



# Multi-objective design of a new sustainable scenario for bio-methanol production in Brazil

Lucas Bonfim-Rocha<sup>a,\*</sup>, Marcelino Luiz Gimenes<sup>a</sup>, Sérgio Henrique Bernardo de Faria<sup>a</sup>, Rodrigo Orgeda Silva<sup>a</sup>, Laureano Jiménez Esteller<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, State University of Maringá, 5790 Colombo Avenue, 87020-900, Maringá, Brazil

<sup>b</sup> Department d'Enginyeria Química, Universitat Rovira I Virgili, Av. Països Catalans 26, 43007, Tarragona, Spain

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## ABSTRACT

The objective of this work is to investigate the technoeconomic feasibility of a new sustainable bio-methanol production scenario from renewable sources using carbon dioxide captured from the fermentation process in ethanol production distilleries, carrying out an integrated analysis of the overall system. The hydrogen required is provided electrolyzing treated water of the distilleries and producing oxygen as a valuable byproduct. Aiming to promote carbon capture processes, an industrial methanol plant was modelled with Aspen Plus<sup>®</sup> and optimized using Matlab<sup>®</sup>. Design parameters were handled taking into account the associated capital costs and applying sensitivity analysis. The response surfaces were obtained according to the amount of bagasse used to cogenerate energy, attempting to maximize the Net Present Value while minimize the CO<sub>2</sub> emissions of each scenario. The results show that the problem of high-energy consumption for electrolysis might be bypassed using co-generated energy, being feasible to implement this process in distilleries able to emit more than 120,000 tonne/harvest of CO<sub>2</sub>. Depending on the distillery size, a range of 1136–1988 tonnes of methanol can be produced per year at production costs in the range of 0.51–0.62 \$/kg with a negative CO<sub>2</sub> balance varying from –2198 to –1814 tonne/yr. The purposed scenario indicates that integrating a methanol plant with an ethanol distillery is an innovative option for carbon mitigation in Brazil compared to other studies, contributing to the sustainable production of methanol.

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## 1. Introduction

In recent years, research activities regarding the global environmental impacts of carbon dioxide (CO<sub>2</sub>) emissions have been intensified. Overall, government policies and some international conferences (e.g., 11th Session of the Conference of the Parties (CMP 11) and 21st Conference of the Parties (COP 21)) aim at minimize the emissions of greenhouse gases (GHG), as it incentives the use of renewable sources. Among the GHG, CO<sub>2</sub> contributes vertiginously to the atmosphere warming because of emissions directly related to human activities, representing 64.3% of the total gases emitted (IPCC, 2013). In order to reduce emissions from the industrial sector, CO<sub>2</sub> reuse as raw material in the production of marketable products, might become not only economically viable but also a profitable business, besides the advantage to replace fossil fuels by

renewable ones (Van-Dal and Bouallou, 2013).

Among various possible chemical products manufactured from CO<sub>2</sub>, methanol is of particular interest as it is a biodegradable fuel that can be used for gasoline blending, biodiesel production or direct methanol fuel cells (Olah, 2013). Beyond that, it may serve as raw material to produce other valuable derivatives, such as formaldehyde, acetic acid, methyl methacrylate, etc. (Cuéllar-Franca and Azapagic, 2015).

Despite the worldwide growth of methanol production and demand, many countries are not self-sufficient (e.g., Brazil) and import it for many purposes (e.g., biodiesel production) (de Mello et al., 2017). More than 80% of the methanol produced worldwide is obtained from natural gas (NG), which is often associated with high GHG emissions (Milani et al., 2015). Two possible pathways of reducing CO<sub>2</sub> emissions and producing bio-methanol are either by the syngas resulting from biomass gasification or by CO<sub>2</sub> hydrogenation in large-scale processes (Cifre and Badr, 2007). Nevertheless, the synthesis from biomass requires additional steps for

\* Corresponding author.

E-mail address: [pg70276@uem.br](mailto:pg70276@uem.br) (L. Bonfim-Rocha).

gasification, followed by cleaning and conditioning steps, which increase costs and environmental impacts (Renó et al., 2011). Therefore, bio-methanol production by CO<sub>2</sub> hydrogenation with hydrogen from renewable sources appears as the cleanest and promising route.

Leonzio (2017) presents a comprehensive literature review focusing on methanol synthesis using carbon dioxide and hydrogen as raw materials. In the last years, several research papers have been published investigating the production of methanol by using CO<sub>2</sub> captured from different sources and comparing their results with conventional production routes. Nevertheless, these works present two main limitations: (i) they usually focus on processes with capture and purification of gases emitted from fossil fuels combustion and biomass, which incorporates more costs and environmental impacts (Kim et al., 2011; Milani et al., 2015; Atsonios et al., 2016; Blumberg et al., 2017); and/or (ii) they rarely approach economic analysis or disregard unfeasible points such as hydrogen production cost and low conversion kinetics (Van-dal and Bouallou, 2013; Matzen et al., 2015; Kiss et al., 2016; Pérez-Fortes et al., 2016).

The work of Matzen et al. (2015) presents the techno-economic analysis of an integral facility of methanol synthesis, using carbon dioxide from ethanol industry and hydrogen obtained by wind energy from electrolytic production. The study of Pérez-Fortes et al. (2016) assessed, via techno-economic and environmental metrics, the production of methanol by CO<sub>2</sub> hydrogenation evaluating the potential of CO<sub>2</sub> reuse on (i) the net reduction of CO<sub>2</sub> emissions of a pulverized coal power plant and (ii) the production cost, in comparison with conventional synthesis in Europe.

In view of pure sources of CO<sub>2</sub>, Brazil is recognized globally by the strong renewable components of its energy matrix. Rochedo et al. (2016) estimates that, in Brazil, ethanol distilleries are the major amount of CO<sub>2</sub> contribution sources with a capture potential of 57.8 Mtonne of CO<sub>2</sub>/yr in 2030. Furthermore, Brazilian policies signed in COP 21 a target reduction that should reach 43% by 2030, in relation to 2005 GHG emissions (Marcovitch, 2015). Consequently, researches realized that the sugar-energy sector plays a key role in this scenario, once sugarcane is used to produce ethanol and bioelectricity, representing almost 16% of the country's energy matrix (UNICA, 2017).

In the last years, commercialization of surpluses of electricity through use of bagasse, leaves and straw present themselves as best alternatives for the use of this waste. However, the bioelectricity price produced by the Brazilian sugarcane mills has been presenting high instability recently. Reports provided by the National Electric Energy Agency, the responsible for conducting public auctions of energy generation projects, show that bioelectricity prices ranged from 118 in 2015 to 63 \$/MWh in 2016 (ANEEL, 2017). According to Brazilian Sugarcane Industry Association (UNICA, 2017), even in the free energy market, where values for bioelectricity above 200 \$/MWh for several weeks in 2014 appear, currently, it presents prices are under 100 \$/MWh. Then, aiming to contour this issue, finding alternative uses for the surplus of biomass or bioelectricity, added to the problems of CO<sub>2</sub> emissions became the rationality of many studies (Dias et al., 2011; Esen and Yuksel, 2013; Mazen et al., 2015).

In this work, we aimed to investigate the challenge of undervalued bioelectricity and CO<sub>2</sub> emissions in sugarcane mills face to the problem of expensive costs for electrolysis, by proposing a novel sustainable scenario for bio-methanol production and evaluating its techno-economic-environmental feasibility.

## 2. Methods

A systematic hybrid methodology for simulation-optimization of chemical processes is applied taking into account economic and environmental aspects. Then, different sizes of distilleries in Brazil are assessed to evaluate the general applicability of the proposed scenario, outlined as indicates Fig. 1 with the representation of mass, energy, and utilities flows. Each step of the proposed scenario is explained in the next sections.

### 2.1. CO<sub>2</sub> source and cogeneration systems

In ethanol distilleries, just after fermentation reactors, the product gaseous stream carries away some ethanol with it, which is treated in the absorption column, recovering ethanol (Silva et al., 2015). The gaseous stream leaving the absorber contains a negligible amount of ethanol, so it is vented to the atmosphere with a high purity CO<sub>2</sub> stream (99% w/w) (Xu et al., 2010). Thus, in this study, the amount of CO<sub>2</sub> released was considered as a non-cost raw material to produce bio-methanol. Besides, to identify the applicability of the scenario once that the undervalued bioelectricity problem occurs in Brazil, sugarcane mills with different capacities are listed in Table 1.

Recent advances in the Brazilian sugarcane sector boosted bioelectricity production from cogeneration, with 9.9 TWh in 2011 and 21.2 TWh in 2016 (UNICA, 2017). The process initially considers a methanol plant annexed to a medium autonomous distillery that crushes 2,750,000 tonne<sub>sugarcane</sub>/yr and cogenerates 20.3 kWh/tonne<sub>bagasse</sub> of bioelectricity (base case) (CONAB, 2017). Regarding the energy allocated for self-consumption and energy for sales, values registered are around 45.3 and 54.7%, respectively.

### 2.2. Water electrolysis unit

Until now, the cleanest method of producing hydrogen has been water electrolysis using electricity from renewable energy sources. Different types of electrolyzers can be found in the literature, each of them with a distinct reaction mechanism to produce hydrogen (Ball and Wietschel, 2008). Broadly, there are three main types of electrolyzers available: alkaline, polymer electrolyte membrane (PEM) and high temperature solid oxide electrolyzers (SOE). Currently, SOE and PEM electrolyzers are at a research and development stage (Bhandari et al., 2014) and have small scales of production. Therefore, alkaline electrolyzers are the most used technology in a worldwide level (Bhandari et al., 2014) and for this reason, it was considered the specifications of this technology (Table 2).

The water electrolysis system considered in this work is composed by the appropriate combination of electrolyzers presented by E4tech Sàrl with Element Energy Ltd (E4TECH, 2014). Appendix A includes the electrolyzers information (i.e., plant capacities, output pressure, electricity consumption, etc.) with data sets for different types of regulatory and pricing environment. In this scenario, a set of electrolyzers are designed operating with surplus energy provided by cogeneration units of Brazilian sugarcane mills. The hydrogen generated from the electrolysis is cooled, purified, compressed, and transported by pipelines to the methanol plant while the oxygen, produced with a ratio of 8 kg of O<sub>2</sub>/kg of H<sub>2</sub>, is stored as a by-product for sale.

### 2.3. Bio-methanol process description

The bio-methanol production process using CO<sub>2</sub> hydrogenation consists of three main steps: gas compression, methanol synthesis,

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