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Comparison of extraction techniques for product diversification in a supercritical water gasification-based sugarcane-wet microalgae biorefinery: Thermoeconomic and environmental analysis

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This study presents a thermoeconomic and environmental assessment of the extraction of lipids and proteins from wet microalgal biomass in a 3G biorefinery by two different technologies: supercritical fluid extraction (SFE) and low-pressure solvent extraction (LPSE). Simulation tools were used to study a sugarcane biorefinery producing ethanol from sugarcane juice (1G) and bagasse (2G); the microalgal growth in an open pond; and the processing of microalgal biomass into lipids, proteins and synthetic natural gas (SNG). Supercritical water gasification (SCWG) of microalgal biomass enables an increase in biofuel production of 10.2% MJ when no extraction process is considered and of 1.9% MJ when LPSE is considered. The heat demand of the proposed biorefinery with LPSE was increased by 87.8% compared with the demand of the sugarcane biorefinery without microalgal growth and processing. When the SFE process is considered, the heat demand of the overall process increased 3.2 times. SFE for wet microalgae processing is not economically attractive, as it increases the total investment by 71%. The CO_2 flow used in the SFE process demonstrated to be a key factor in the thermoeconomic viability of the process. Regarding the wet processing of microalgae prior to SCWG, the best alternative studied was the use of LPSE technology.

1. Introduction

Sugarcane is a very important biomass for the Brazilian economy. It is used to produce electricity, ethanol and sugar in biorefineries. Although it is considered an environmental friendly sector due to the biofuel and bioenergy production, the expansion of sugarcane crop and industrial processing are linked to different environmental impacts, such as land competition with food crops, the displacement of farming to protect forest environments, and a high water footprint. Managing social and environmental risks is important for sugarcane growers and processors and food companies due to regulatory pressures as well as shareholder and consumer expectations for sustainably produced goods. The use of process "wastes" to increase biofuel and bioproduct productivity of sugarcane biorefineries, without increasing the amount of sugarcane harvested, is a necessary action being investigated by different authors (Filoso et al., 2015; Sindhu et al., 2016).

The integration of 3rd-generation biofuels into sugarcane biorefineries using microalgal biomass growth is opportune because it decreases the CO_2 generated in the process and provides a new use for the produced vinasse. Microalgae-based fuels have been studied since the late 1970's because microalgae do not require cultivable land or fresh water for cultivation, are not edible, can be grown to increase their biomass several fold irrespective of the seasonal conditions, present a strong ability to fix atmospheric CO_2 and can

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Abbreviations

1G	First-generation biofuel
2G	Second-generation biofuel
3G	Third-generation biofuel
C_{op}	Operating costs of the plant (US$/y)
C_{tot}	Yearly total costs (US$/y)
i	Interest rate
IPCC07	Intergovernmental panel on climate change 07
LCA	Life cycle analysis
LPSE	Low-pressure solvent extraction
n	Lifetime assumed for the investment
SCWG	Supercritical water gasification
SFE	Supercritical fluid extraction
SNG	Synthetic natural gas
S/F	Solvent mass-to-feed mass ratio
ΔT_{min}	Minimum temperature difference
τ	Annualization factor

be used in water treatment (Langholtz et al., 2016). Even though the technology for biofuel production is technically feasible, one of the key technical challenges that needs to be overcome before the large-scale introduction of microalgae technology to biofuel production and greenhouse gas mitigation is the efficient processing of microalgal biomass. A major obstacle to the efficient processing of microalgae is their water content (Brennan and Owende, 2010).

The possibility of annexing microalgal biomass production to existing sugarcane mills is currently being evaluated in the industrial environment and scientific community. According to Klein et al. (2018), between the years 2012 and 2014, partnerships between Brazilian sugarcane mills and international companies were evaluating the integration of microalgal production with sugarcane biorefineries, but until 2018, no microalgal production processes were in operation. According to the authors, microalgae companies still lack large-scale facilities for cultivation and microalgae post-processing. The existing infrastructure of sugarcane mills in Brazil could assist in the establishment of pilot plants and industrial-scale units and stimulate the development of this technology for biomass production.

Different studies have focused on the environmental benefits of integrating microalgal production and sugarcane processing in Brazil, most of them studied the integration of vinasse as a nutrient for microalgal growth (Sydney et al., 2016; Brasil et al., 2017). The integration of microalgal growth in the sugarcane biorefinery process to produce third-generation biofuels has been proven to be energetically, environmentally and/or economically synergetic by some authors (Lohrey and Kochergin, 2012; Moncada et al., 2014; Souza et al., 2015; Maranduba et al., 2015). These studies evaluated the biodiesel production from microalgae integrated to conventional ethanol and/or sugar production processes using process simulation tools, resulting in a positive environmental impact on sugarcane biorefineries. Lohrey and Kochergin (2012) concluded that the main bottleneck of microalgae biodiesel production was the drying step, which makes colocation with sugar mills an attractive option due to the available infrastructure and excess bagasse. In the study by Moncada et al. (2014), the integration of microalgae biodiesel and a sugarcane biorefinery presented high economic profitability. While the study of Souza et al. (2015) highlighted the significant technical and economic barriers associated with microalgae biodiesel production technology and therefore the need for economic incentives and the production of other microalgae-based products of greater benefit.

Microalgae contain compounds such as lipids, pigments (carotenoids), proteins and carbohydrates, which all can be used in different markets. The production of other microalgae-based products of greater benefit prior to biofuel production could be a key element that increases the economic viability of integrated biorefineries. In this context, selective fractionation of the main target compounds directly from wet microalgal biomass could be an interesting route, as dewatering microalgae requires a great amount of energy (Grima et al., 2003).

Therefore, the main goal of this study was to investigate using computational simulation tools the integration of microalgal growth with a sugarcane biorefinery, evaluating the possible routes of wet microalgae processing to produce biofuel and/or extract high-added-value compounds. The use of CO_2-rich off-gases generated from a theoretical Brazilian sugarcane biorefinery producing first- and second-generation ethanol (ethanol obtained from sugarcane bagasse through enzymatic cellulose hydrolysis) to grow microalgae was evaluated. Furthermore, the production of synthetic natural gas (SNG) by supercritical water gasification (SCWG) of the microalgal biomass leftover after lipid/protein extraction using supercritical CO_2 (supercritical fluid extraction, SFE) or ethanol (low-pressure solvent extraction, LPSE) was evaluated.

2. Methodology

The approach used in this study is based on the quantitative results generated by professional process simulators using up-to-date literature information on sugarcane and microalgae processing. The overall investigated process is shown in Fig. 1. In this integrated sugarcane-microalgae biorefinery, the production of electricity, first-generation ethanol, second-generation ethanol from sugarcane bagasse and possible products from microalgae (synthetic natural gas, lipids and/or proteins) was considered.

2.1. *Process design and simulation*

2.1.1. *Sugarcane biorefinery*

The commercial flowsheeting software Aspen Plus v. 8.4 (Aspen Technology Inc., USA) was used to simulate the ethanol production process of both first- and second-generation ethanol in the sugarcane biorefinery. A description of the model of conventional ethanol production, as well as the property models used, was fully described in detail by Albarelli et al. (2015) and Mian et al. (2015). Briefly, the first-generation ethanol production consisted of the following steps: sugarcane cleaning, juice extraction, juice treatment and concentration, glucose fermentation, ethanol distillation and dehydration (Fig. 1). For process simulation, the available technology in modern ethanol distilleries in Brazil, such as dry sugarcane cleaning, concentration in multi-effect evaporators, sterilization of the sugarcane juice before entering the fermentation system, and ethanol dehydration using monoethylene glycol, was considered. Fifty percent of the sugarcane bagasse produced after juice extraction in the conventional ethanol production process is used for cellulosic ethanol production. Of the remaining bagasse, 41% is used as fuel for heat and power production in a cogeneration system, and 9% goes toward other uses (filtration of juice and spare bagasse in the cogeneration system). In the second-generation ethanol production process, physical and chemical treatments break the lignin-cellulose-hemicellulose matrix of bagasse and increase the cellulose susceptibility to hydrolysis. Dextrose is produced by the enzymatic hydrolysis of bagasse cellulose, and the resulting sucrose solution is concentrated. The concentrated solution is then mixed with the concentrated juice obtained from the first-generation process, and the resulting