\$ 40/tonne CO₂eq achieved in 2006 and in 2013, respectively, under the European Union Emissions Trading System (NYTimes, 2013; Sandbag, 2016). The increase in the revenues provided by the commercialization of CBios with fuel distributors in Brazil was considered in the discounted cash flows analyses previously performed in Chapters 4 and 5. The main metric chosen for the analysis was the NPV/I ratio, which is a normalized index useful in the comparison of scenarios with contrasting initial investments.

The method was applied to the following scenarios of Chapters 4 and 5: BASE1, BASE2, BASE3, P1, P2, C1, C2, B1, B2, B3, and B4. Initially, the discussion developed in the next section is carried out for "closed" plants, i.e. biorefineries with verticalized agricultural-industrial phases through the substitution of fossil diesel in sugarcane operations with microalgal biodiesel. A brief comparison with the results obtained for "open" plants, i.e which produce sugarcane biomass with conventional diesel and commercialize the full amount of microalgal biodiesel to the market, is also performed.

6.3 Results and discussion

6.3.1 Verticalized agricultural-industrial biorefineries

Using the methodology described in the previous section, the main figures regarding CO_2 mitigation with the biorefineries in question operating in "closed" mode are summarized in Table 6.2. Among the assessed alternatives, only scenarios B2 and B4 have both ethanol and biodiesel as outputs to the market; the other biorefineries produce ethanol as the sole biofuel capable of earning decarbonization credits. The amount of ethanol produced in all scenarios is able to substitute at least 230 million L/year of gasoline type A, while the

commercialized biodiesel in scenarios B2 and B4 can dislocate around 20 million L/year of fossil diesel.

Biodiesel production impact in scenarios B2 and B4 remained between 20 and 21 g CO₂eq/MJ, thus representing a reduction of 76-77% in comparison to fossil diesel (Matsuura et al., 2017). Batan et al. (2010) also determined significant reductions in climate change impacts from either soybean or microalgae biodiesel in comparison to fossil diesel. The overall balance of microalgae-derived biodiesel, specifically, benefits from lower N₂O emissions than other crops since the aerobic growth of microalgae restricts the venting of this compound in the atmosphere. Campbell et al. (2011) identified that microalgal biodiesel could be produced with a lower impact than canola biodiesel even when CO₂ is delivered to cultivations with trucks over 100 km. In addition, Clarens et al. (2011) calculated lower impacts for microalgae biodiesel in comparison to canola biodiesel and stressed that identifying new destinations for coproducts obtained from microalgal biomass is imperative for a higher overall process sustainability. Chen et al. (2018b) determined, for systems in the United States, biodiesel emissions from tallow, soybean, and canola, of around 21, 22, and 31 g CO2eq/MJ, respectively. Impacts determined for microalgae biodiesel in this work stand either at par or below these values. For comparison, soybean biodiesel in Brazil presents an impact of over 44 g CO₂eq/MJ (Matsuura et al., 2017).

Through the utilization of Equations 4 to 8, it was estimated that each biorefinery was able to mitigate from 490 to 542 thousand tonnes CO₂eq/year with the supply of biofuels to the market, depending on the scenario. Among base configurations, scenario BASE3 presented the best mitigation potential in view of the inherent lower climate change potential of anhydrous ethanol due to biomethane utilization in the agricultural phase of sugarcane production. The same reasoning can be applied to integrated sugarcane-microalgae biorefineries: the substitution of 100% of the fossil diesel used in sugarcane production with microalgal biodiesel shows its benefits in the climate change impact of anhydrous ethanol. With a virtually unchanged ethanol production in comparison to scenarios BASE1 and BASE2, in which only fossil diesel is used in sugarcane operations. Further reductions in CO_2 emissions can also be perceived in scenarios B2 and B4: since biodiesel is an output of the biorefinery to the market, the impacts of sugarcane production and processing are also partially allocated to this product. Finally, the increase in revenues is also shown in Table 6.2, within the range described in Section 6.2. As can be seen, the figures vary from as low as R\$ 5 million (US\$ 1 million) up to R\$ 70 million (US\$ 21 million), according to the scenario and the practiced CBio price.

| Scenario | BASE1 | BASE2 | BASE3 | P1 | P2 | C1 | C2 | B1 | B2 | B3 | B4 |
|---|--------------------|--------|--------|--------|--------|-----------|--------|-----------|--------|-----------|-----------|
| Anhydrous ethanol production (million L/y) | | 347.2 | 347.2 | 343.6 | 343.6 | 343.6 | 343.6 | 346.1 | 342.5 | 346.1 | 342.4 |
| Climate change impact, with use phase (g CO ₂ eq/MJ) | 21.7 | 21.7 | 18.9 | 18.6 | 18.2 | 18.5 | 18.2 | 17.9 | 18.8 | 17.9 | 18.3 |
| | | | | | | | | | | | |
| Biodiesel production to market (million L/y) | | - | - | - | - | - | - | - | 17.3 | - | 17.5 |
| Climate change impact (g CO ₂ eq/MJ) | - | - | - | - | - | - | - | - | 20.8 | - | 20.2 |
| | | | | | | | | | | | |
| Dislocated gasoline, type A (million L/y) | | 234.8 | 234.8 | 232.4 | 232.4 | 232.4 | 232.4 | 234.1 | 231.6 | 234.1 | 231.6 |
| Dislocated fossil diesel (million L/y) | - | - | - | - | - | - | - | - | 14.0 | - | 14.2 |
| | | | | | | | | | | | |
| Fossil-only, total emissions (thousand tonnes CO ₂ eq/y) | | 654 | 654 | 648 | 648 | 648 | 648 | 652 | 689 | 652 | 689 |
| Biobased-only, total emissions (thousand tonnes | | 164 | 143 | 130 | 136 | 130 | 137 | 135 | 151 | 135 | 147 |
| $CO_2 eq/y)$ | | 104 | 145 | 137 | 150 | 137 | 157 | 155 | 151 | 155 | 177 |
| Reduction in total emissions (thousand tonnes CO ₂ eq/y) | 490 | 490 | 511 | 508 | 511 | 509 | 511 | 517 | 538 | 517 | 542 |
| | | | | | | | | | | | |
| Credits from CBio commercialization - R\$ million/y (U | J S\$ milli | on/y) | | | | | | | | | |
| <i>CBio price: R</i> \$ 10/tonne CO ₂ eq | 4.9 | 4.9 | 5.1 | 5.1 | 5.1 | 5.1 | 5.1 | 5.2 | 5.4 | 5.2 | 5.4 |
| (US\$ 3/tonne CO2eq) | (1.5) | (1.5) | (1.5) | (1.5) | (1.5) | (1.5) | (1.5) | (1.6) | (1.6) | (1.6) | (1.6) |
| <i>CBio price: R\$ 40/tonne CO</i> ₂ <i>eq</i> | 19.6 | 19.6 | 20.4 | 20.3 | 20.5 | 20.3 | 20.4 | 20.7 | 21.5 | 20.7 | 21.7 |
| $(US\$\ 12/tonne\ CO_2eq)$ | (5.9) | (5.9) | (6.1) | (6.1) | (6.1) | (6.1) | (6.1) | (6.2) | (6.4) | (6.2) | (6.5) |
| <i>CBio price: R\$ 70/tonne CO</i> 2eq | 34.3 | 34.3 | 35.8 | 35.6 | 35.8 | 35.6 | 35.8 | 36.2 | 37.7 | 36.2 | 38.0 |
| (US\$ 21/tonne CO2eq) | (10.2) | (10.2) | (10.7) | (10.6) | (10.7) | (10.6) | (10.7) | (10.8) | (11.3) | (10.8) | (11.3) |
| CBio price: R\$ 100/tonne CO2eq | 49.0 | 49.0 | 51.1 | 50.8 | 51.1 | 50.9 | 51.1 | 51.7 | 53.8 | 51.7 | 54.2 |
| (US\$ 30/tonne CO2eq) | (14.6) | (14.6) | (15.3) | (15.2) | (15.3) | (15.2) | (15.3) | (15.4) | (16.1) | (15.4) | (16.2) |
| CBio price: R\$ 130/tonne CO2eq | 63.7 | 63.7 | 66.5 | 66.1 | 66.5 | 66.1 | 66.5 | 67.2 | 69.9 | 67.3 | 70.5 |
| (US\$ 39/tonne CO2eq) | (19.0) | (19.0) | (19.9) | (19.7) | (19.9) | (19.7) | (19.9) | (20.1) | (20.9) | (20.1) | (21.0) |

 $Table \ 6.2-Main\ environmental\ results\ and\ economic\ impacts\ of\ the\ RenovaBio\ Program\ on\ verticalized\ biorefineries.$



Figure 6.2 presents the effects of an additional revenue due to the commercialization of CBios on the cash flow of the biorefineries presented in Chapter 4.

Figure 6.2 – NPV/I ratio evolution with varying CBio prices in biorefineries of Chapter 4.

At the highest considered CBio price, the income from its commercialization would mean an increase of at least 2 p.p. in the IRR of all biorefineries and of at least 0.16 in all NPV/I ratios, in comparison to the values presented in Chapter 4. The highest benefits are seen in base scenarios (BASE1 and BASE2), since the lower the CAPEX, the easier to achieve a high NPV. Taking the current carbon credit price in the international market (of around US\$ 9/tonne CO₂eq or R\$ 30/tonne CO₂eq) as the basis for the CBio price, this would lead to highly unprofitable scenarios, such as P2 and C2, to achieve at least a positive NPV and, therefore, a positive NPV/I ratio. Wiesberg et al. (2017) calculated a carbon pricing of around US\$ 140/tonne CO₂eq for (standalone) Brazilian microalgae plants using flue gasderived CO₂ to be economically feasible.

A similar trend can be observed in Figure 6.3 for the biorefineries considered in Chapter 5. In this plot, a *quasi*-linear behavior of the increase in the NPV/I ratio with increasing CBio prices also appears. Again, base scenarios are among the ones with the highest benefits, especially biorefinery BASE3. Finally, integrated biorefinery B4 only achieves a positive NPV/I ratio with a CBio price of R\$ 130/tonne CO₂eq (US\$ 39/tonne CO₂eq) or higher.



Figure 6.3 – NPV/I ratio evolution with varying CBio prices in biorefineries of Chapter 5.

6.3.2 Non-verticalized agricultural-industrial biorefineries

The same assessment was carried out for non-verticalized biorefineries, i.e. which use fossil diesel for the production of sugarcane and commercializes the full biofuels production to the market. This analysis is not applicable to base scenarios (BASE1, BASE2, and BASE3), being only used for co-located biorefineries. Table 6.3 summarizes the main results obtained.

Inherently higher climate change impacts for anhydrous ethanol production are observed in all scenarios since the production of sugarcane bears the impacts of using fossil diesel – even though the amount of impacts allocated to anhydrous ethanol is lower due to a lower participation in the total revenues of the biorefinery in view of the commercialization of biodiesel. As a result, a higher amount of CO₂ is mitigated in such biorefineries, in spite of higher impacts on fossil depletion (as shown in Chapters 4 and 5). Ultimately, open scenarios would be able to earn around 4.4% more revenues due to the commercialization of CBios as a consequence of the slightly higher potential in reducing CO₂ emissions (in comparison to Table 6.2).

| Scenario | P1 | P2 | C1 | C2 | B1 | B2 | B3 | B4 |
|---|------------|--------|--------|--------|-----------|--------|-----------|-----------|
| Anhydrous ethanol production (million L/y) | 343.6 | 343.6 | 343.6 | 343.6 | 346.1 | 342.5 | 346.1 | 342.4 |
| Climate change impact, with use phase (g CO ₂ eq/MJ) | 22.2 | 21.8 | 22.2 | 21.9 | 19.0 | 19.6 | 19.0 | 19.3 |
| | | | | | | | | |
| Biodiesel production to market (million L/y) | 17.0 | 17.0 | 17.0 | 17.0 | 5.1 | 22.4 | 5.1 | 22.6 |
| Climate change impact (g CO ₂ eq/MJ) | 24.7 | 24.2 | 24.7 | 24.3 | 21.0 | 21.7 | 21.0 | 21.3 |
| Dislocated encoling teme A (million I (n) | 222.4 | 222.4 | 222.4 | 222.4 | 224.1 | 021.6 | 024 1 | 221.6 |
| Dislocated gasonne, type A (minion L/y) | 12.7 | 232.4 | 12.7 | 12.7 | 234.1 | | 234.1 | 251.0 |
| Dislocated fossil diesel (million L/y) | 13./ | 13.7 | 13.7 | 13./ | 4.1 | 18.1 | 4.1 | 18.3 |
| Fossil-only, total emissions (thousand tonnes CO ₂ eq/y) | 690 | 690 | 690 | 690 | 665 | 702 | 665 | 702 |
| Biobased-only, total emissions (thousand tonnes CO ₂ eq/y) | 178 | 175 | 179 | 176 | 147 | 161 | 147 | 158 |
| Reduction in total emissions (thousand tonnes CO ₂ eq/y) | 512 | 515 | 512 | 515 | 518 | 541 | 518 | 544 |
| Credits from CBio commercialization - R\$ million/y (US | \$/million | y) | | | | | | |
| <i>CBio price: R\$ 10/tonne CO</i> ₂ eq | 5.1 | 5.2 | 5.1 | 5.1 | 5.2 | 5.4 | 5.2 | 5.4 |
| (US\$ 3/tonne CO2eq) | (1.5) | (1.6) | (1.5) | (1.5) | (1.6) | (1.6) | (1.6) | (1.6) |
| <i>CBio price: R\$ 40/tonne CO</i> ₂ eq | 20.5 | 20.6 | 20.5 | 20.6 | 20.7 | 21.6 | 20.7 | 21.8 |
| (US\$ 12/tonne CO2eq) | (6.1) | (6.1) | (6.1) | (6.1) | (6.2) | (6.4) | (6.2) | (6.5) |
| <i>CBio price: R\$ 70/tonne CO</i> 2eq | 35.8 | 36.1 | 35.8 | 36.0 | 36.3 | 37.9 | 36.3 | 38.1 |
| (US\$ 21/tonne CO2eq) | (10.7) | (10.8) | (10.7) | (10.7) | (10.8) | (11.3) | (10.8) | (11.4) |
| CBio price: R\$ 100/tonne CO2eq | 51.2 | 51.5 | 51.2 | 51.5 | 51.8 | 54.1 | 51.8 | 54.4 |
| (US\$ 30/tonne CO2eq) | (15.3) | (15.4) | (15.3) | (15.4) | (15.5) | (16.1) | (15.5) | (16.2) |
| CBio price: R\$ 130/tonne CO2eq | 66.6 | 67.0 | 66.5 | 66.9 | 67.4 | 70.3 | 67.4 | 70.7 |
| (US\$ 39/tonne CO2eq) | (19.9) | (20.0) | (19.9) | (20.0) | (20.1) | (21.0) | (20.1) | (21.1) |

Table 6.3 – Main environmental results and economic impacts of the RenovaBio Program on non-verticalized biorefineries.

Scenarios with AD of vinasse (BASE3 and B1 to B4) could also benefit from CBios through supplying biomethane to the national gas grid. In this way, such sugarcane production systems would not use biomethane to substitute fossil diesel and, as presented in Chapters 4 and 5, would have inherently higher impacts associated with anhydrous ethanol. However, the environmental benefit of establishing such biorefineries would be seen in the use phase of both biodiesel and biomethane.

6.4 Preliminary conclusions

The RenovaBio Program presents itself as a promising, innovative policy in many aspects (biofuels demand planning and boosting energy security in Brazil), but also for its potential in leveraging both incipient technologies and well-established ones. As well as for standalone producers of ethanol, biodiesel, or other biofuels, integrated sugarcane-microalgae biorefineries would be able to significantly increase their economic feasibility with credits earned from the commercialization of CBios. Ultimately, with the deployment of the Program in the next few years, every single biorefinery in the country will pursue the production of biofuels with ever lower impacts, since this would lead to the emission of additional CBios for commercialization. This is a clear case of a "market pull" type of innovation, in which the market requires products with better characteristics, and is also a long-term target of the National Biofuel Policy.

CHAPTER 7 CONCLUSIONS

7.1 General conclusions

The present work concerning the establishment of industrial-scale biorefineries integrating sugarcane mills and microalgae plants hints at the best possible process configurations and integration strategies. The sole fact of extending the operation of a sugarcane mill from 200 to 330 days represents a huge step towards increasing the economic return in view of the lower CAPEX involved. This option is technically feasible and its deployment in industrial scale would represent a breakthrough in the sugar-energy sector.

The co-location of microalgae plants with sugarcane mills leads to several different outcomes. The verticalization of the industrial production with the sugarcane agricultural phase leads to integrated biorefineries with lower CO_2 emissions and simpler logistics due to the dismissal of fossil diesel procurement for an in-house biodiesel production. The best reactor system for photoautotrophic microalgae growth appears to be covered raceways in view of its comparatively lower CAPEX and maintenance costs. The heterotrophic cultivation of microalgae with sugarcane vinasse in closed stirred vessels also yields higher biomass productivities with a relatively low overall cost. In general, the high intensity in terms of inputs (such as EE and chemicals) and the high CAPEX involved must be tackled to improve the overall economic feasibility of such projects, since integrated sugarcane-microalgae biorefineries tend to have a lower return on investment than base sugarcane mills.

The inclusion of AD of vinasse for biogas production (and sequential upgrading to biomethane) in integrated biorefineries highly improves the environmental impacts of anhydrous ethanol production. A reduction in NaOH consumption for pH adjustment in vinasse digesters is imperative for further reduction of environmental impacts associated with ethanol production in integrated biorefineries, as well as for an improvement in economic indices. Integrated sugarcane-microalgae biorefineries which substitute 100% of the fossil diesel in sugarcane operations with 70% biomethane and 30% microalgal biodiesel show a promising economic performance, as well as more positive environmental indices than those currently obtained in Brazilian sugarcane mills. This is exemplified by the results of scenario B1, which stand among the best of all integrated biorefineries considered in this Thesis: the associated economic impacts are higher than a conventional sugarcane mill (scenario BASE1), while the climate change impact related to the production of anhydrous ethanol is around 18% lower than that obtained in current autonomous distilleries in Brazil.

The production of a liquid fertilizer from concentrated vinasse for a partial substitution of conventional NPK in sugarcane cultivation does not appear to be an attractive

option for integrated sugarcane biorefineries. Adding this process to sugarcane mills tends to worsen both economic and environmental performances, due to intrinsic process inefficiencies.

The new National Biofuel Policy (RenovaBio) is expected to bring several benefits to the Brazilian energy sector, among which the predictability for future biofuels demand stands out. Incipient technologies, such as microalgae facilities in demonstration scale, could be leveraged with the mechanism created by the RenovaBio Program; established plants, especially sugarcane mills and biodiesel producers, would also take advantage of the emission of decarbonization credits.

In an overall analysis, further Research and Development funding for low-carbon biofuels should be put in place by the government and the private sector alike to boost the technological development of microalgae processes. Moreover, policymakers should prioritize the creation of legal measures to support innovation, thus aiding the establishment of flagship plants and encouraging further deployment of integrated sugarcane-microalgae biorefineries to arrive at fully-commercial nth plants.

7.2 Suggestions for future work

In view of the many steps involved in the deployment of pilot and industrial-scale microalgae plants, both standalone facilities or integrated with sugarcane biorefineries, several themes should be approached for further development of the subject:

Microalgae cultivation

- Investigation on the potential of using other CO₂ sources for use in industrial plants by microalgae, especially flue gas from sugarcane LCM combustion in the CHP unit.
- Development of experimental work on biogas upgrading with microalgae cultivations.
- Establishment of pilot plants of microalgae cultivation with biogas-derived CO₂ integrated with sugarcane mills.

Microalgae downstream

- Further studies on biomass separation techniques (harvest).
- Development of pilot-scale plants of *in situ* transesterification of microalgal lipids.
- Investigation of distinct uses for microalgal biomass:
 - *Carbohydrates*: ethanol fermentation; AD; other bioproducts.
 - *Lipids*: renewable diesel and renewable jet fuel (drop-in hydrocarbons).
 - *Other fractions*: isolation of pigments, nutraceuticals, and high value-added compounds.

AD of vinasse

- Use of the liquid phase (digestate) for use as culture medium.
- Reduction of NaOH/NaHCO₃ consumption for high-yield biogas production.
- Maximization of CH₄ content in biogas (either through process optimization or the use of nanomaterials and/or packed reactors).

Process integration

- Use of liquid fertilizer from vinasse as a nutrient source for microalgae growth.
- Potential use of microalgae debris (biomass after lipid extraction) as a carbon source for biogas production and/or ethanol fermentation.

Modelling, simulation, and sustainability assessment

- Development of rigorous models for CO₂ absorption with solvents using the Aspen Plus® (AspenTech) software, with focus on flue gases from power plants and CHP units in sugarcane mills.
- Development of rigorous models for temperature control in both open and closed PBRs for microalgae growth.
- Development of user-friendly software specific to microalgae cultivation and processing.

- Use of multi-criteria analysis to aid decision-making processes while simultaneously considering environmental and economic impacts.
- Broadening of the understanding of economic impacts through the use of tools that are able to assess the economy as a whole (for example, input-output models).
- Inclusion of land-use change (LUC) impacts in the environmental impacts of ethanol production.

Policymaking

• Inclusion of microalgae-derived biofuels in both publicly- and privately-funded projects for financing.

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Annex A.1

TECNOLOGIA | PESQUISA

Microalgas e Cana-De-Açúcar: Uma Parceria em Potencial

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Resumo

A utilização de microalgas para produção de biocombustíveis apresenta potencial para ser alternativa promissora, uma vez que o seu cultivo proporciona produtividades em carboidratos e lipídios superiores às matérias-primas vegetais convencionalmente utilizadas na obtenção de etanol e biodiesel, respectivamente. No atual estágio de desenvolvimento, a produção autônoma de microalgas em larga escala ainda envolve altos custos e é de difícil viabilização econômica. Uma das estratégias possíveis para que tais processos industriais se apoiem, inicialmente, e se tornem autossuficientes, a longo prazo, é através da sua integração com um sistema sólido e robusto. No Brasil, a produção de microalgas pode se beneficiar largamente de uma parceria com o setor sucroenergético. Usinas de cana-de-açúcar poderiam atuar como fornecedoras de carbono (CO2 e vinhaça) e de utilidades (energia elétrica e vapor de processo) para o cultivo de microalgas, assim diminuindo os custos operacionais da nova unidade.

Summary

The utilization of microalgal biomass for the synthesis of biofuels is a potential promising alternative for the next decades, since its production reaches carbohydrate and lipid productivities far superior to those of vegetable raw material conventionally employed in the obtention of ethanol and biodiesel, respectively. In the current stage of development, large-scale, stand-alone microalgae production still involves high costs and presents marginal economic viability. One of the strategies to promote the feasibility of these processes in the beginning and their self-sufficiency in the future is through its integration to a solid, robust industrial system. In Brazil, microalgae production can largely benefit from a partnership with the sugar-energy sector. Sugarcane mills could act as sources of both carbon (CO₂ and vinasse) and utilities (electrical energy and process steam) for microalgae cultivation, thus reducing operational costs of the new unit.

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Palavra Chave:

Cana-de-açúcar, microalgas, integração de processos, biorrefinaria, bioprodutos

Introdução

Uma biorrefinaria consiste em uma instalação que realiza a conversão da biomassa em diversos produtos de interesse de mercado, como biocombustíveis, bioprodutos e eletricidade. Um dos agentes com maior potencial de utilização são as microalgas, dada a sua rápida taxa de crescimento e grande acúmulo de carboidratos, lipídios, proteínas e outros compostos. Embora seja um dos temas mais pesquisados da atualidade, a produção de microalgas em escala industrial só é viável em determinados casos e para produtos de alto valor agregado. Esse panorama pode ser modificado através da operação conjunta de cultivos de microalgas com unidades de grande porte que possam auxiliar na redução de custos de processo. Nestas condições, existem poucos casos no mundo com uma probabilidade maior de sucesso que na estratégia de integração com a indústria sucroenergética brasileira, capaz de fornecer matéria-prima e energia para a produção de microalgas. Tendo isso em vista, o presente artigo visa a mostrar os principais aspectos referentes ao estabelecimento de um conceito real e plausível de biorrefinarias de microalgas e cana-de-açúcar.

Microalgas

As microalgas são definidas como micro-organismos unicelulares e realizadores de fotossíntese, que podem se desenvolver como células individuais isoladas ou associadas em pequenas colônias e são encontradas tanto em água doce como em ambientes marinhos. Atualmente, são conhecidas mais de 40 mil espécies de microalgas e cianobactérias – micro-organismos unicelulares eucarióticos e procarióticos, respectivamente. Entre os maiores grupos de microalgas, os mais frequentemente citados são conhecidos devido a suas propriedades de fixação de CO₂, tratamento de efluentes ou produção de substratos para síntese de biocombustíveis (KUMAR et al., 2010). A Tabela 1 mostra as produtividades estimadas em óleo para microalgas e cultivos tradicionais. Em determinados casos, pode-se observar que a produtividade teórica em óleo pelas microalgas é de algumas ordens de grandeza maior que por cultivos amplamente difundidos, como a soja.

TABELA 1 – PRODUTIVIDADE ESTIMADA EM ÓLEO PARA DIVERSAS BIOMASSAS

| BIOMASSA | Produtividade em óleo (L/ha.ano) |
|--------------|----------------------------------|
| Milho | 172 |
| Soja | 446 |
| Canola | 1190 |
| Pinhão-manso | 1892 |
| Сосо | 2689 |
| Palma | 5950 |
| Microalgas | 58700-136900 |

Fonte: adaptado de CHISTI, 2007

As microalgas podem ser classificadas e diferenciadas segundo a maneira pela qual se dá o seu metabolismo, utilizando fontes orgânicas ou inorgânicas de carbono com ou sem a presença de luz. Dos quatro tipos de metabolismo possíveis em microalgas, dois são vistos como os mais viáveis para cultivos de microalgas em larga escala: fotoautotrófico e heterotrófico.

O metabolismo fotoautotrófico envolve a utilização de luz solar como a única fonte de energia pelas microalgas, que é convertida em energia química através da fotossíntese juntamente com CO_2 como fonte de carbono. Este regime metabólico é bastante similar à fotossíntese realizada por plantas para seu crescimento. Já o cultivo heterotrófico é definido pela utilização de compostos de carbono presentes no meio de cultura – como açúcares, glicerol e outras moléculas orgânicas de baixa massa molar – como única fonte de energia e de carbono (KUMAR et al., 2010).

Independentemente do regime metabólico, os demais nutrientes necessários ao crescimento das microalgas devem estar presentes no meio de cultura. Além de nitrogênio, fósforo e enxofre, os principais elementos constituintes da matéria orgânica de microalgas (além do carbono), micronutrientes como potássio, magnésio e ferro também são necessários, embora em quantidades menores.

Em larga escala, a obtenção de produtos de interesse comercial a partir da biomassa de microalgas passa por diversas etapas, conforme esquematizado na Figura 1.



O cultivo de microalgas deve ser feito de modo a simular as melhores condições possíveis para crescimento dos microorganismos. Os parâmetros de cultivo influenciam diretamente a composição da biomassa de microalgas, sendo que eles podem ser modulados para uma maior produção de determinado composto. Para tal, são empregados tanto reatores abertos ao meio ambiente quanto reatores fechados, escolha que é feita dependendo da espécie de microalga que é empregada, dos produtos que se deseja obter e do espaço físico disponível.

Em geral, sistemas abertos são os mais utilizados, uma vez que são mais baratos e mais fáceis de construir e operar que biorreatores fechados. Dentre eles, se destacam as lagoas do tipo raceway – canais ovais de recirculação de ciclo fechado com pequena profundidade (20 a 50 cm) e grande comprimento. Apesar de terem baixos requerimentos energéticos e manutenção mínima, estes reatores apresentam grandes perdas de água por evaporação, penetração limitada de luz no meio de cultura, baixa eficiência de utilização de CO_2 e alta possibilidade de

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contaminação do cultivo por espécies invasoras, o que acarreta baixa produtividade da microalga desejada. As limitações dos sistemas abertos levaram ao desenvolvimento de reatores fechados, projetados para o crescimento de microalgas de forma isolada do meio externo. Os principais projetos incluem fotobiorreatores tubulares, de placas paralelas e de colunas, cada um com suas peculiaridades e aplicações específicas. Por serem fechados, estes reatores apresentam bom aproveitamento de luz solar, baixos riscos de contaminação e baixa perda de água. Tais fatores promovem a obtenção de concentrações de microalgas muito maiores que em sistemas abertos e, por consequência, maiores produtividades de biomassa.

No entanto, existem certas desvantagens inerentes, como as altas tensões de cisalhamento sobre as células, o elevado consumo de energia para bombeamento do meio de cultura e os altos custos de construção e operação (estes últimos podendo ser até uma ordem de grandeza maiores que os de reatores abertos). Mesmo assim, a maior produtividade de microalgas pode compensar os custos de produção e justificar o seu uso industrial (BRENNAN e OWENDE, 2010).

A etapa seguinte ao cultivo corresponde à separação da biomassa de microalgas do meio de cultura através do emprego de diferentes operações de separação sólido-líquido, normalmente em dois estágios: uma concentração inicial, realizada por floculação, sedimentação por gravidade ou flotação, e um espessamento através de técnicas como filtração e centrifugação. Após a secagem das microalgas, a ruptura das células é realizada para liberação dos compostos que constituem a biomassa de microalgas através de homogeneizadores de alta pressão, autoclavagem ou lise ácida ou alcalina (BRENNAN e OWENDE, 2010).

Dependendo do composto desejado, os blocos básicos constituintes das microalgas passam por diferentes operações unitárias até que se obtenha o produto final. Lipídios são normalmente extraídos com solventes orgânicos ou em condições supercríticas. A partir deste ponto, o óleo de microalgas pode sofrer as conversões pelas quais os óleos vegetais tradicionalmente passam, como transesterificação para obtenção de biodiesel e epoxidação para síntese de resinas. No caso de carboidratos, a hidrólise de polissacarídeos é realizada, em geral, para liberação de extração de compostos. Há, ainda, a possibilidade da extração de compostos de alto valor agregado, como pigmentos (astaxantina e β -caroteno), ácidos graxos (ácidos docosahexaenoico e eicosapentaenoico) e aminoácidos.

Usinas de cana-de-açúcar como base para integração de processos

Na Figura 2, são mostrados os principais fluxos de massa e energia provenientes de usinas de cana-de-açúcar que poderiam ser empregados por processos de produção de biomassa de microalgas. Esses pontos serão detalhados a seguir.

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Fonte de Carbono

Através da fotossíntese, microalgas são capazes de fixar carbono contido em diferentes fontes: (1) CO_2 atmosférico; (2) CO_2 de gases de exaustão; (3) CO_2 fixado na forma de carbonatos solúveis (KUMAR et al., 2010).

Para cultivos autotróficos, os níveis atuais de CO_2 atmosférico (de cerca de 400 ppm) não são suficientemente elevados para sustentar altas taxas de crescimento de microalgas ou altas densidades celulares, sendo que alimentações gasosas com maior concentração de CO_2 devem ser empregadas. Tendo isso em vista, usinas de cana-de-açúcar são fontes interessantes de CO_2 por apresentarem, pelo menos, duas correntes gasosas com alto teor do gás.

A mais abundante delas é originada na combustão de bagaço ou palha em caldeiras para geração de vapor. O gás de exaustão obtido contém cerca de 14% (v/v) de CO₂, podendo ser injetado nos biorreatores para crescimento das microalgas após remoção de material particulado e resfriamento. Outra corrente consiste na saída gasosa dos fermentadores, que é composta por CO₂ em alta pureza – acima de 98% (v/v). Nesse caso, é possível que uma etapa



de diluição da corrente com ar atmosférico ou com o gás de exaustão da caldeira seja necessária anteriormente à sua injeção no cultivo de microalgas.

No caso de microalgas heterotróficas, o principal efluente líquido de usinas de cana-de-açúcar, a vinhaça, pode ser utilizado como fonte de carbono nos cultivos. Apesar de a fertirrigação com vinhaça ser altamente difundida no Brasil e ser permitida pela atual legislação, ela é considerada como o método mais simples para se lidar com esse efluente abundante (MORAES et al., 2014), sendo o seu uso em cultivos de microalgas uma aplicação mais nobre.

As principais características da vinhaça obtida a partir do processamento de cana-de-açúcar são mostradas na Tabela 2. Além do carbono, denotado pelas demandas biológica (DBO) e química (DQO) de oxigênio, as microalgas podem se valer dos outros compostos presentes na vinhaça como nutrientes para seu crescimento: nitrogênio, fósforo, potássio e, em menor quantidade, cobre, cádmio e ferro.

TABELA 2 – COMPOSIÇÃO DE VINHAÇAS DE DIFERENTES FONTES DE AÇÚCAR

| | Caldo de Cana | Melaço de cana |
|-----------|---------------|----------------|
| DBO (g/L) | 16,7 | 39,5 |
| DQO (g/L) | 30,4 | 84,9-95 |
| N (mg/L) | 102-628 | 153-1230 |
| P (mg/L) | 71–130 | 1–190 |
| K (mg/L) | 1733–1952 | 4893-11000 |

Fonte: adaptado de ESPAÑA-GAMBOA et al., 2011

Fonte de Energia

Em geral, a principal necessidade energética em plantas de microalgas se resume a energia elétrica, utilizada no acionamento de equipamentos: impelidores em reatores abertos e fechados, bombas para o deslocamento de meio de cultura, de suspensão de microalgas ou de água de reposição, centrífugas para separação de biomassa, sopradores para injeção de CO₂ no cultivo ou para sistemas de separação por flotação e extratores de lipídios.

O uso de vapor de processo pode ser necessário em casos específicos, como quando do emprego de tecnologias de conversão da biomassa de microalgas (produção de biodiesel, por exemplo) ou na esterilização de meios de cultura com carbono orgânico para cultivos heterotróficos. A integração entre essas unidades também pode se valer de correntes com calor residual provenientes da usina de cana-de-açúcar para prover parte da energia térmica da produção de microalgas. Opções interessantes para tal são a vinhaça, que sai da coluna de retificação a alta temperatura, e o vapor vegetal obtido na concentração do caldo de cana-de-açúcar.

Conclusões

Nesse artigo, foi apresentado o potencial de integração mássica e energética entre os processos de processamento de cana-deaçúcar e de microalgas para viabilização técnico-econômica do último. No entanto, para que este conceito de biorrefinaria seja colocado em prática, é imperativo que o setor esteja aberto a novas tecnologias, principalmente àquelas que possam trazer maior segurança à indústria sucroenergética em situações de mercado adversas, assim como prover retornos financeiros ainda maiores que os experimentados atualmente.

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Annex A.2

Table A.2.1 – General parameters for microalgae production and processing.

| Parameter | Value | Reference | |
|---|--|--|--|
| Operation period | 330 days | Assumption | |
| Average daily light period | 12 h | Assumption | |
| CO ₂ required for algae growth | 1.83 kg CO ₂ /kg microalgae | Chisti (2007) | |
| Microalgae composition (proteins; lipids; carbohydrates) | 50%; 30%; 20% | Assumption | |
| Harvest - Settling | | | |
| Overall efficiency | 90% | Davis et al. (2016) ^a | |
| Final microalgae concentration | 15 kg/m ³ | Uduman et al. (2010) ^b | |
| Energy consumption | 0.1 kWh/m ³ | Uduman et al. (2010) ^c | |
| AlCl ₃ consumption | 0.01 kg/m ³ | Davis (2011) ^d | |
| Harvest - Centrifugation | | | |
| Overall efficiency | 95% | Mohn (1988) ^e | |
| Final microalgae concentration | 220 kg/m ³ | Mohn (1980) ^e | |
| Energy consumption for high- density cultivations | 8 kWh/m ³ | Mohn (1980) ^e | |
| Energy consumption for low- density cultivations | 16 kWh/m ³ | Extrapolation from Mohn (1980) ^f | |
| Culture medium blowdown after harvest | 5% | Assumption | |
| Supercritical lipid extraction | | | |
| Extraction efficiency | 98% | Personal | |
| Final meal moisture | 15% | communication with | |
| Power consumption | 0.23 MW/tonne microalgae | industrial supplier | |
| Biodiesel production | | | |
| Biodiesel yield | 0.956 kg/kg oil | Aspen Plus® simulation | |
| Glycerin output | 0.118 kg/kg oil | Aspen Plus® simulation | |
| Operational level (stream factor) | 90% | Assumption | |
| Power consumption for water recirculation | 0.8 kW/acre | Davis et al. (2016) ^g | |

^a Target dewatering efficiency for large-scale algal facilities. Main assumptions: initial microalgae concentration of 0.5 g/L, concentration factor of 20, and settlers of trapezoidal profile.

^b Upper limit for total solids in gravity settlers.

^c Energy consumption in low lamella separators.

^d Minimum AlCl₃ dosage to initiate microalgae flocculation (*Nannochloris oculata*, at pH 5.3, and initial cell concentration of 10⁷ cells/mL) determined by Davis to be 0.025 g/L of AlCl₃.6H₂O.

^e Parameter for a continuous decanter bowl centrifuge, concentration factor of 11, tested with a series of microalgae species (*Scenedesmus* genre, *Coelastrum proboscideum*, among others). ^f For initial microalgae concentrations lower than 2 g/L, a higher energy consumption was considered.

^g Estimated pumping power for 12-inch pipes, elevation of 7.3 m and a 10% head loss.

Table A.2.2 – Main parameters for modeling and simulation of photoautotrophic growth of microalgae in covered raceways.

| Parameter | Value | Reference |
|--|-----------------------|--|
| Microalgae productivity | 250 kg/ha.day | Davis et al. (2011) ^a |
| Final microalgae concentration | 0.5 kg/m ³ | Davis et al. (2011) ^a |
| Growth surface area | 0.81 ha/raceway | Rogers et al. (2014) ^b |
| Raceway depth | 0.15 m | Assumption |
| Mixing energy | 0.22 W/m^2 | Rogers et al. (2014) ^c |
| CO ₂ uptake | 90% | Brown (1996) ^d |
| Area increase due to auxiliary equipment | 15% | Lohrey and Kochergin (2012) ^e |

^a Consideration for large-scale photoautotrophic growth of a generic microalga species in open ponds, given that the algal facility receives sufficient amounts of solar radiation.

^b Determined pond size so as not to exceed paddlewheel capability. Broad study considerations: large-scale photoautotrophic growth of a generic microalga species (with composition following the Redfield ratio) in open ponds, with average microalgae productivity of 150 kg/ha.day, culture density of 0.5 g/L, 10% harvesting rate, 80% lipid extraction efficiency, and 25% lipid content.

^c Baseline scenario of the study for energy consumption in paddlewheels: raceway velocity of 0.3 m/s and liner manufactured in polyethylene.

^d Minimum CO₂ capture efficiency for large open ponds operated under optimum conditions.

^e Consideration for large-scale photoautotrophic growth of microalgae in covered raceway ponds in integration with sugarcane mills.

Table A.2.3 – Main parameters for modeling and simulation of photoautotrophic growth of microalgae in flat-panel PBRs.

| Parameter | Value | Reference |
|--|-----------------------------|---|
| Microalgae productivity | 1.25 kg/m ³ .day | Davis et al. (2011) ^a |
| Areal footprint | 200 m ³ /ha | Davis et al. (2011) ^a |
| Final microalgae concentration | 4 kg/m^3 | Davis et al. (2011) ^a |
| Mixing energy | 53 W/m ³ | Sierra et al. (2008) ^b |
| CO ₂ uptake | 95% | Improvement over CO ₂ uptake in raceways ^d |
| Area increase due to auxiliary equipment | 15% | Lohrey and Kochergin (2012) ^c |

^a Consideration for large-scale photoautotrophic growth of a generic microalga species in closed PBRs, given that the algal facility receives sufficient amounts of solar radiation.

^b Required power supply to ensure an adequate mass transfer capacity to avoid build-up of photosynthetically-derived O_2 . Study considerations: maximum biomass productivity of 2 g/L.day, with 50% carbon content in the biomass and a photosynthetic ratio of 1 mol O_2 /mol CO_2 .

^c Since Brown (1996) indicates possible carbon capture efficiencies between 90-99% in large open ponds, the estimated figure of 95% can be considered a conservative one for the performance of closed PBRs.

^d Consideration for large-scale photoautotrophic growth of a generic microalga species in covered raceway ponds in integration with sugarcane mills.

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| | |

| Parameter | Value | Reference |
|--|---------------------|--|
| Initial microalgae concentration | 1 kg/m^3 | Mattos and Bastos (2016) ^a |
| Final microalgae concentration | 4 kg/m ³ | Mattos and Bastos (2016) ^a |
| Batch time | 30 h | Mattos and Bastos (2016) ^a |
| Reactor H/D ratio | 1.5 | Assumption |
| Mixing energy | 1 hp/m ³ | Personal communication with Paulo Mantelatto (2016) |
| ^a Microalga species: Dasmodasmus sp.: Inoculum growth: BGN medium pH 7.5, 25 °C | | |

Table A.2.4 – Main parameters for modeling and simulation of heterotrophic growth of microalgae in large-scale stirred vessels.

^a Microalga species: *Desmodesmus* sp.; Inoculum growth: BGN medium, pH 7.5, 25 °C, aeration of 1 VVM, $3 \times g$ mechanical stirring, photo flux of 45 µmol/m².s up to 1 g/L microalgae concentration; Heterotrophic cultivation: vinasse at pH 7.0, 25 °C, aeration of 1 VVM, $3 \times g$ mechanical stirring.

Annex A.3

Table A.3.1 – Main parameters for the AD of sugarcane vinasse and upgrading of biogas to biomethane.

| Parameter | Value | Reference |
|--|---|--|
| Vinasse COD | 21 kg/m ³ | Moraes et al. (2014) ^a |
| COD removal | 85% | Personal communication with Bruna Moraes (2016) |
| CH ₄ production | 0.32 m ³ CH ₄ /kg COD removed | Personal communication with Bruna Moraes (2016) |
| Biogas composition, v/v (CH4; CO ₂ ; H ₂ S) | 76%; 23%; 1% | Improvement over Moraes et al. (2014) values ^b |
| Volumetric organic load (VOL) | 26.5 kg/m ³ .day | Souza et al. (1992) ^c |
| Diesel/biomethane equivalence | 0.722 kg diesel/Nm ³ biomethane | Heating value equivalence |
| PSA unit power consumption | 0.25 kWh/Nm ³ | Petersson and Wellinger (2009) ^d |

^a Typical value for vinasse generated in autonomous ethanol distilleries.

^b Conservative values considered in the study, v/v (CH₄; CO₂): 60%; 35%.

^c Average value for 50 days of operation of a 75-m³ pilot UASB reactor of São Martinho Mill (Pradópolis, SP), using *in natura* vinasse as the carbon source.

^d EE consumption for raw biogas compressed to 8 bar, with previous removal of H_2S , and for the production of biomethane with 96+% v/v CH₄.