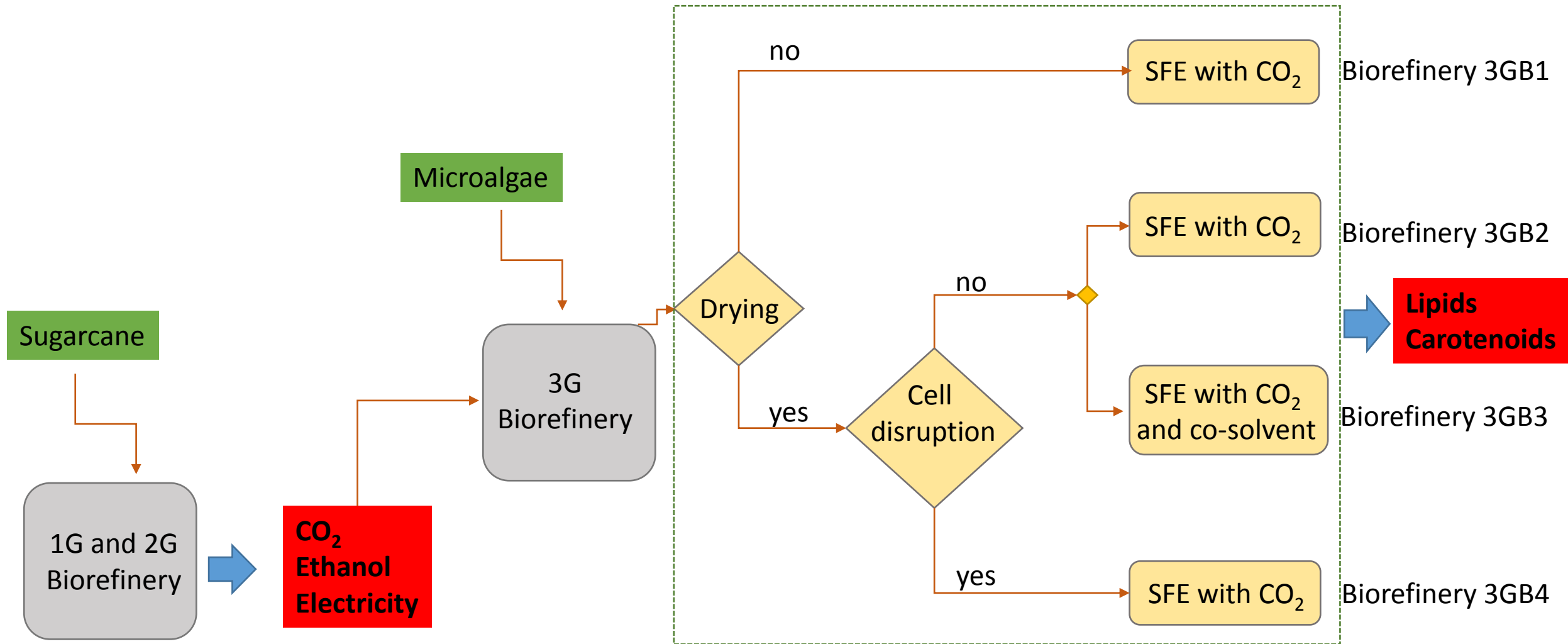


*Investigated Supercritical Fluid Extraction (SFE) processes*



### **Highlights**

- Synergy between microalgae supercritical CO<sub>2</sub> extraction and sugarcane biorefinery
- Development of a supercritical fluid-based microalgae-sugarcane biorefinery concept
- Use of heat, electricity, ethanol and CO<sub>2</sub> generated from a sugarcane biorefinery

# Product Diversification in the Sugarcane Biorefinery Through Algae Growth and Supercritical CO<sub>2</sub> Extraction: Thermal and Economic Analysis

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## ABSTRACT

The sugarcane sector in Brazil has undergone a major modernization in the last thirty years. Embracing the biorefinery concept, this sector is investigating bioproduct diversification and mostly putting a lot of effort and investment on second generation ethanol production. In this context, the investigation of the integration of a third generation biofuel production using microalgae to the sugarcane biorefinery seems an important starting point. This study evaluates the integration of microalgae growth and processing to a sugarcane biorefinery producing first and second generation ethanol using process simulation tools. Microalgae are cultivated using CO<sub>2</sub> produced during fermentation of ethanol and it is processed using supercritical fluid extraction technology in order to obtain lipids rich in high added-value compounds, carotenoids. The results showed that the integration of microalgae biomass processing without previously drying with the sugarcane biorefinery producing ethanol is not attractive from the thermo-economic point. When considering the extraction of dried microalgae the extraction process could be thermal integrated to the sugarcane biorefinery producing ethanol without the need of buying external fuel. The amount of CO<sub>2</sub> used as solvent to the supercritical fluid extraction was the main factor that influenced the economic viability of the process. When a microalgae pretreatment by cell disruption was accomplished or an extraction co-solvent, ethanol, was used, it was possible to decrease the amount of CO<sub>2</sub> used in the process and an increase in process yields was consequently achieved. The use of a co-solvent in the extraction increased in 1.4 and 2.4 times lipids and carotenoids extraction, respectively, and presented a lower investment when comparing with microalgae extraction without cell disruption.

**KEYWORDS:** process simulation; supercritical fluid extraction; cellulosic ethanol; biofuel; pinch analysis; process design.

## Abbreviations

$\dot{m}$  mass flow [kg/year]

$\dot{v}$  volume flow [L/year]

1G first generation

2G second generation

3G third generation

carot carotenoids

$c_{\text{fix}}$  carbon fixation

COM COst of Manufacturing

ENP electricity net power [kWh]

FC Fixed Costs

GE General Expenses

$i$  interest rate

LHV Low heating value [MJ/kg]

ma microalgae

MATLAB MATrix LABoratory

MUSD million US dollars

$n$  Project lifetime

S/F Solvent mass to Feed mass ratio

SFE    Supercritical fluid extraction

VC    Variable Cost

## **1 Introduction**

The sugarcane sector moves a big share of the Brazilian economy. This industry conventionally produces sugar, ethanol and electricity. Nevertheless, in the last decades, it has undergone a major modernization to optimize the production process and envision increasing biofuel and other bioproducts production using process by-products and/or process wastes [1]. Hydrolysis of cellulose from sugarcane bagasse is one important topic under research and with few trial plants already working [2-3], as hydrolyzing cellulose produces sugar monomers that can be converted to ethanol enabling higher ethanol production per agriculture area. The economic feasibility of cellulosic ethanol, also called second generation ethanol, production processes is still a challenge when compared to conventional ethanol production, but product diversification plays an important role in enhancing its economic feasibility [4,5]. Consequently, the sugarcane sector has embraced the biorefinery concept and the search for economically and environmentally feasible processes integrated to the conventional mills are being evaluated by researchers and the industry.

Microalgae culture has been proposed as a method for production of biofuels coupled to CO<sub>2</sub> fixation as a greenhouse gas mitigation strategy [6]. A significant research effort, starting in the late 1970's, promoted microalgae use as a renewable energy resource to a variety of biofuel end products (e.g. methane, hydrogen, ethanol, biobutanol, renewable diesel, gasoline and jet fuel) [7]. Compared to other biomass types, the use of microalgae is interesting as they present high photosynthesis efficiency, offer the opportunity to utilize land and water resources that are, currently, unsuited for any other use [8,9]. Microalgae contain compounds such as lipids, pigments (carotenoids), proteins and carbohydrates, which all can be used for different markets. A smart development of microalgae-biorefinery concept would take advantage of biomass

composition and consider high added-value compounds recovery, as carotenoids recovery, prior biofuels production, creating an important revenue generation.

The integration of microalgae in the sugarcane biorefinery as a third generation biofuel production process has been proven to be synergetic by some authors, providing an important starting point [10-11]. Most of the studies evaluated the biodiesel production from algae integrated to the conventional ethanol and/or sugar production processes resulting in a positive environmental impact for the sugarcane biorefinery. However, the economic attractiveness of the process was not a common sense between the authors. Moncada et al. [10] calculated a high profitability for the integrated microalgae-sugarcane biorefinery. Meanwhile, Souza et al. [11] highlighted the significant technical-economic barriers associated with algae biodiesel and therefore the need of economic incentives and the production of other algae-based products with higher benefit, such as carotenoid pigments. In this extend, carotenoids extraction directly from wet microalgae could be an interesting route as dewatering microalgae requires a great amount of energy and is responsible for 20% to 30% of lipid extraction cost considering conventional solvent extraction technology [12].

Analyzing the prospection of the microalgae-sugarcane biorefinery using computational simulation tools in order to access energy requirements and costs evaluating different biofuels and bioproducts/processes possibility is an important step to overcome bottlenecks and propose a feasible integrated biorefinery. In this context, the present study aims at evaluating the integration of first, second and third generation biofuel production in a biorefinery producing ethanol from sugarcane juice and bagasse and extraction products from microalgae, grown from fermentation CO<sub>2</sub>. The proposed biorefinery concept will be analyzed thermal-economically using flowsheet modeling software and process integration will be performed through Pinch analysis. It will be



evaluated the roll of product diversification in the sugarcane biorefinery by evaluating a high added-value product, carotenoids, production from microalgae using supercritical technology comparing different operational strategies (direct use of wet biomass, use of biomass pretreatment and use of ethanol as co-solvent during the supercritical CO<sub>2</sub> extraction) simultaneously with biofuels. Supercritical fluid extraction (SFE) has demonstrated to be an ideal clean technology to be used as part of a holistic biorefinery for the recovery of bioactive compounds from plants and other vegetal materials, prior to its chemical conversion, indicating that SFE can be effectively used during the first-step in biorefinery concepts [13]. Additionally, the benefits of constructing a SFE plant in close proximity to an alcoholic fermentation facility that produces high purity CO<sub>2</sub> as a by-product and ethanol, was already recently demonstrated by our research group [14,15], thus this paper aims to contribute to analyze the impact of some ideas of different researchers to guide future investigation towards the more promising direction.

## **2 Material and methods**

### **2.1 Process description**

The proposed microalgae-sugarcane biorefinery is evaluated following the simplified process representation (Fig. 1). In this biorefinery it was considered the production of electricity, first generation ethanol, second generation ethanol from sugarcane bagasse and lipids/carotenoids from microalgae. Four different configurations were evaluated regarding the Supercritical Fluid Extraction (SFE) process of lipids/carotenoids and the biorefinery with microalgae growth and processing was compared to the biorefinery without microalgae production. The summary of the technologies listed for each case studied are displayed in Table 1.

### **2.1.1 Ethanol production in the sugarcane biorefinery**

The ethanol production process, both first and second generation ethanol, in the sugarcane biorefinery was simulated using the commercial flowsheeting software Aspen Plus [16].

For the first generation ethanol production, the process is comprised of the following steps: sugarcane cleaning, juice extraction, juice treatment and concentration, glucose fermentation, ethanol distillation and dehydration. For process simulation, it was considered the available technology in modern ethanol distilleries in Brazil, such as sugarcane dry cleaning, concentration in multi-effect evaporators, sterilization of the sugarcane juice before entering the fermentation system, ethanol dehydration using monoethylene glycol. The description of the model for the conventional ethanol production, as well as the property models used, was fully described in details elsewhere [5,17]. Sugarcane bagasse, produced after juice extraction in the conventional ethanol production process, is used 50% to cellulosic ethanol production. The remaining is used 41% as fuel for heat and power production and 9% to other uses. In the second generation ethanol production process, the bagasse goes through a physical and chemical treatment to break the lignin-cellulose-hemicellulose matrix and increase cellulose availability to the hydrolysis process. During the enzymatic hydrolysis, cellulose is converted into sugar monomers and the resulting sucrose solution is concentrated. The concentrated solution is then mixed with the concentrated juice obtained at the first generation process and the resulting solution is sent to fermentation. From this point, first and second generation ethanol are sent to the distillation and dehydration system of conventional ethanol production. Table 2 shows the main parameters considered for the simulation.

### **2.1.2 Process waste to energy as fuels and the cogeneration system**

For the cogeneration system, the following were considered as fuels: sugarcane leaves (33 t/h), 41% w/w of sugarcane bagasse, lignin cake and biogas. Lignin waste generated at the hydrolysis process. Liquid process waste with high organic load was considered to biogas production in an upflow anaerobic sludge blanket biodigester as described elsewhere [22]. The cogeneration system was modeled as a steam-based cycle including condensing extraction steam turbines supplying heat and power to the process. Live steam considered at 793 K and 9 MPa and condensing extraction steam turbines are simulated. The entire system is integrated with the process design when the heat cascade problem is solved.

### **2.1.3 Microalgae growth in an open pond system**

A mathematical model for cultivation of algae in open pond developed in MATLAB software [23] was used, the model details are found in [21]. The microalgae cultivation model is developed considering an open pond system in which the water surface is exposed to solar radiation using an equation oriented modeling approach. In the cultivation model, the open pond is provided with water, a CO<sub>2</sub>-rich gas stream and nutrients. The carbon consumption rate is dictated by the microalgae growth process and the CO<sub>2</sub>-rich gas injection is minimized in order to close the CO<sub>2</sub> balance and to permit the constant growth process without carbon shortage. The total nitrogen is not considered as a limiting factor for the photosynthesis process, being kept at a constant level with addition of ammonium as nitrogen source. The occupied area by the open pond can be changed to maximize the use of CO<sub>2</sub> available. The model depends on the following parameters: the area occupied by the open pond, the depth of the open pond,

the location and weather data at this location (irradiation, temperature), an initial microalgae concentration and the algae characteristics. The microalgae characteristics are the ones from *Chlorella vulgaris* and the weather data are the ones for Petrolina (Brazil). The assumed microalgae composition of *Chlorella vulgaris* is given in Table 2. The CO<sub>2</sub> source for the algae growth is the gases produced in the fermentation process for ethanol production, considering a 5% loss. The CO<sub>2</sub> is injected in the open pond during the day and is discharged to the atmosphere during the night.

#### **2.1.4 Lipids and carotenoids extraction from microalgae using supercritical CO<sub>2</sub>**

It was investigated four technological pathways to microalgae processing using SFE (Fig. 2):

Biorefinery 2G: producing ethanol and electricity from sugarcane,

Biorefinery 3GB1: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from wet microalgae with supercritical CO<sub>2</sub>, Biorefinery

3GB2: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub>,

Biorefinery 3GB3: Biorefinery producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub> with ethanol as co-solvent,

Biorefinery 3GB4: Biorefinery producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried cell-disrupted microalgae with supercritical CO<sub>2</sub>.

The simulation of the SFE plant was performed using the commercial flowsheeting software Aspen Plus [16].

In all alternatives evaluated, it was considered a prior dewatering of the biomass to achieve solid concentration of 3%. When biomass was used in the wet SFE system (Biorefinery 3GB1), no more preprocessing techniques were considered. When biomass was used with low moisture content, it was considered two sequential centrifuges to decrease water content to 67 % and 44 %, consecutively. The biomass was then air dried using heated air at 373 K until achieve a 8 % of moisture. When cell disruption was considered (Biorefinery 3GB4), a milling process was simulated at the MATLAB programming level [23], so the electricity demand for this process was taken into account.

In the SFE process, CO<sub>2</sub> solvent sent to the process was initially cooled to 247 K and compressed to the desired pressure. It was then heated to the extraction temperature reaching the supercritical conditions. Later, the extraction vessel was packed with the vegetable biomass. Then supercritical CO<sub>2</sub> was passed through the vessel. As the process was studied in a stationary regimen, it was considered multiple SFE unities working in parallel to achieve a continuous inlet and outlet material flow. For the analysis, it was considered 2 supercritical extractors operating in parallel. After the extraction process, the lipid extract diluted in supercritical CO<sub>2</sub> was sent to a depressurization tank to separation. At this stage, the pressure is reduced to 7 MPa and temperature is set at 302 K, gasifying the carbon dioxide and separating it to be recycled to the process.

When a co-solvent extraction (Biorefinery 3GB3) was considered, ethanol was used in a fraction of 5 % of the solvent inlet flow. It was heated and pressurized to the desired conditions, and then mixed with CO<sub>2</sub> before entering the extraction vessel. After extraction, CO<sub>2</sub> is separated in two flash tanks working in the temperature and pressure to maximize separation and minimize cost [24], first vessel at 4 MPa and 303 K and

second at 0.1 MPa and 298 K. Ethanol was separated from the extracted compounds by evaporation and recycled to the process. Table 3 summarizes the parameters used in simulation.

## **2.2 Process modeling**

Process modeling is developed following a systematic process design methodology that is described in detail elsewhere [5]. Initially, data is gathered on the processes to be evaluated through literature. Then, mass balance, energy balance and compounds specific equations are modeled in Aspen Plus flowsheeting software [16]. A thermo-economic model of the process is built in MATLAB [23]. In the thermo-economic model, energy integration is performed on the basis of the pinch analysis methodology [27]. The optimal utility integration is obtained when the combined production of fuel, power and heat are maximized, which minimizes the operating cost by solving the heat cascade problem using a mixed integer linear programming technique developed by Marechal and Kalitventzeff [28]. The economic model consists in the evaluation of the total investment cost. The major process units are sized and their purchase cost is calculated using correlations from literature [29] and [30]. For more details, see supplementary material. After completing the models construction, the alternatives studied are evaluated based on the process performance indicators.

## **2.3 Process performance indicators**

The process was analyzed based on productivity, energetic and economic performance indicators.

**Productivity performance indicator:** The productivity performance indicator was calculated based on the mass balance results of the flowsheeting software used. It was evaluated the biorefinery products and intermediary products productivity per mass of sugarcane used in the process.

**Energetic performance indicator:** The energetic performance indicators considered were the total heat demand of the analyzed biorefinery, calculated after energy integration using the Pinch method and optimization of utility use [28], and the electricity net power (ENP) (Eq. 1) of the biorefinery.

$$ENP = \dot{E}_{produced} - \dot{E}_{consumed} \quad \text{Eq. 1}$$

**Economic performance indicator:** To evaluate the process in terms of economic parameters, the performance indicators calculated were total investment cost and cost of manufacturing (COM), as presented hereafter.

To calculate the total investment was calculated by the economic model as described in “Section 2.2 Process modeling”. In the model, the cost the major process equipment are roughly sized and their purchase cost is calculated and adjusted to account for specific process pressures and materials using correlations from literature [29,30]. The total investment is then calculated using multiplication factors to take into account indirect expenses like installation costs, contingencies and auxiliary facilities.

COM estimation for the biorefineries was calculated based on the methodology of Turton et al. [29]. Variable cost (VC), fixed costs (FC) and general expenses (GE) are calculated in terms of five main costs: total investment cost, cost of utilities, cost of operational labor, cost of waste treatment and cost of raw materials. The COM was calculated as presented in Equation 2.

$$COM = (VC + FC + GE) * (1 + 0.03COM + 0.11COM + 0.05COM) \quad \text{Eq. 2}$$

In which 0.03COM represents the royalties; 0.11COM the distribution and selling and 0.05COM the research and development investments. To enable a better visualization of the impact of each process, ethanol production 1G and 2G and microalgae production and processing, at the COM, it was calculated separating the processes as follow

COM<sub>sc</sub> – COM related to the sugarcane use, is the COM calculate for the 1G and 2G ethanol production process. It was calculated considering the total investment calculated in Biorefinery 2GB and as raw-material sugarcane, sugarcane leaves and enzymes. The number of workers necessary to this part of the process was calculated in 16 and the cost of each worker is of 52900 USD/year [29].

COM<sub>ma</sub> – COM related to the microalgae use, is the COM calculate for the microalgae growth and extraction process. It was calculated considering the total investment calculated for each Biorefinery 3GB subtracting the investment calculated for Biorefinery 2GB. Raw-materials considered were electricity net power, microalgae nutrients (diammonium phosphate and NH<sub>3</sub>) and cold demand under 298 K. The number of workers for this block of the process was calculated in 5 [29].

It was also evaluated the COM divided by the amount of products produced in a year as presented in Equations 3, 4 and 5, being named specific COMs.

$$COM_{ethanol} = \frac{COM_{sc}}{V_{ethanol}} \quad \text{Eq. 3}$$

$$COM_{lipid} = \frac{COM_{ma}}{m_{lipid}} \quad \text{Eq. 4}$$



$$COM_{carot} = \frac{COM_{ma}}{m_{carotenoid}} \quad \text{Eq. 5}$$

Table 4 shows the data used to perform the economic analysis.

### 3 Results and discussion

#### 3.1 Thermal integration of the proposed Biorefineries

Fig. 3 shows the gran composite curves for each biorefinery configuration evaluated. Heat demand of the process is integrated in order to decrease the heat consumption to the minimum possible for all configurations. It is possible to see that Biorefinery 2GB presents good heat integration, it is self-sufficient in terms of energy and uses less energy than the available by the burning of the fuels available. It is used as fuel for the cogeneration system: sugarcane leaves, part of sugarcane bagasse (41% of the total bagasse produced, while 50% is sent to the 2G process and the remaining is used in different parts of the process), biogas produced from process wastes (xylose stream from cellulose hydrolysis process and vinasse from ethanol purification) and lignin waste (from cellulose hydrolysis). From the total heat supplied to the process 38% comes from the leaves, 25% from the burned bagasse, 19% from biogas and 18% from the lignin cake. The higher heat consumption are found in the ethanol purification columns and the sugar concentration after cellulose hydrolysis. Concerning the produced glucose by cellulose hydrolysis, it is necessary to concentrate the cellulose hydrolysate before sending it to fermentation. The multiple effect evaporators (region right under 400 K), for both 1G and 2G ethanol production, integration is optimized in order to reduce to the minimum steam consumption possible [35]. The optimization results showed that the best integration could be found considering that only the 1<sup>st</sup> and

3<sup>rd</sup> effects of the multiple effect evaporator for juice concentration (1G) was activated and that only the 1<sup>st</sup> effect for hydrolysate concentration (2G), when employing 50% of bagasse to 2G ethanol production was activated, being the evaporators integrated with the dehydration system between 348 and 415 K, and with the distillation between 341 and 388 K. Then, the total heat demand of the Biorefinery 2GB was  $2.1 \times 10^2$  MW.

When the SFE of wet biomass is considered (Biorefinery 3GB1), the heat demand of the overall process increases 3.2 times in comparison with the stand-alone sugarcane biorefinery (Biorefinery 2GB), which leads to the need of 8.1 times more sugarcane bagasse for the cogeneration system. The thermal demand for CO<sub>2</sub> heating is 7.1 times higher than the highest heat demand of the sugarcane biorefinery. Comparing the thermal demand for CO<sub>2</sub> heating with the average heat flows of the Biorefinery 2GB, of which 96% is under 31 MW, it would be 31.2 times higher. This high thermal demand is not due to the high temperature increase as extraction is taken place at 333 K [25] but due to the large CO<sub>2</sub> mass-flow necessary for the process. As a lot of thermal energy is necessary for the SFE process at Biorefinery 3GB1, the optimum solution to the multiple effect of the evaporation system was to concentrate only using the 1<sup>st</sup> effect of the multiple effect evaporator of 1G and 2G. To enable an efficient SFE from wet microalgae integration to the sugarcane 1G and 2G biorefinery it would be necessary to investigate the use of lower solvent mass to feed mass ratios (S/F) during the supercritical CO<sub>2</sub> extractions.

When microalgae are previously dewatered and dried the total flow of CO<sub>2</sub> necessary to extraction reduces drastically [26], 16.7 times for Biorefineries 3GB3 and 3GB4 and 13.3 for Biorefinery 3GB2. With that, it is possible to integrate the SFE process with the 1G and 2G ethanol production without the need of external fuel to supply the heat demand. The grand composite curves for the process when low moisture microalgae are

used for SFE present similar format to Biorefinery 2GB with small changes under 370 K. It was possible to notice that drying biomass was not a barrier to the thermal integration of the process. The integration of the SFE process with the ethanol process occurs between 285 and 370 K. The SFE process exchange heat with different low temperature processes of the ethanol production as heat-flows from fermentation and second generation ethanol production. The heat demand of the SFE process after thermal integration was of 52.6, 69.2 and 80.8 MW for Biorefineries 3GB2, 3GB3 and 3GB4, respectively. For the Biorefinery 3GB2 a higher amount of CO<sub>2</sub> solvent is used as a higher S/F is considered, even though it presents a better thermal integration reducing the cooling demand of the integrated biorefinery. The introduction of an ethanol as co-solvent in the supercritical CO<sub>2</sub> extraction process increases the thermal demand of the SFE process but with the energy integration, no increase on the total heat demand of the biorefinery is observed.

### ***3.2 Biorefinery productivity parameters***

The results for the raw-material consumption and productivity of final and intermediary products are presented in Table 5. Intermediary products are consumed in the process. First and second generation ethanol production in a biorefinery perspective, as studied in the Biorefinery 2GB, using process wastes as fuel to the cogeneration system enables an energy self-sufficient process without the need of external fuel or electricity. By using 50 % of the generated bagasse after crushing to second generation ethanol production, the overall ethanol production increased in 11 %. The cultivation of algae using the fermentation CO<sub>2</sub> results in a productivity of 8.9 t of microalgae per hour (in dry basis, d.b.) with a total occupied area for the open pond of 850 ha. During the year, the mean concentration of algae calculated was 344.6 g/m<sup>3</sup> and the diammonium

phosphate and nitrogen consumption was of 6.2 and 10.6 t/ha. By algae cultivation it was possible to capture 64.2 kg of CO<sub>2</sub>/t sugarcane resulting in a reduction of 161,832.9 t of CO<sub>2</sub>/year. Although CO<sub>2</sub> produced by fermentation is considered in many environmental analysis biogenic, as it is related to the natural carbon cycle, decreasing CO<sub>2</sub> production has always and important significance in the environmental footprint of the process. Although microalgae cultivation being known for its possible use of marginal land, in the case of the sugarcane biorefinery, there are few not used areas as the mills are located in the middle of the sugarcane cultivation. The undesired areas for sugarcane cultivation are usually slope areas, in which mechanical harvesting is not possible. These areas would also not be compatible with open pond installation. Therefore, unless the sugarcane mill presents some area not used for sugarcane cultivation for a determined reason, the installation of the open pond system would have an impact on the total amount of sugarcane inlet in the process. Sugarcane plantation usually produces 75 t of sugarcane/ha [36]. With the installation of the open pond system, it would be displaced 63.75 t of sugarcane plantation. This means 5.3 days less of work in the biorefinery, reducing in 2.9 % the yearly ethanol and electricity production, which would affect in 2.9 % the overall economic benefit of the biorefinery. Although the installation of the open pond system would probably interfere in the productivity of the biorefinery, all analysis were accomplished considering no reduction on the working days.

The results of lipids and carotenoids extraction from microalgae using SFE technology are displayed for Biorefineries 3GB1, 3GB2, 3GB3 and 3GB4 (Table 5). Initially, wet microalgae SFE extraction using CO<sub>2</sub> was investigated (Biorefinery 3GB1). Wet microalgae extraction could be interesting as dewatering microalgae requires a great amount of energy and is responsible for 20 % to 30 % of lipid extraction cost

considering conventional solvent extraction technology [12]. The wet microalgae processing could be an interesting alternative of biomass valorization by extraction of high added-value compounds prior to synthetic natural gas (SNG) production in a supercritical water gasification system [21]. The results for the biorefinery using wet SFE showed that when this technology is considered the biorefinery is not self-sufficient in thermal demand and extra bagasse is necessary to fulfill the thermal demand. The overall amount of lipids produced is also lower than when considering dried microalgae as biomass to the SFE (Table 5). When a previews microalgae dewatering and drying is considered, no external bagasse is necessary to be used as fuel to the cogeneration system, but electricity production at the cogeneration system is not enough and external electricity needs to be bought. Higher amounts of lipids could be extracted by using dried algae to SFE, being even higher the amount of lipids and carotenoids extracted when ethanol was considered as co-solvent to the process (Biorefinery 3GB4) (Table 5). Concerning electricity consumption, the biorefineries that considered microalgae extraction presented a much higher demand than the stand alone sugarcane biorefinery (Biorefinery 2GB) (Table 5). When SFE from wet algae in an integrated microalgae-sugarcane biorefinery (Biorefinery 3GB1) was considered the electricity demand is 18 times higher than the not integrated biorefinery, and for the SFE from dried microalgae the increase is only between 2.8 and 3.6. The main electricity consumption step for the proposed supercritical fluid-based 3G biorefineries is the CO<sub>2</sub> pumping system at the SFE process. It is responsible for around 60% of the electricity demand when dried microalgae is used and 92% when wet biomass is used. Ethanol production is only decreased when SFE is considered with the used of co-solvent (Biorefinery 3GB4), as fresh ethanol is necessary for SFE process to replace ethanol losses (Table 5).

### ***3.3 Evaluation of economic process indicators***

Fig. 4 shows the total investment cost necessary for the evaluated alternatives. The highest investment is found when SFE is conducted with wet microalgae. In this situation, the total investment is 71% higher than the stand alone sugarcane biorefinery. Although processing of wet biomass would be interesting for valorization of microalgae before supercritical water gasification [21], as already discussed, the use of this technology with such high S/F ratio integrated to the ethanol production process would not be attractive from the thermal-economic point of view.

The use of dried microalgae for SFE presented total investment around 24% lower than the use of wet microalgae. The cost for the open pound system was calculated in 6.1 MUSD, representing around 1.3 % of the total investment. The amount of CO<sub>2</sub> used in the extraction process highly influences the SFE investment. When a higher CO<sub>2</sub> flow is used (S/F = 450), Biorefinery 3GB2, the investment for the SFE system increased 39% comparing when cell disruption is considered (S/F = 300), Biorefinery 3GB3, taking in to account the increase in the investment due to the milling system necessary. Therefore, it is possible to see, in terms of investment cost, that it is favorable to consider a pretreatment of microalgae or use of co-solvent in order to decrease the CO<sub>2</sub> flow during the SFE process. The reduction of CO<sub>2</sub> flow by using a pretreatment step, such as cell disruption, or co-solvent also presented the advantage of decreasing electricity consumption and increased both lipids and carotenoids extraction that impacts on the cost of manufacturing (COM) and economic viability of the process. Table 6 shows the COM for the proposed integrated microalgae-sugarcane biorefineries considering low moisture microalgae processing. The highest specific COM is found for ethanol production mainly due to the high variable cost of which sugarcane price is a

big share. A slight higher  $COM_{\text{ethanol}}$  is found when SFE with co-solvent is considered as lower ethanol final production is obtained. Higher  $COM_{\text{lipid}}$  is found also for SFE with co-solvent as with this system the  $CO_2$  losses are higher during ethanol separation and fresh  $CO_2$  is needed in the process. In this first analysis, the selling of the final product as an extract rich in lipids (considering the price of 0.9 USD/kg [32]) would not be economically attractive for this process as the revenue would be lower than the  $COM_{\text{ma}}$ , COM related to the microalgae use, calculated. While, the selling of the SFE product, as an extract rich in carotenoids, would present higher economic attractiveness. Considering carotenoids price of 3 USD/g [33], the benefit would be 5.2, 5.7 and 8.3 times higher than the  $COM_{\text{ma}}$  for the Biorefineries 3GB2, 3GB3 and 3GB4, respectively, representing a good possibility of profitability. When the price for carotenoids is reduced to 0.3 USD/g [33], the benefit for carotenoids selling is of 41.5, 40.7 and 71.8 MUSD/year for the Biorefineries 3GB2, 3GB3 and 3GB4, respectively. It represents, that even with the lowest price for carotenoids considered, Biorefineries 3GB3 and 3GB4 would present economic feasibility since the revenue would be higher than  $COM_{\text{ma}}$ .

2G and 3G biofuel production economic difficulties when compete with 1G biofuels and oil-derived fuels is well known. This shows that obtaining a product, such as a extract, with a high valuable compound prior to biofuel production could increase it economical feasibility of the biorefinery. Even though a post processing would be necessary to separate lipids and carotenoids depending on the local market demands, or this flow could be considered entirely for bioactive compound selling and the residual biomass, protein and carbohydrates, could be used either directly as fuel to the cogeneration system increasing electricity production or as raw material to a gasification process.

As a final remark, it is important to stress that the current and futures perspectives for the sugarcane mills in Brazil are strongly considering electricity production and selling to the grid. A great investment was accomplished in the last two decades by sugarcane mills to install new cogeneration technologies and higher pressures burners to enable higher electricity production. The evaluated SFE processes integrated to the biorefinery proved to be very electricity consuming disabling the production of surplus electricity to be sold to the grid.

#### **4 Conclusions**

Microalgae growth in the sugarcane biorefinery enable CO<sub>2</sub> capture of 64.2 kg of CO<sub>2</sub>/t sugarcane increasing investment on 1.8 % compared with the biorefinery without microalgae growth. Supercritical fluid extraction (SFE) from microalgae was an efficient way to extract high value-added compounds, such as lipids and carotenoids. The CO<sub>2</sub> flow used in the process is a key factor to the process thermo-economic viability. Reducing CO<sub>2</sub> flow initially by biomass drying and then by use of pretreatment (cell disruption) or extraction co-solvent decreases electricity consumption and total investment of the biorefinery and increases both lipids and carotenoids recovery. Although the processing of microalgae without dewatering would be interesting to perform an extraction of bioactive compounds prior to supercritical water gasification of microalgae, it presented energetic or economic limitations not been attractive to integrate in the sugarcane biorefinery. SFE process from dried microalgae using ethanol as co-solvent proved to be one of the best alternatives as it presented the highest carotenoids and lipid productivity at a low electricity consumption, presenting a low COM and a possible high profitability. The sale of the carotenoids-rich extract



proved has the better economic attractiveness when compared to the alternative option of focus on sell a lipids-rich extract.

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<http://www.energybiosciencesinstitute.org/~BAT/PDFs/EBI-BAT-AR03-2010-bracaneexpansion.pdf>

## Figure caption

Fig. 1 - Simplified process representation of the proposed microalgae-sugarcane biorefinery

Fig. 2 – Process configurations evaluated for microalgae processing using supercritical fluid extraction

Fig. 3 – Gran composite curves obtained after energy integration for each biorefinery configuration evaluated. Biorefinery 2G: producing ethanol and electricity from sugarcane, Biorefinery 3GB1: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from wet microalgae with supercritical CO<sub>2</sub>, Biorefinery 3GB2: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub>, Biorefinery 3GB3: Biorefinery producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub> with ethanol as co-solvent, Biorefinery 3GB4: Biorefinery producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried cell disrupted microalgae with supercritical CO<sub>2</sub>.

Fig. 4 – Total investment necessary for each biorefinery configuration evaluated. Biorefinery 2G: producing ethanol and electricity from sugarcane, Biorefinery 3GB1: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from wet microalgae with supercritical CO<sub>2</sub>, Biorefinery 3GB2: producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub>, Biorefinery 3GB3: Biorefinery producing ethanol and electricity from sugarcane and lipids/carotenoids-rich extract from dried microalgae with supercritical CO<sub>2</sub> with ethanol as co-solvent, Biorefinery 3GB4: Biorefinery producing ethanol and

electricity from sugarcane and lipids/carotenoid-rich extract from dried cell disrupted microalgae with supercritical CO<sub>2</sub>.

## **Table caption**

Table 1 - Summary of the technologies listed for the studied biorefineries

Table 2 - Main parameters adopted for simulating the sugarcane biorefinery and microalgae growth

Table 3 - Main parameters adopted for simulating microalgae processing

Table 4 - Main parameters used in the economic analysis

Table 5 - Raw material consumption and productivity parameters of products and intermediary products

Table 6 - Cost of manufacturing (COM) for the evaluated biorefinery and economic benefit

**Table 1**

<b>Biorefinery</b>	<b>2GB</b>	<b>3GB1</b>	<b>3GB2</b>	<b>3GB3</b>	<b>3GB4</b>
Conventional ethanol production (1G ethanol production)	X	X	X	X	X
Cellulosic ethanol production (2G ethanol production)	X	X	X	X	X
Biogas production from 1G and 2G process liquid waste (i.e. xylose liquid effluent and vinasse)	X	X	X	X	X
Cogeneration system using as fuel bagasse, leaves, biogas, hydrolysis solid waste	X	X	X	X	X
Algae growth using fermentation CO <sub>2</sub>		X	X	X	X
Dewatering and drying			X	X	X
Cell disruption (Milling)				X	
Supercritical CO <sub>2</sub> extraction		X	X	X	
Supercritical CO <sub>2</sub> extraction with co-solvent (ethanol)					X

Note: 2GB – Sugarcane biorefinery producing 1<sup>st</sup> and 2<sup>nd</sup> generation ethanol; 3GB – Sugarcane biorefinery producing 1<sup>st</sup> and 2<sup>nd</sup> generation ethanol and microalgae growth.



Table 2

Parameter	Value	Unit
<b>CONVENTIONAL ETHANOL PRODUCTION PROCESS</b>		
<i>Sugarcane juice extraction and treatment<sup>a</sup></i>		
Sugarcane processed	500	t/h
Efficiency of dirt removal on sugarcane cleaning	60	%
Efficiency of sugars extraction on the mills	97	%
Sugarcane bagasse moisture content	50	% w/w
Recovery of sugars on juice treatment	99.4	%
<i>Ethanol production and recovery<sup>b</sup></i>		
Fermentation yield	89	%
Ethanol recovery on distillation and dehydration	99.7	%
<b>CELLULOSE HYDROLYSIS PROCESS</b>		
<i>Bagasse catalyzed steam explosion pretreatment<sup>c</sup></i>		
pretreatment temperature	463	K
reaction time	5	min
Hemicellulose–xylose conversion	61.4	%
cellulose-glucose	4.1	%
xylose-furfural	5.1	%
hemicellulose-acetic acid	9.2	%
soluble lignin extraction	50	%
<i>Bagasse saccharification through enzymatic hydrolysis<sup>c</sup></i>		
Reaction time	24	h
Hydrolysis solid loading	5	%

Temperature	323	K
Enzyme load <sup>*</sup>	30	mg/g Cellulose
Cellulose–glucose conversion	69.2	%
Hemicellulose-xylose conversion	35.7	%
<b>MICROALGAE GROWTH</b>		
<b><i>Chlorella vulgaris</i> composition<sup>d</sup></b>		
Lipids	22	% dry weight
Proteins	57	% dry weight
Carbohydrates	21	% dry weight
<b>Process parameters<sup>e</sup></b>		
Open pond depth	0.3	m
pH in the pond	8	
Ratio of CO <sub>2</sub> injected	3.3	kg/kg microalgae
Initial microalgae concentration	360	g/m <sup>3</sup>
Hydraulic retention time	4	days
Electric power for paddle wheel	2.7	kW/ha
Electric power for CO <sub>2</sub> injection	1.66	kW/ha
Electric power for water pumping	0.5	kW/ha
Electricity for centrifugation	1	kWh/m <sup>3</sup>

<sup>a</sup> Data from Rein [18]; <sup>b</sup> Data from Albarelli et al. [5]; <sup>c</sup> Data from Carrasco et al. [19], <sup>d</sup> Data

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from Becker [20], <sup>c</sup> Data from Mian et al. [21].

\* the enzyme load accounts for cellulose and  $\beta$ -glycosidase

**Table 3**

<b>SFE process of biorefinery</b>	<b>3GB1<sup>a</sup></b>	<b>3GB2<sup>b</sup></b>	<b>3GB3<sup>b</sup></b>	<b>3GB4<sup>b</sup></b>	
Solid concentration after harvesting	3	3	3	3	%
Water content after drying	--	8	8	8	%
Milling process to cell disruption	no	no	yes	no	
Solvent mass to Feed mass ratio (S/F)	5,000	450	300	300	g/g
Percentage of CO <sub>2</sub> in the solvent	100	100	100	95	%
Percentage of Ethanol in the solvent	0	0	0	5	%
<b><i>SFE equipment</i></b>					
Extraction pressure	33	60	60	60	MPa
Extraction temperature	333	333	333	333	K
Lipid extraction*	41.00	51.81	67.52	73.10	%
Carotenoid extraction	n.a.	1.47	1.56	3.55	mg/g of biomass (d.b.)
<b><i>CO<sub>2</sub> recovery</i></b>					
Flash 1 pressure	7	7	7	4	MPa
Flash 1 temperature	302	302	302	303	K
Flash 2 pressure	0.1	0.1	0.1	0.1	MPa
Flash 2 temperature	298	298	298	298	K
<b><i>Ethanol recovery</i></b>					
Ethanol recovery pressure	--	--	--	0.016	MPa
Ethanol recovery temperature	--	--	--	348	K
<sup>a</sup> Soh and Zimmerman [25]; <sup>b</sup> Safi et al. [26]					
* percentage of lipid extracted from the total lipid available in biomass					

**Table 4**

Data	Value	
<i>Economic data</i>		
Project lifetime	25	years
Construction and startup	2	years
Depreciation	10	years
Interest rate	15	% year
Days worked in a year	210	days/year
<i>Products selling price</i>		
Ethanol	0.72 <sup>a</sup>	USD/L
Electricity	51 <sup>a</sup>	USD/MWh
Lipid	0.9 <sup>b</sup>	USD/kg
Carotenoid	0.3 - 3.0 <sup>c</sup>	USD/g
<i>Raw-material buying price</i>		
Sugarcane	35.18 <sup>d</sup>	USD/t
Sugarcane-leaves	15.02 <sup>d</sup>	USD/t
Enzyme	4.24 <sup>e</sup>	USD/kg
Diammonium phosphate	325 <sup>b</sup>	USD/t
NH3	300 <sup>b</sup>	USD/t
CO <sub>2</sub> to SFE	300 <sup>f</sup>	USD/t
Electricity	70.6 <sup>a</sup>	USD/MWh
Cold demand under 293K	0.028 <sup>g</sup>	USD/kWh

<sup>a</sup> Data from UNICA [31]; <sup>b</sup> Data from Williams and Laurens [32]; <sup>c</sup> Data from Spolaore et al. [33]; <sup>d</sup> Data from Albarelli et al. [5]; <sup>e</sup> Data from Humbird et al. [34]; <sup>f</sup> Data from Santos et al. [14]; <sup>g</sup> Data from Pereira and Meireles [35]

Table 5

Biorefinery	2GB	3GB1	3GB2	3GB3	3GB4	
<b>Raw-materials</b>						
Sugarcane inlet	500	500	500	500	500	t sc/h
Leaves inlet <sup>a</sup>	0.07	0.07	0.07	0.07	0.07	t/ t sc
Electricity consumption	47.89	926.01	220.30	174.54	181.45	kWh/t sc
Extra bagasse necessary as fuel <sup>a</sup>	0	0.77	0	0	0	t/t sc
<b>Intermediary products</b>						
CO <sub>2</sub> to algae growth	0	3.3	3.3	3.3	3.3	kg CO <sub>2</sub> /kg microalgae
Algae	0	17.77	17.77	17.77	17.77	kg (d.b.)/t sc
Biogas from waste gasification <sup>a, b</sup>	0.17	0.17	0.17	0.17	0.17	kg/t sc
Lignin solid waste <sup>a</sup>	23.87	23.87	23.87	23.87	23.87	kg/t sc
Bagasse to cogeneration <sup>a</sup>	0.10	0.10	0.10	0.10	0.10	t/t sc
Bagasse to 2G process	0.12	0.12	0.12	0.12	0.12	t/t sc
<b>Products</b>						
Ethanol	86.60	86.60	86.60	86.60	85.77	L/t sc
Net electricity	112.39	-926.01	-60.01	-14.25	-21.16	kWh/t sc
Lipids	0	1.60	2.03	2.64	2.86	kg (d.b.)/ t sc
Carotenoids	0	n.i.	26.16	27.69	63.10	g/t sc
Protein + Carbohydrate	0	16.17	17.27	16.66	19.12	kg/ tsc

sc = sugarcane

n.a. = not informed

<sup>a</sup> used as fuel to the cogeneration system<sup>b</sup> liquid streams used to biogas production were the vinasse, obtained after distillation, and pentose-rich liquor, obtained after SO<sub>2</sub>-catalyzed steam explosion pretreatment

Table 6

	3GB2	3GB3	3GB4	
<i>Ethanol production COM</i>				
Variable cost	122.4	122.4	122.4	MUSD/year
Fix cost	56.7	56.7	56.7	MUSD/year
General production cost	3.2	3.2	3.2	MUSD/year
<b>COM<sub>sc</sub></b>	<b>216.9</b>	<b>216.9</b>	<b>216.9</b>	<b>MUSD/year</b>
<b>COM<sub>ethanol</sub></b>	<b>0.99</b>	<b>0.99</b>	<b>1.00</b>	<b>USD/L</b>
<i>Microalgae production and processing COM</i>				
Variable cost	13.5	15.8	33.8	MUSD/year
Fix cost	20.9	15.4	15.8	MUSD/year
General production cost	1.2	0.9	0.9	MUSD/year
<b>COM<sub>ma</sub></b>	<b>42.3</b>	<b>38.2</b>	<b>60.1</b>	<b>MUSD/year</b>
<b>COM<sub>lipid</sub></b>	<b>8.29</b>	<b>5.74</b>	<b>8.35</b>	<b>USD/kg</b>
<b>COM<sub>carot</sub></b>	<b>125.74</b>	<b>82.23</b>	<b>52.51</b>	<b>USD/kg</b>
Revenue of lipid and SFE waste selling	26.36	26.98	30.57	MUSD/year
Revenue of carotenoid* and SFE waste selling	219.54	218.76	501.12	MUSD/year

\*Considering carotenoid selling price of 3 USD/g

Figure 1

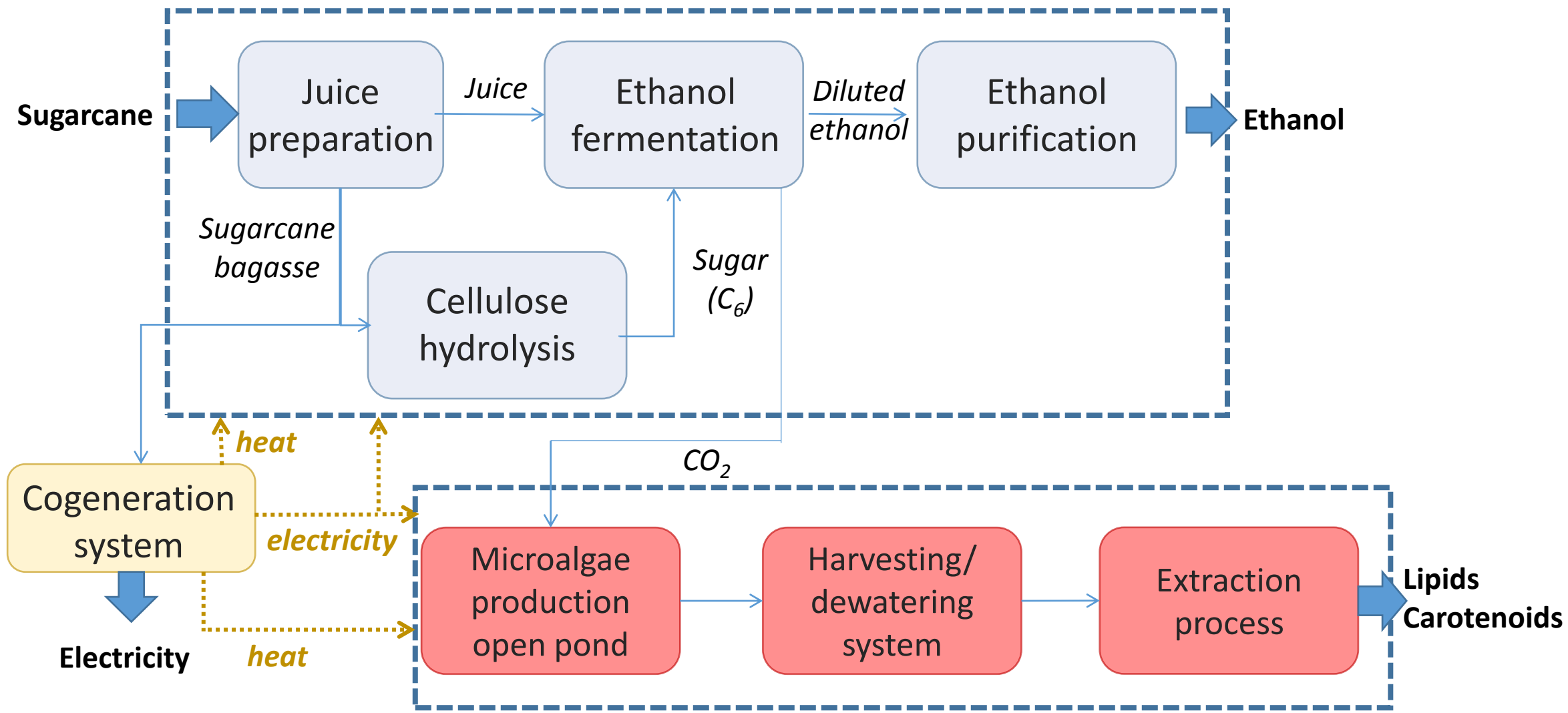




Figure 2

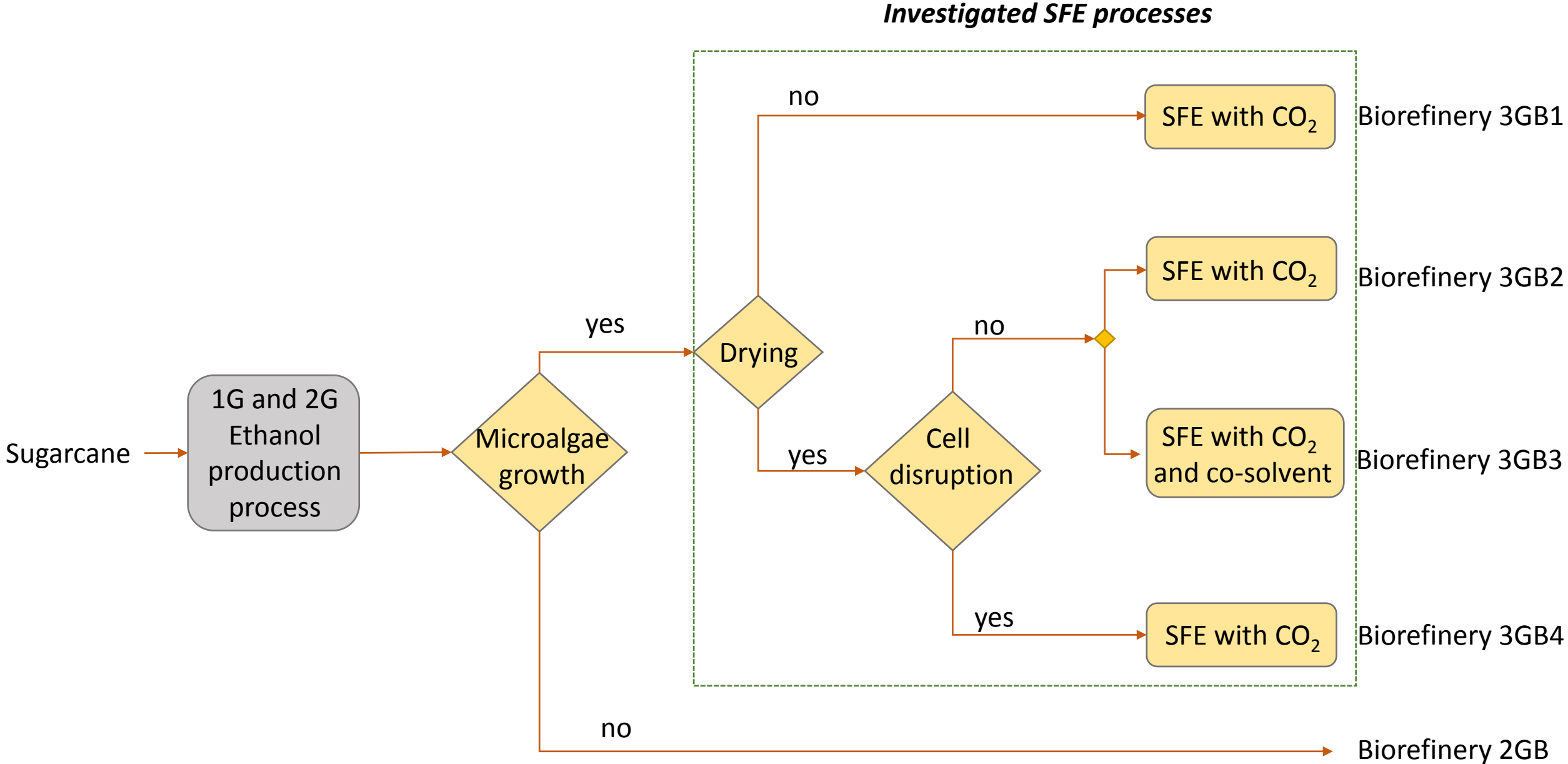


Figure 3

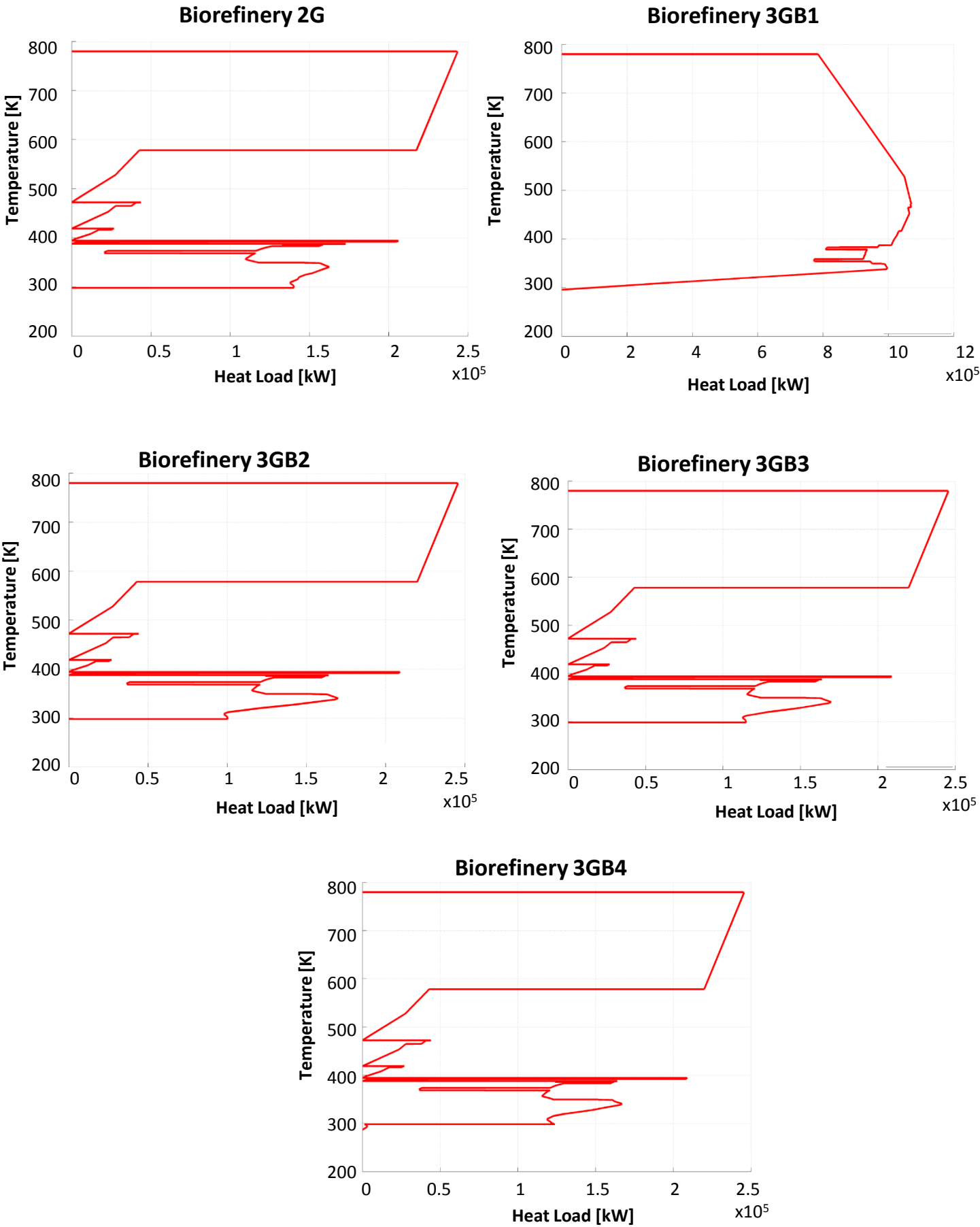
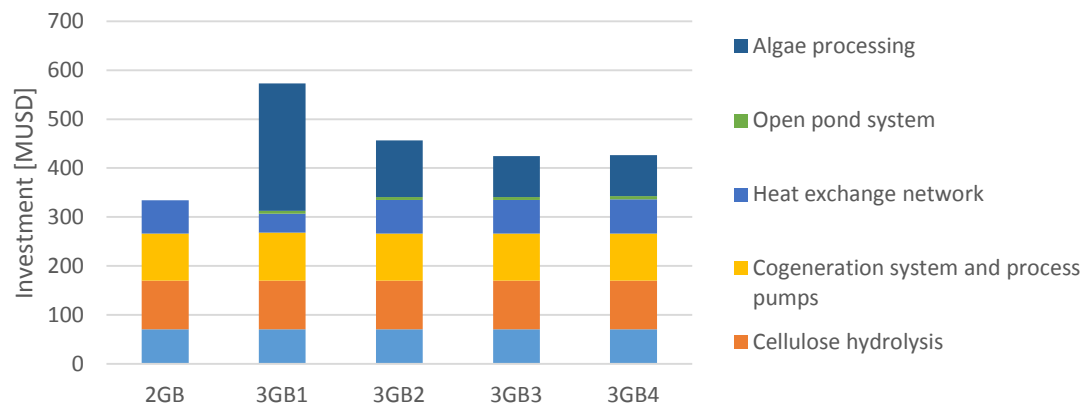


Figure 4



## Supplementary Material

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