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Modeling and environmental implications of methanol production from biogenic CO_2 in the sugarcane industry

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ABSTRACT

This article presents a comprehensive model for the industrial production of methanol through the direct hydrogenation of biogenic CO_2 from a biorefinery. Carbon capture and transformation to methanol are modeled through process simulation, ensuring that the H_2 used for CO_2 reduction, as well as electrical power requirements, are renewable. The environmental assessment is performed *via* a cradle-to-gate life cycle assessment study. The approach is applied to a typical large-scale sugar-ethanol complex in Argentina. The results show that the production of green methanol is a good option for the decarbonization of the industry and the methanol market. The sustainability of the overall process largely depends on the sustainability of the agricultural tasks that form the basis of the biorefinery. This is an unavoidable aspect that is not taken into account in many environmental studies on the production of CO_2-based products, which leave aside the origin of the CO_2.

1. Introduction

Climate change is one of the major global environmental concerns. During the last decade, CO_2 emissions increased exponentially, resulting in values 60% higher than the reference values contemplated in the Kyoto protocol [1]. The decarbonization necessary to not surpass the limits established in the Paris Agreement —2 °C of global warming over pre-industrial values—, requires reductions in CO_2 emissions of up to 50% [2]. Given that industrial activities represent 20% of global emissions, it is necessary to develop and apply decarbonization technologies, especially in those processes that generate large volumes of greenhouse gases (GHG) emissions: oil refining, chemical, iron, cement industries and power plants [3].

Carbon capture and storage (CCS) and carbon capture utilization (CCU) technologies have become the object of intensive study in recent years [4], due to their potential to reduce CO_2 emissions. CCU encompasses a broad set of chemical processes and technologies that use CO_2 as a raw material to produce compounds of commercial interest, which are attractive as a way of replacing petrochemical feedstocks [5,6]. However, to verify their potential for climate change mitigation, it is necessary to carry out an exhaustive analysis of the associated activities and their environmental implications. In this sense, the Life Cycle Assessment (LCA) has proven to be an effective tool when estimating the potential environmental impacts of a product, process or activity throughout its entire life cycle [7]. A recent study by Da Cruz et al. [8] highlights the need to collect primary data when analyzing CCU technologies and, in addition, performing a critical analysis on the possible reduction of environmental impact using an LCA approach. CO_2 can be employed to produce a wide variety of single carbon compounds (C_1) such as urea, methanol, formic acid and methane [9]. These pathways include a hydrogenation stage in which H_2 used can be obtained by water electrolysis, generating industrial quality oxygen as a by-product [10]. Both the electrolytic stage and the CO_2 transformation processes require considerable amounts of energy, this being one of the limitations to the development of decarbonization technologies [11].

Particularly optimistic in this context is the production of methanol. Methanol is a promising liquid energy carrier with potential use in various applications, either as a fuel or as a platform molecule for the synthesis of heavier alcohols, dimethyl ether, formaldehyde, acetic acid, olefins, gasoline and more complex chemicals [7]. The conventional *via* for methanol production (steam reforming of natural gas or coal) has a high environmental impact process [12]. The synthesis of methanol from CO_2 hydrogenation, where H_2 is produced by electrolysis of water powered by renewable electricity [13] and CO_2 is derived from

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renewable carbon sources [14,15] offers a valuable opportunity to decarbonize the chemical industry and economic sector that currently depend on fossil methanol.

Bio-methanol production from different raw materials is a trendy topic studied from different standpoints. Leonzio [6] presents an exhaustive review of the literature regarding CO_2 capture and reuse technologies, including the production of methanol from CO_2 and H_2. The CO_2-based methanol production had been analyzed previously by Matzen et al. [16]. They had considered processes which involve streams of pure CO_2 as feedstock, presenting a scheme for methanol production by direct hydrogenation of CO_2. The study of Pérez-Fortes et al. [17] proposes a methanol production scenario from renewable sources. A simulation of the CO_2 hydrogenation process is developed in CHEMCAD®. Furthermore, Do et al. [18] present a technical-economic analysis of methanol synthesis, using CO_2 captured from waste gases (combustion gases from a coal-fired power plant) and H_2 obtained from renewable energy.

The availability of high-purity CO_2 gases from fermentative processes is a technical advantage for the production of chemical products because the raw material conditioning stage is straightforward. There are few studies in the literature that analyze this source of CO_2, including the one by Bonfim-Rocha et al. [15]. It considers a process to produce methanol from CO_2 coming from sugar-to-ethanol fermentation and renewable H_2 in a Brazilian autonomous distillery. The process is modeled in Aspen Plus® and a technical, economic and environmental analysis is carried out. The work of Zang et al. [19] analyzes the production of fuels and power generation from CO_2 generated in the fermentative process of ethanol production. The authors propose the use of H_2 as raw material using an external source of electricity for its production, but the system analyzed does not include the stages of electrolysis, sugar fermentation and CO_2 capture.

Several studies include LCA to estimate the environmental impact of the methanol process, among them, Adnan and Kibria [20], Matzen and Demirel [21] and Wang and Demirel [22]. Particularly, Meunier et al. [23] explore the LCA environmental impacts of “green” methanol production by catalytic hydrogenation of CO_2 using process simulation tools. Van-Dal and Bouallou [24] model the same route of the previous process and carry out a carbon balance as an environmental analysis. Moreover, González-Garay et al. [25] simulate the methanol production from different energy sources, and analyze the results in a broader context considering planetary boundaries.

Given the abovementioned context, the sugarcane industry arises as an excellent opportunity to properly integrate a methanol production process and decarbonize the chemical sector. Usually, three main products are obtained: sugar, bioethanol and bioenergy (heat and electricity). On a smaller scale, some other by-products may be generated. Large CO_2 emissions are generated by the combustion of biomass in the boilers and the fermentation of sugary musts. Moreover, fermentation gases are 99% biogenic CO_2, and a suitable raw material for green methanol. In order to guarantee the successful incorporation of methanol production to the current biorefinery schemes, it will be necessary to ensure the direct applicability of existing technologies, in a sustainable manner from a life cycle standpoint.

One of the critical barriers to implement C_1 processes in the sugarcane industry, from the point of view of environmental sustainability, is the access to clean energy supply. The sugarcane industry is characterized by being self-sustaining from an energy point of view, since the energy necessary for the production of sugar and ethanol comes from the combustion of bagasse, the lignocellulosic residue of the sugarcane milling. Likewise, this activity can even achieve energy surpluses, which could be used to partially cover the power requirements of the CCU technologies to be installed. As the surplus energy originates from biomass, the reducing agent (H_2) employed for the CO_2 transformation processes can be obtained in a cleaner way, thus avoiding the use of H_2 of fossil origin. Therefore, by applying CCU technologies for the production of C_1, sugarcane biorefineries could become carbon sinks and, simultaneously, offer the market carbon neutral and even carbon negative products [26].

This paper presents a comprehensive study of the industrial production of methanol by direct hydrogenation of CO_2 from the sugar-alcohol industry. The process has been designed supported by process simulation, being H_2 considered to come from an alkaline electrolyzer. The outcomes from the simulations are used to evaluate selected key performance indicators as well as to feed a cradle-to-gate LCA. For the case study, the carbon capture system is sized using real data from an industrial facility. The originality of this work is twofold: (i) raw materials and energy for the production of methanol are essentially “green” (biogenic CO_2 is generated in an ethanol distillery attached to a sugar mill, and H_2 is produced using biomass-based energy from the same industry); and (ii) the environmental assessment includes from biomass production until methanol at the plant gate.

2. Proposed approach

The general approach applied is depicted in Fig. 1. The production of methanol from industrial CO_2 is evaluated through technical and environmental performance indicators. For the former, a process model is developed considering H_2 production, CO_2 capture and conversion to methanol (see Section 2.2). For the latter, a LCA is carried out on the stages of agriculture, sugar mill, distillery, H_2 production and CO_2 capture and conversion, through several impact categories (see Section 2.3).

Two possible ways to synthesize "bio-methanol" in large-scale processes are the production of methanol from synthesis gas obtained from biomass gasification and the reduction of biogenic CO_2, with H_2 of renewable origin [28]. In this work, we focus on the latter given the large amounts, and high purity of biogenic CO_2 emissions produced in the fermentation step of ethanol production in a sugar-alcohol facility. Fig. 2 shows schematically the processes considered and the main streams of mass and energy involved in this study.

2.1. Calculation basis

To show the capabilities of the proposed process, it is considered a methanol plant attached to a medium-capacity sugar-alcohol complex [29] located in northwestern Argentina. It processes 1.3 million tonnes of raw sugarcane per year. Bagasse (82.3 t/h) is fed into the boilers to produce steam and electricity through cogeneration systems. Part of the renewable electricity (approximately 75%) is used to cover the factory needs itself, and the surplus (2 MWh/h), to operate the electrolysis unit for H_2 production and to fulfill the electrical demand of the distillery and the CO_2 capture and conversion sections.

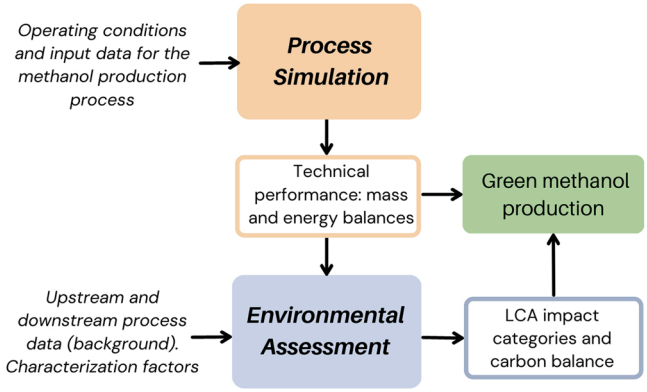

Fig. 1. Outline of the general approach (modified from [27]).

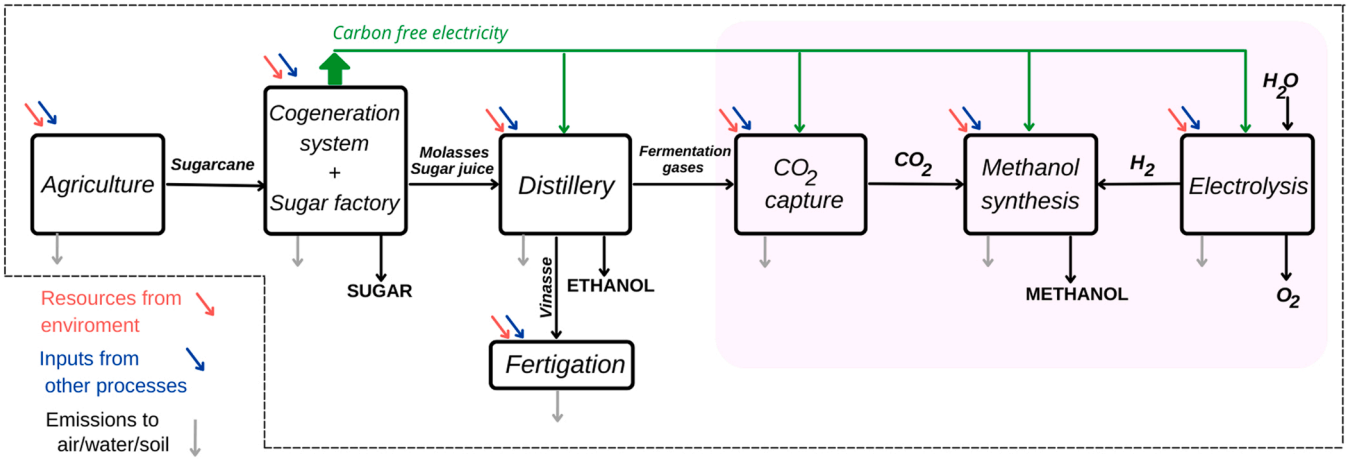

Fig. 2. Simplified diagram of the CO_2-based methanol production process. The shaded area represents the processes modeled by simulation. The dashed line encloses the processes included in the LCA.

2.2. Process simulation

On analyzing the applicability of a CCU technology in the sugar-alcohol industry, process simulation provides a powerful tool to study existing alternatives, assess possible improvements and optimize process variables [30]. The shaded area in Fig. 2 represents the H_2 production unit by water electrolysis and the biogenic CO_2 capture and conversion pathway, processes that are modeled by the process simulation software UniSim® Design R490 [31].

2.2.1. Water electrolysis unit

In order to manufacture a "greener" product thus reducing life cycle CO_2 emissions, the H_2 stream must be supplied to the process in a renewable form. An alkaline electrolyzer is considered for H_2 production due to its great stability, lower operation costs and higher power capacity compared to other technologies [32]. Afterwards, to reduce life cycle emissions, renewable electricity obtained from biomass combustion is provided to the alkaline electrolyzer. Additionally, oxygen is co-produced along H_2 in the electrolytic process in a ratio of eight to one.

2.2.2. Thermodynamic models and kinetic parameters

To model the CO_2 to methanol process, the Peng Robinson equation is used considering a non-ideal vapor phase, while the NRTL model [33] is selected to calculate the properties of liquid phase. Catalytic kinetics is described by the Langmuir-Hinshelwood-Hougen-Watson formalism [34]. The model parameters for the catalyst ($Cu/ZnO/Al_2O_3$) are derived from previous work [24].

The transformation process is ruled by two reactions given by the following equations:

$$CO_2 + 3\,H_2 \rightleftarrows CH_3OH + H_2O \;\Delta H_{298\,K} = -87\;kJ/mol \quad (1)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \;\Delta H_{298\,K} = +41\;kJ/mol \quad (2)$$

The first reaction (Eq. (1)) is exothermic and occurs with a decrease of the number of moles, so according to Le Chatelier's principle, the methanol formation is favored by relatively low temperatures (200–300 °C) and high pressures (50–100 bar). The second reaction (Eq. (2)) is undesirable because it consumes the same reactants as the first one.

2.2.3. Flowsheet synthesis

The methanol synthesis and purification scheme is similar to the one proposed by Pérez-Fortes et al. (2016) [17]. The technical evaluation is carried out based on some selected indicators calculated from the simulation outcomes. Mass balance metrics evaluate the mass demand of the individual inputs and outputs, including the overall conversion of CO_2 and H_2. The energy balance metrics evaluate the needs for heat and electricity, and the possibility of energy integration. Heat recovery is enhanced by means of pinch analysis, which is also used to design the heat exchanger network, considering a minimum approach temperature of 10 °C.

2.3. Environmental Assessment

The LCA evaluates the environmental performance of products and processes to identify environmental critical points (*i.e.* processes or flows responsible for a significant part of the overall impact), and to compare impacts between different systems [23]. Requirements and guidelines to perform the LCA are taken from the international standards ISO 14040 and ISO 14044 [35,36] by following the four LCA phases: goal and scope definition, life cycle inventory analysis, life cycle impact assessment and interpretation [21]. The goal of the study is to evaluate the environmental profile of the methanol obtained from direct hydrogenation of biogenic CO_2. A cradle-to-gate scope is selected for LCA calculations. The system boundaries include the agriculture, sugar mill and distillery stages, as well as the H_2 production and the CO_2 capture and conversion processes (Fig. 2). The production of one kilogram of high-purity methanol is considered as the functional unit.

The agriculture stage includes all the activities related to the agricultural production of sugarcane with a high technological level (planting, cultivation and harvesting), considering both sugarcane plant and ratoon. A yield of 75 t sugarcane/ha is assumed [37]. Trucking of the harvested sugarcane from the fields to the sugar factory through an average distance of 50 km is also included .

In the sugar mill stage, four valuable outputs are obtained: white sugar, raw sugar, molasses and sugarcane juice. Both juice and molasses are intermediate products consumed in the distillery stage. As a multi-product system, a criterion for assigning environmental loads on the products must be considered. Here we follow a sequential assignation approach through the stages to obtain the environmental load of the functional unit. First, a mass allocation factor [36] is used for the sugar mill (24.4% white sugar, 29.3% raw sugar, 12.2% molasses and 34.1% sugarcane juice). An economic allocation is not an option since the market price of intermediates is unavailable. The bagasse generated in the milling is used as fuel to produce steam and electricity to fulfill the process needs. Therefore, the bagasse receives no environmental load.

The distillery stage uses molasses and sugarcane juice as raw material, which transfer their environmental burden to the products of this stage: ethanol, fusel oil and fermentation gases. The distillery subsystem includes the fermentation and distillation stages. Through a batch

fermentation process, fermentable sugars are transformed into an ethanol solution and a high purity CO_2 gas stream. The ethanol solution (7–10 vol%) is centrifuged and sent to the distillation stage where azeotropic ethanol is obtained (96 vol%) along with a small amount of fusel oil. CO_2 is captured from the gas stream for methanol synthesis. In this stage, we also follow a mass allocation method of the environmental loads [36] (50.45% ethanol, 0.45% fusel oil and 49.10% fermentation gases). After the distillation operation, large amounts of vinasse are generated, approximately 13 liters per liter of ethanol produced [37,38]. Although vinasses can receive different treatments to reduce its contaminant load, this study considers its disposal in the fields through a fertigation system. An average distance between the distillery and the fields of 10 km is considered.

For H_2 production, demineralized water and electrical energy are consumed, and industrial quality oxygen is obtained as a co-product. For this multi-product process, the mass allocation results in 11.1% for H_2 and 88.9% for O_2.

Life cycle inventory (LCI) analysis covers life cycle emissions to the air, land and water, acquisition of raw material and waste production in reference to the functional unit. Primary data is collected through interviews with sugarcane growers and sugar producers in Tucumán. Results will be limited to the average values used to represent the local reality of the sugar-alcohol activity. The mass and energy flows associated with the CO_2 capture and conversion sections come from the simulation model. Those associated with H_2 production by electrolysis of water are modeled using data from the literature [39]. LCI data of background processes are retrieved from Ecoinvent v3.5 database [40] using global datasets whether local data are missing. A cut-off rule of 1% is used and infrastructure is not taken into account. The contribution of the catalyst to the different impact categories is not considered in the analysis as it is reported as negligible [23]. The LCI and impact assessment phases are calculated with the support of SimaPro® 9.1.0.11 [41].

Several works in the literature claim that two impact indicators should be included in LCA studies of CCU processes: global warming (GW) and fossil resource scarcity (RS) [10,42,43]. In this study, three additional impact categories are also considered by using the ReciPe (H) midpoint model [44]: terrestrial acidification (TA), freshwater eutrophication (FE) and stratospheric ozone depletion (OD). Furthermore, Ecoinvent v3.5 database is used to provide the impacts of two extra methanol production processes, the fossil-based conventional process and the biomass *via* syngas process, which have been harmonized to carry out a comparative analysis with the process proposed in this work.

In the LCA standard, direct and indirect fossil CO_2 emissions are considered to contribute to GW because they involve a release of fossil carbon into the atmosphere. Nevertheless, zero impact is assigned for biogenic CO_2 emissions because biogenic CO_2 captured through photosynthesis during biomass growth is assumed to be reabsorbed at the end of the product life cycle. In this work, a biogenic CO_2 balance is carried out, accounting for all the biogenic CO_2 flows involved, to complement the LCA and evaluate the potential for CO_2 capture.

3. Results and discussion

3.1. Process simulation

Fig. 3 shows a simplified flowsheet of the system modeled by simulation. Three sections can be distinguished: H_2 production, CO_2 capture and conditioning, and CO_2 conversion.

3.1.1. H_2 production

The production of H_2 from alkaline water is conducted at 3 MPa and 50 °C with a specific electrical power consumption of 50 kWh/kgH_2, consistent with values reported in the literature [13,39].

The supply of electrical energy for water electrolysis is a key factor, since it determines the H_2 production capacity and, therefore, the methanol production. In the scenario presented, the mill's surplus renewable electricity is used to meet the overall energy requirements of the methanol plant. Note that the energy consumption in a process that combines sugar and ethanol production —which is the case in this research— is higher than in an autonomous distillery scheme [15]. So, there is a trade-off between the energy availability of the cogeneration systems for the production of H_2 and the production of sugar. The electrolyzer provides a constant H_2 flow of 37.3 kg/h, corresponding to an energy consumption of approximately 1860 kWh/h. O_2 is released to the air while H_2 is compressed to 75 bar.

3.1.2. CO_2 capture and conditioning

The gaseous stream, called "Fermentation gases", at 38 °C and 1 bar, is water washed in an absorption column to recover some ethanol (Fig. 3). After that, the gas stream leaves the absorber with 99% purity CO_2. The amount of convertible biogenic CO_2 is calculated from the capacity of the electrolyzer. The remaining CO_2 is vented to the atmosphere. The CO_2 to be processed is compressed through four stages with intermediate cooling. The compressors are modeled as adiabatic units with a 0.75 isentropic efficiency. The compression ratio per stage is approximately 2.5, close to that proposed by Turton et al. [45], leading to a pressure of 75 bar at the end of the compression tandem.

3.1.3. CO_2 conversion

The pressurized CO_2 and H_2 streams are mixed with a recycle stream

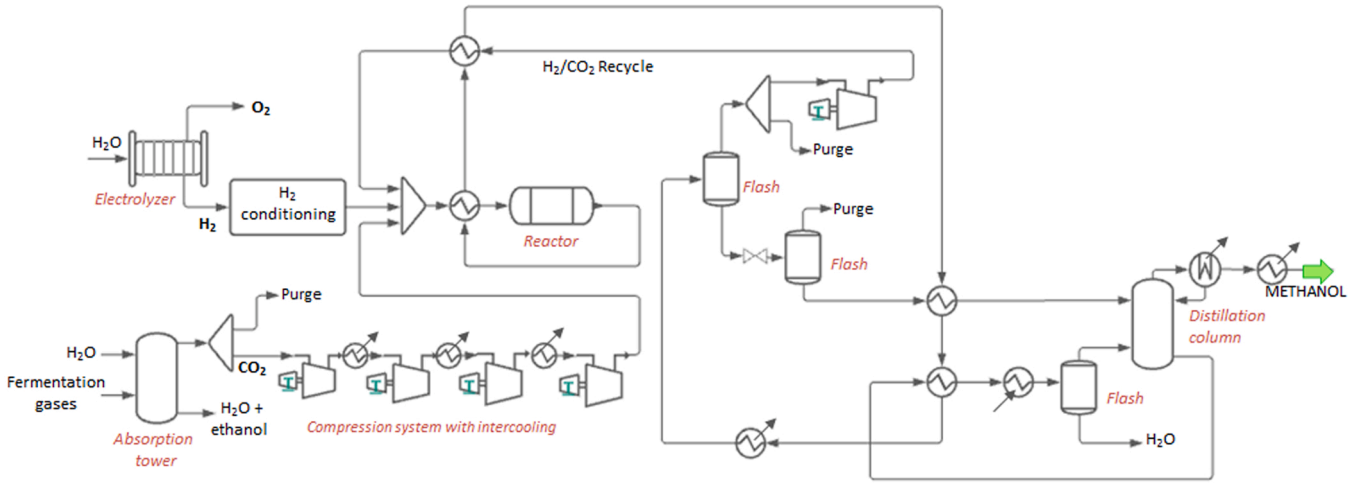

Fig. 3. Methanol production flowsheet by CO_2 hydrogenation.

and heated to reach the reactor inlet temperature of 210 °C. The reactor is modeled as an ideal adiabatic plug flow reactor. The heat of reaction is harnessed to preheat the feed stream to the reactor and for distilling the methanol-water mixture.

The reactor output, with 12 wt% methanol content, at 287 °C, is cooled in successive heat exchangers to 35 °C, condensing almost all the methanol and water. The gas and liquid phases are then split in a flash separator. The gas stream, composed mainly of H_2 and carbon oxides, is recycled to the reactor to increase the selectivity of the desired product [17]. Approximately 1% of the recycle stream is purged to prevent inert gases buildup. The liquid phase is expanded at 1.2 bar and gases are removed in a second flash unit.

The condensate is a mixture of 63 wt% methanol. It is fed to a distillation column where methanol and non-condensable compounds go to the top, while water is separated at the bottom. The operating conditions of this unit allow reaching the specifications of purity and recovery of methanol. The distillate stream is cooled up to 25 °C. The remaining inert gases are purged. Table 1 provides the design and operating conditions of the reactor and distillation column.

Table 2 shows the key performance indicators for this process including some power consumption figures. An overall conversion of CO_2 to methanol of 94.9% is achieved. In the reactor, the selectivity for methanol is high, 98.0%, at 75 bar, 210 °C and with a H_2/CO_2 ratio of 3.5 in the reactor inlet. Pure liquid methanol (99.1 wt%) is produced at 1 bar and 25 °C and pure water (99.9 wt%) is recovered at 1.1 bar and 102 °C. The consumption of raw materials is close to the minimum, stoichiometric value, while the use of utilities (steam and electricity) is also very low. It is noteworthy that reported results come after heat integration of the proposed process (CO_2 capture and conversion sections), including required cooling and heating auxiliary services. Cooling services are covered by water from cooling towers or refrigeration cycles with ammonia, and heating services by medium pressure steam.

3.2. Environmental assessment

Fig. 4 shows the environmental profile of the proposed process for the synthesis of methanol that considers a cradle-to-gate scope: agriculture, sugar industry, distillery, H_2 production, CO_2 capture and conversion. The percentage of contribution of the different stages to the system under analysis is represented in the y-axis. The five selected environmental impact categories appear in the x-axis: global warming (GW), stratospheric ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), and fossil resource scarcity (RS).

The results show the importance of the emissions generated in the sugarcane fields in the total environmental impacts of renewable methanol production, since the agriculture stage is the main contributor in all impact categories and represents 82.7% of GW, 99.7% of OD, 98.2% of TA, 97.7% of FE and 75.7% of RS.

It should be noted (Fig. 4) that emissions associated with auxiliary services are shown in the "Heat" category and contribute insignificantly (<1%) to the global warming impact category. For its part, the contribution of the sugar factory stage is low because emissions from the cogeneration system are mostly carbon neutral since they come from bagasse combustion. In the agriculture stage, the sources of GHG (mainly 66.6% N_2O, 31.2% fossil CO_2 and 1.6% CH_4) are primarily related to the decomposition of fertilizers (81.8%) and less, to urea production and diesel combustion in transportation vehicles and agricultural machinery. These constitute the main environmental hotspots regarding climate change. Since the impacts in GW are high, there are some points that could be modified to reduce even more the carbon footprint profile, such as replacing or reducing nitrogen fertilizers applied to the sugarcane crop and minimizing diesel consumption by improving the supply chain and replacing fossil fuels. In this vein, a sensitivity analysis is performed to determine the relationship between the dose of nitrogen applied to sugarcane (in the form of urea) and the high emissions of GHG. The results show that a reduction in the addition of urea to the soil significantly and linearly decreases the GW ($5{\cdot}10^{-3}$ kg CO_2eq/%dose reduction). Hence, it is important to evaluate alternatives to the traditional way of fertilizing sugarcane with urea.

In addition, emissions associated with nitrogenous fertilizers applied to sugarcane cultivation contribute to the environmental impact categories TA and OD, in particular emissions of nitrous oxide (N_2O), other nitrogen oxides (NO_x) and ammonia (NH_3).

N_2O emissions have a significant impact on OD, accounting for 99.7%. Hence, the analysis suggests that both the ozone layer integrity and the climate would benefit from reductions in N_2O emissions.

Similar results can be observed TA, in which NH_3 emissions due to the fertilization of agricultural systems with urea are the main responsible for the high impacts in this environmental category. The main emission is NH_3 (93.2%), followed by NO_x (4.7%) and sulfur dioxide (2.1%).

The main substances that contribute to the RS category are natural gas (57%), oil (37.6%) and coal (5.5%), with the production of high-pressure natural gas being the process with the greatest influence (48.7%).

Furthermore, the analysis shows that the impacts of the biorefinery on FE are mainly due to the water emissions of phosphorus oxides coming from sugarcane growing (84.80%) and, to a lesser extent, from the processes of production of triple superphosphate (4.52%) and urea (5.58%). A strategy to reduce these emissions could include a more efficient use of phosphate fertilizers in the crop.

The sugar factory, distillery, and CO_2 capture and conversion stages do not contribute to the different categories of environmental impact, since the substances emitted into the air, soil and water have a zero impact factor and the electricity consumed is 100% renewable. The impacts associated with the H_2 production stage are far outweighed by the impacts of the other contributing categories, so they are considered negligible. This result is consistent with the electricity source (biomass) selected for water electrolysis.

Table 1
Design and operating conditions of the reactor and the distillation column for methanol production.

Equipment		Value	Unit
Reactor	Inlet temperature	210	°C
	Pressure	75	bar
	Reactor length	15	m
	Reactor volume	42	m^3
	Bed apparent density	887.5	kg/m^3
Distillation column	Number of plates	30	–
	Feed stage (from top)	24	–
	Reflux ratio	1.2	–
	Feed temperature	80	°C
	Condenser pressure	1.0	bar

Table 2
Key performance indicators and power consumption figures for the proposed methanol production process.

Parameter	Value	Unit
Methanol production rate	4.46	t/day
H_2 use (per unit of methanol product)	0.20	kg/kg
CO_2 use (per unit of methanol product)	1.49	kg/kg
Recycle to feed ratio (recycle/feed)	4.88	mol/mol
H_2:CO_2 ratio (feed/reactor inlet)	3.0/3.5	mol/mol
H_2 conversion in reactor (per pass)	16.90	%
CO_2 conversion (per pass)	19.99	%
CO_2 conversion (overall process)	94.90	%
Renewable electricity available	2000	kW
Power of H_2 feed compressor (30–75 bar)	19.77	kW
Power of CO_2 feed compressor (1–75 bar)	31.00	kW
Power electrolysis consumption	1840	kW
Power for refrigeration cycle	108.8	kW
Heat duty of reboiler (distillation column)	44.18	kW

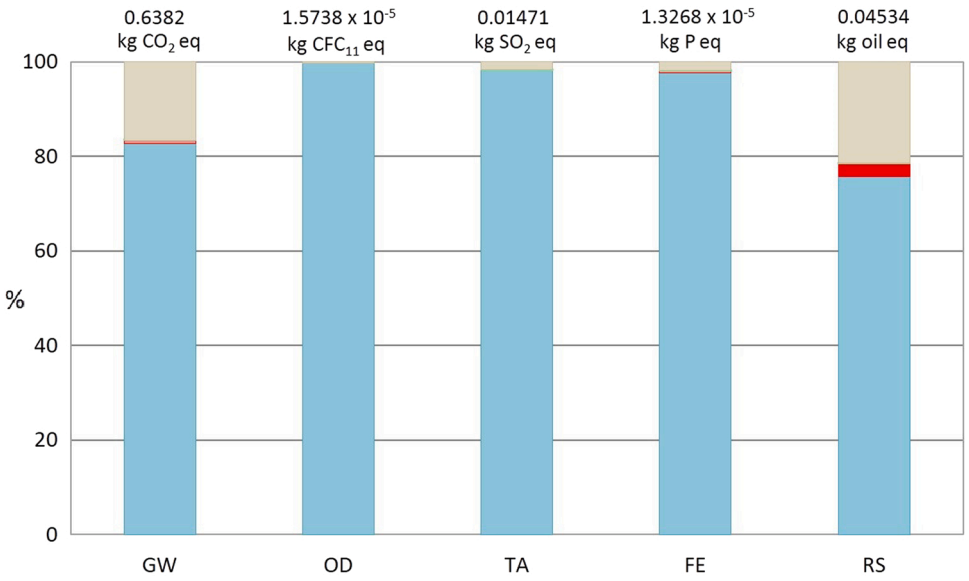

Fig. 4. LCA environmental profile of green methanol. Above each bar: absolute impact values per kg of methanol (Agriculture, Heat, Sugar factory + Distillery + CO_2 capture + Methanol synthesis + Electrolysis, others). The acronyms in the abscissas stand for: global warming (GW), stratospheric ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE) and fossil resource scarcity (RS).

The process "others" in Fig. 4 includes the emissions associated with the processes of transporting sugarcane to the industry and vinasse to the field, and the production of the N source (urea) used in the fermentation.

Figs. 5 and 6 show the comparison at a characterization and normalization level, respectively, between the environmental impacts of one kilogram of methanol produced by three different routes: (i) methanol from biogenic CO_2 and renewable H_2 (this work), (ii) methanol from syngas derived from biomass gasification and (iii) methanol production from natural gas by steam reforming (conventional process). Fig. 5 presents the comparison of the results, in percentage, referred to the highest impact value.

The CO_2-based methanol production process produces a higher impact on the GW category compared to the conventional route. As mentioned, this result is associated with the release of CO_2 emissions in the agriculture stage. In contrast to this work, other LCA studies presented in the literature consider CO_2 as an industrial waste with no associated environmental impact and, therefore, its environmental climate change profile for the methanol production is significantly reduced. For example, Meunier et al. [23] present a comparison between the climate change category impacts of the conventional methanol production process and the CO_2 coming from a cement plant to methanol conversion process, without including the carbon capture section and its previous stages. The GW of the CO_2-based process is lower than in the conventional methanol production, demonstrating more than 50% reduction in CO_2 emissions.

In the categories of FE and RS, the environmental impacts of the proposed process are considerably lower than the production of methanol by other means, especially in RS, which exhibits a reduction of more than 90% compared to the conventional process.

Fig. 6 shows the normalization of each impact category by using the normalization factors of the ReCiPe model, the impact of an average

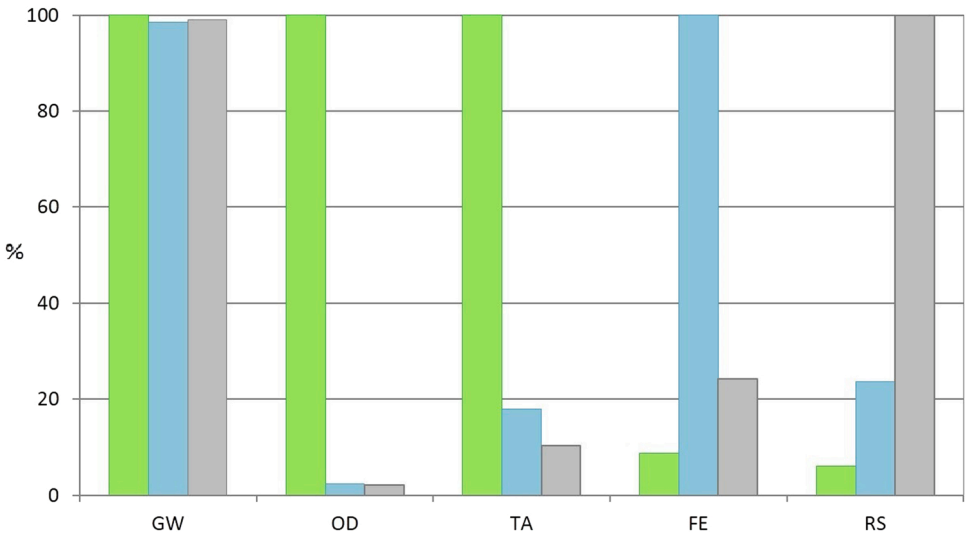

Fig. 5. Comparison between the environmental impacts of methanol production processes at characterization level (CO_2-based methanol, Biomass *via* syngas methanol and Fossil-based methanol). 100% represents the highest value for each impact category. GW: global warming, OD: stratospheric ozone depletion, TA: terrestrial acidification, FE: freshwater eutrophication, RS: fossil resource scarcity.

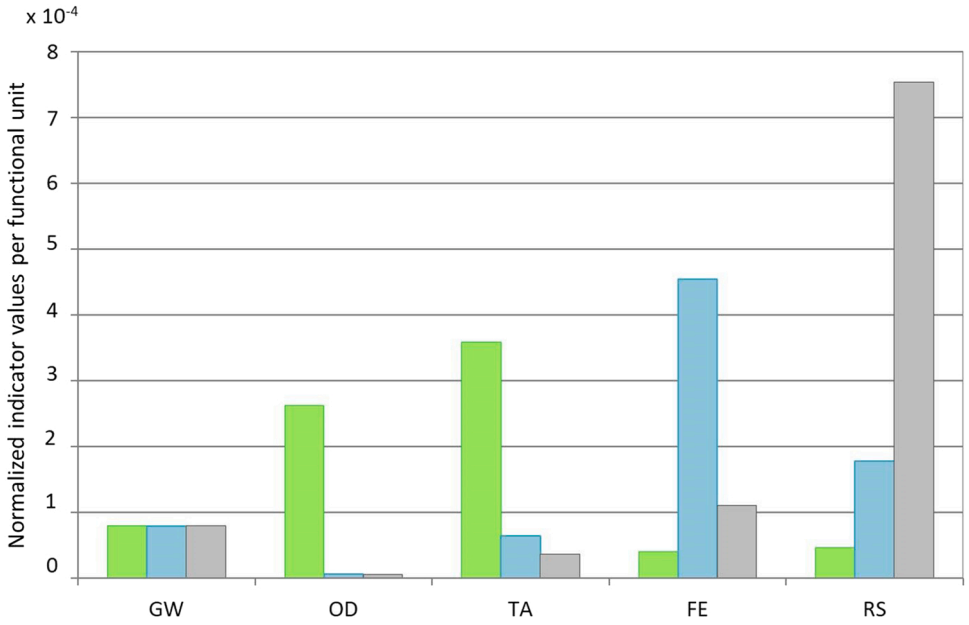

Fig. 6. Comparison between the environmental impacts of methanol production processes at normalization level (■ CO_2-based methanol, ■ Biomass *via* syngas methanol, ■ Fossil-based methanol). GW: global warming, OD: stratospheric ozone depletion, TA: terrestrial acidification, FE: freshwater eutrophication, RS: fossil resource scarcity.

world citizen (ReCiPe 2016 Midpoint (H) V1.04/World (2010) H/ Normalization [44]). The most relevant categories would be RS and FE, in which the CO_2-based methanol performs quite better than the other production processes.

Finally, Fig. 7 presents a Sankey diagram for the biogenic CO_2 flows involved in the proposed methanol production scheme. In the agriculture stage, sugarcane takes large volumes of CO_2 from the atmosphere through photosynthesis. The CO_2 absorption of millable sugarcane is calculated at about 48,770 $kgCO_2$/ha, a value lower than that reported by Carminati et al. [46]. These authors consider that the CO_2 sequestered by the plantation corresponds, according to the photosynthesis chemical equation, to 0.781 $kgCO_2$/kg sugarcane. From here, biogenic CO_2 is released and distributed following different paths throughout the processes that ultimately lead to methanol. The Sankey diagram reveals the opportunities for generating products from biomass-based CO_2. Several flows of biogenic CO_2 are released at different points of the methanol production process. In the sugar-alcohol industry, direct emissions are found in the combustion of bagasse (cogeneration system) and the fermentation of sugar (distillery). The bagasse combustion process represents the main source of biogenic CO_2 emissions from this industry. Therefore, to improve the sustainability of the sugarcane sector, it is important to evaluate capture-storage and capture-use options associated with this carbon source. For example, a greater production of green methanol could be obtained if biogenic CO_2 generated in the combustion of bagasse and H_2 obtained by electrolysis with some renewable source of electrical energy are selected as raw materials. Thus, a mixed production scheme for "full green" methanol and "gray" methanol should be evaluated, using renewable CO_2 and H_2 produced by electrolysis with electricity from the industry and alternatively with electricity from the grid (from a non-renewable source).

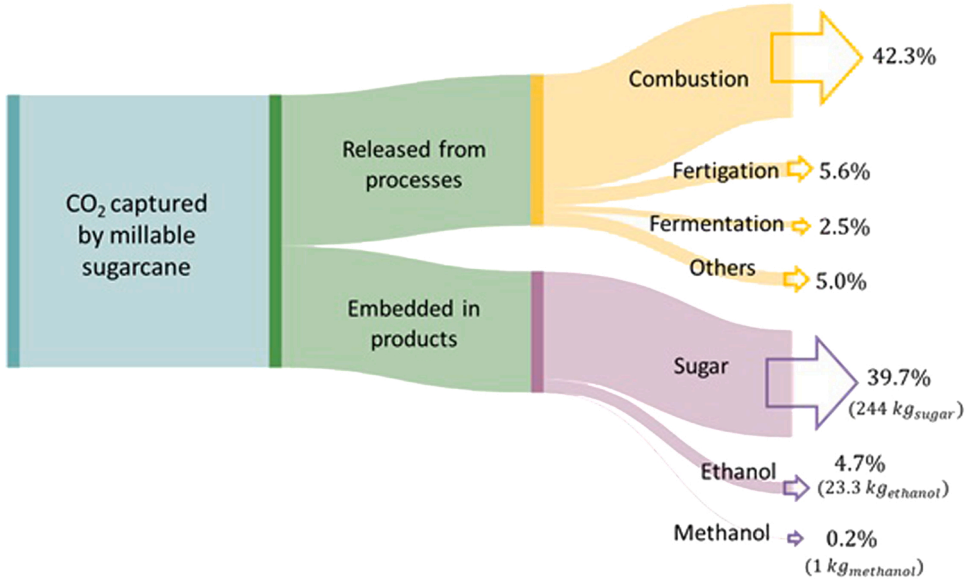

Fig. 7. Sankey diagram of biogenic CO_2 fate for the sugarcane biorefinery complex including methanol synthesis.

4. Conclusions

In this work the environmental implications of methanol production from biogenic CO_2 in a biomass biorefinery are explored. The carbon capture and transformation to methanol are modeled through process simulation. At all times, it has been ensured that H_2 used for the reduction of CO_2, as well as the electrical energy required for the process, are renewable. The environmental assessment is performed *via* a cradle-to-gate LCA study.

The approach is applied to a typical average large-scale sugar-ethanol complex from northwestern Argentina. The environmental competitiveness of green methanol production is demonstrated as an option for the decarbonization of the industry and the methanol market in the scenario considered. No less important is the fact that the addition of a new product to the biorefinery scheme results in a decrease in the impacts of each existing product.

The sustainability of the overall process strongly depends on the sustainability of the agricultural tasks that form the basis of the biorefinery, in this case, sugarcane growing. It is precisely the use of fertilizers and the consumption of fuel at that stage that gives rise to the predominant environmental impact of the methanol produced. This is an unavoidable aspect that is not taken into account in many environmental studies on the production of CO_2-based products, which leave apart the CO_2 origin.

As future work, other process combinations will be evaluated, including the use of other CO_2 sources from the same industry, as well as different renewable and non-renewable energy sources.

CRediT authorship contribution statement

Ana María CUEZZO Methodology, Software, Visualization, Writing – original draft, Investigation, **Paula Zulema ARAUJO** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Investigation, **Jonathan WHEELER** Conceptualization, Methodology, Writing – original draft, Investigation, **Fernando Daniel MELE** Conceptualization, Methodology, Project administration, Funding acquisition, Writing – review & editing, Writing – original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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