Techno-Economic and Environmental Analysis of Carbon, Capture and Utilization of fermentation CO_2 from Ethanol Distilleries

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ABSTRACT

The sugar and ethanol industry has a well-established sector in Brazil. Currently this sector has looked to improve processes and define further different product portfolios under a biorefinery perspective. BECCS designs with the capture of the CO_2 from ethanol fermentation suggest a relevant potential for carbon mitigation in Brazil. This study evaluated an innovative way to convert the biogenic CO_2 from the fermentation process to methanol. Three scenarios were considered comprising possible biorefinery designs for the combined production of ethanol with methanol. The potential carbon mitigation of all scenarios was evaluated on a life cycle basis, as well as the economic feasibility for the methanol production unit. Results showed that CO_2 capture is technically feasible, and the minimum selling price for methanol presented competitive values to the market price. Lastly, the environmental performance of the ethanol processes, considering the combined methanol production, could assure at least 72% of the GHG reduction compared to fossil gasoline.

KEYWORDS

Bioenergy with carbon capture and storage (BECCS), byproduct valorization, life cycle assessment (LCA), techno-economic analysis, methanol production, sugarcane biorefinery**.**

1. INTRODUCTION

The current pursuit for decarbonizing the global economy is directly related to an ambitious (and necessary) target for limiting the global temperature rise to below 1.8°C by 2100. To achieve this target, it is suggested net-zero emission emissions from the global energy sector by 2070, which can be carried out by a box of measures, from the fuel shifting to avoiding demand [1]. The Carbon Capture, Utilization and Storage (CCUS) techniques correspond to almost 20% of the potential carbon reduction by 2070. It is expected to implement CCUS in existing assets of power generation and heavy industries in the coming years. However, the

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decarbonizing potential would expand from 2040 with carbon removal from the atmosphere and carbon offsetting through Bioenergy with Carbon Capture And Storage (BECCS) [1].

Among the different BECCS designs, the capture of the carbon dioxide (CO_2) from ethanol fermentation, which is more concentrated than other streams, suggests a relevant potential for carbon mitigation in Brazil [2], since its well-consolidated sugarcane ethanol industry, that is responsible for supplying 20% of the national transport sector and 6% of the power demand through bagasse use [3].

Furthermore, Brazil is currently under a new policy for biofuels promotion (Renovabio program) [4], based on the potential carbon reduction of a specific biofuel on a life cycle basis. In the policy framework, the process design, including the use of residual feedstocks and the generation of power surplus, has an important influence on the overall performance of biofuel production. It is supposed that the carbon capture techniques and its eventual use as feedstock for other products could increase the ethanol industry portfolio and improve the environmental performance of the whole supply chain.

In this context, the capture and the later use of CO_2 for methanol production – which is considered a chemical building block for several products and is obtained mainly from fossil resources [1] – is well evaluated in several studies, as cited by Khojasteh-Salkuyeh et al. [5]. For instance, different methanol production pathways have been developing, such as conventional natural gas reforming, CO_2 hydrogenation, dry reforming, and tri-reforming, as shown in Figure 1. Details of each process unit (*e.g.*, *Methanol* synthesis, Separation and Purification, and Heat recovery) are discussed in Nguyen and Zondervan [6].

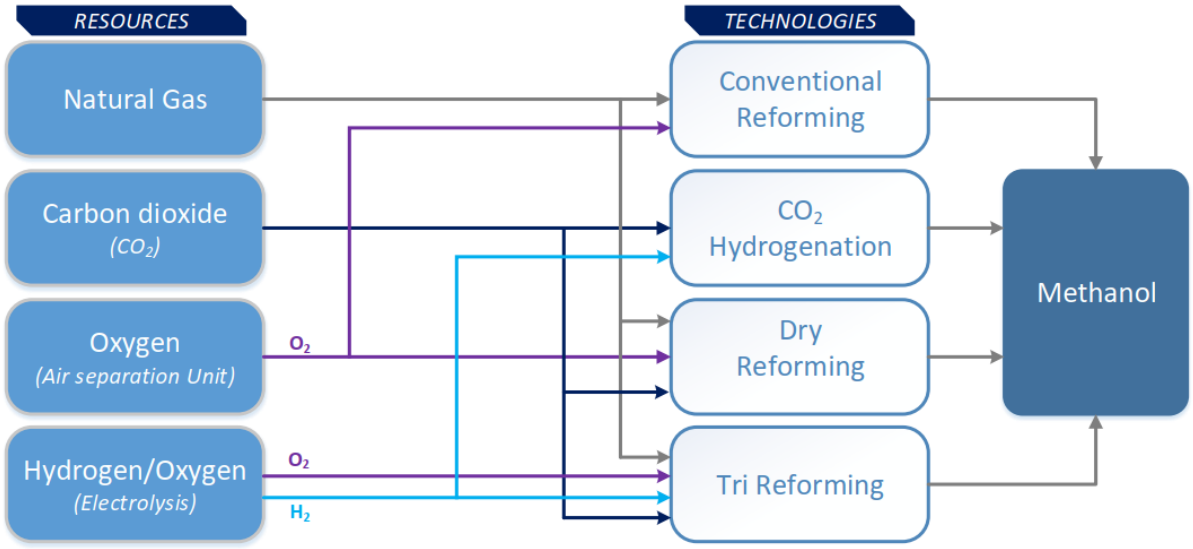

Figure 1. Schematic process of the methanol production routes [5]

Hence, this brief study evaluated the potential carbon mitigation and the techno-economic performance of the additional methanol production from fermentation processes of an ethanol distillery in the Brazilian context.

2. PROCESS DESCRIPTION

The carbon capture and utilization process for methanol production was assumed integrated into the ethanol distillery. Figure 2 shows the flow diagram of CCU at the biorefinery. Sugarcane stalks, and/or lignocellulosic material (LCM) composed by sugarcane straw and bagasse – in case of 2G ethanol production –goes to an autonomous distillery. During fermentation stages, a pure CO_2 stream is released; thus no penalty (at the separation step) was calculated, and it passes directly to compression stages. After compression, CO_2 goes to the methanol plant with hydrogen to produce methanol.

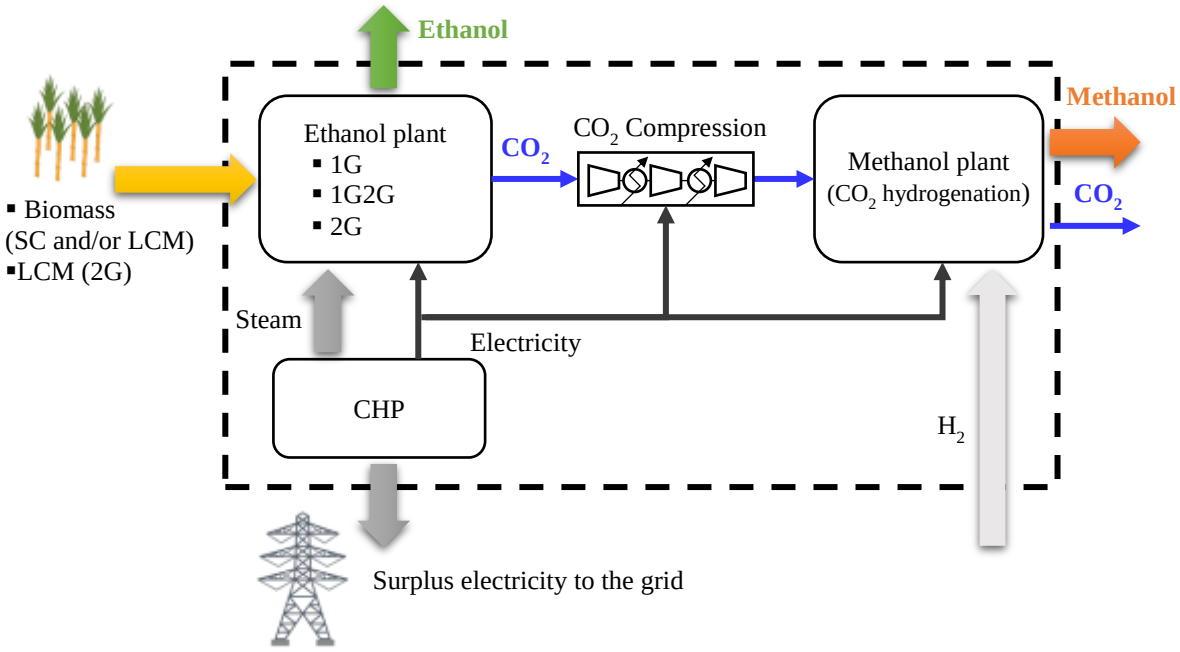

Figure 2. Simplified flow diagram CCU process at the biorefinery.
1G: first generation ethanol; 2G: second generation ethanol; 1G2G: combined production of 1G and 2G ethanol; CHP: combined heat and power; SC: sugarcane stalks; LCM: lignocellulosic material.

2.1. Biorefinery scenarios

The biorefinery system considered in this study is a facility that integrates sugarcane processing with biomass conversion to produce fuels and power. Three scenarios are considered for ethanol production based on a virtual biorefinery proposed by Bonomi et al. [7], and their main parameters are summarized in Table 1.

Conventional ethanol production – 1G

It is a facility in which ethanol is produced from sugarcane juice, and all remaining biomass, bagasse, and straw go to the cogeneration power plant for electricity generation. The combined heat and power (CHP) unit operates all year with 90% of the capacity factor with the CEST (condensing extraction steam turbine) technology.

Integrated ethanol production (1G2G)

For the 1G2G scenario, the 1G plant has the same configuration and operational conditions as the 1G autonomous distillery. The 1G sector of the plant operates for 200 days, while cogeneration and 2G sectors operate for 330 days. During harvest season, 2G sector runs with bagasse and straw coming directly from 1G plant, and during the off-season, 2G plant operates

with stocked bagasse and straw mixture. The CHP unit produces steam only to meet process requirements in backpressure turbines.

Ethanol production from LCM – 2G

The 2G facility is annexed to an autonomous distillery and uses only the surplus lignocellulosic material (bagasse and straw) for ethanol production. Electricity associated with this scenario is provided by the 1G distillery that burns only the amount of biomass required to supply its process steam demand.

Table 1. Characteristics of the biorefinery scenarios

Parameter	1G	1G2G	2G
Milling capacity (t/h)	833	833	-
Total annual milling capacity (Mt/year)	4.0	4.0	4.0[a]
Distillery operation (h)	4800	7920[b]	7920
Ethanol production (ML/year)	342	497	154
CO_2 production during fermentation (t/h)	55.3	72.4 (harvest)[c] 16.1 (off-season)	15.8
CO_2 production during fermentation (Mt/y)	0.266	0.397	0.125
Surplus electricity (kWh/t feedstock)[d]	186	62	244

[a] 2G production of ethanol considers using surplus lignocellulosic material (bagasse and straw) from an optimized 1G autonomous distillery associated with a mill processing 4 million tons of sugarcane per year

[b] Considering a 200-days harvest season and the off-season of 130 days.

[c] Including CO_2 stream from both 1G and 2G processes.

[d] Sugarcane is the feedstock for 1G and 1G2G scenarios. Lignocellulosic material (dry basis), comprising sugarcane residues (bagasse and straw) is the feedstock for the 2G scenario.

3. METHODS

3.1. Technical assumptions

In all scenarios, the surplus electricity from ethanol distillery would be used for supply the CO_2 compression duty and methanol production demand. The parameters for the compression stage were estimated following the model proposed by McCollum and Ogden [8]. The CO_2 stream would be compressed until 92 bar, adequate pressure to enter the methanol reactor.

It was assumed that the methanol plant would be located at the biorefinery site. For that reason, it was not considered transportation logistics. Moreover, CO_2 was assumed as an ideal gas and the compression process was divided into five stages with intermediate cooling (at 40°C) and isentropic efficiency of about 85% per stage.

In turn, the CO_2 hydrogenation was assumed for methanol production. During the hydrogenation of CO_2 into methanol (CH_3OH), the main reaction (*methanol synthesis*), shown in relation (1), includes the hydrogenation of CO_2 and CO and the reverse water-gas shift. In this case, a high-purity hydrogen from an external source was assumed to be delivered at the pressure of 92 bar.

$$CO_2+3H_2 \leftrightarrow CH_3OH+H_2O \quad (1)$$

For the methanol synthesis, it was assumed that CO_2 enters at 92 bar and 40 °C. Next, conversion takes place in a catalytic reactor, fed with CO_2 and hydrogen, at a temperature of 200–300 °C and pressure of 50–100 bar, in the presence of $Cu/ZnO/Al_2O_3$ catalyst, and a methanol purity of 99.5 wt% was adopted in the process conversion [5].

3.2. Economic performance assessment

The economic assessment considered only the methanol unit integrated into ethanol distilleries. The methanol unit scale is directly related with available CO_2 stream at ethanol fermentation processes. Cost estimations were done based on a literature review for the CO_2 hydrogenation technology. All costs are presented in €$_{2019}$ and for all equipment, the useful life is 25 years. The interest rate was 12% and taxes were calculated to be coherent with references for biorefinery scenarios in Brazil. The minimum selling price (MSP) for methanol was calculated to evaluate feasibility.

Capital expenditures (CAPEX) were estimated from the values taken from Nguyen and Zondervan [6] in the function of the CO_2 outlet stream from the ethanol plant. Equation 2 presents the relation adopted, where C represents the capital cost, Q the capacity, α is the scaling factor, and *ref* indicates the reference case. The Chemical Engineering Plant Cost Index-CEPCI was adopted to update data to the year of reference [9]. Equation 2 shows the cost estimate correlation used on the evaluation [10]. This analysis represents an estimated class 5 (Accuracy -25% to +40%) according to the American Association of Cost Engineering (AACE).

$$C = C_{ref} \cdot \left(\frac{Q}{Q_{ref}} \right)^{\alpha} \quad (2)$$

Regarding the operation costs, no cost was attributed to CO_2, as it is an output emission in ethanol production. In the case of hydrogen, the assumed cost was 1,395 € considering steam methane reform [11]. As electricity is provided by the CHP annex, no cost was attributed. For heating duties, the cost was assumed at 41 €/MWh [12]. Other expenses were considered in the function of fixed capital investment: 3.5% for labor and 3% for maintenance.

3.3. LCA assessment

From a biorefinery perspective, the Life Cycle Assessment (LCA) aimed to evaluate the GHG emissions associated to 1.0 $MJ_{ethanol}$ considering an additional methanol production from CO_2 released in the fermentation process. The three different scenarios, as above described, were analyzed assuming the 1G ethanol production as a baseline scenario.

The LCA was carried out on cradle-to-gate boundaries, *i.e.*, from acquiring the raw materials to products delivered at the industry gate. The global warming potential (GWP) factors reported by IPCC AR5 [13] were assumed. For the background database, similar emission factors were taken from RenovaCalc [14].

The multiple products – mostly, ethanol, methanol, and power surplus – were handled in two different ways: i) by energy allocation, as assumed in RenovaBio [14]; and ii) by system expansion, considering the credits related to the power surplus displacing marginal power generation in the Brazilian grid (0.465 $kgCO_2/kWh$, Capaz et al., 2021) and the conventional methanol production (0.620 $kgCO_2/kWh$, Ecoinvent, 2016). In general, lignocellulosic feedstock was accounted for with null burden from upstream, except its transportation. Land-use change (LUC) aspects were not considered here.

4. RESULTS AND DISCUSSION

Potential for reducing CO_2 emissions considering the replacement of fossil methanol by biogenic methanol; the impacts on power surplus generation (and electricity exported to the grid) considering the capture of biogenic carbon were evaluated. Besides, the techno-economic analysis was focused on the assessment of the methanol production unit.

4.1. Techno-economic analysis

Table 2 summarizes the main outcomes for the methanol production unit. Thus, the inlets and outputs balances for the configuration systems are given. Moreover, the economic performance results (Table 3) in terms of the CAPEX per unit of methanol produced, surplus electricity, and MSP of methanol were determined.

Table 2. Results for the methanol production unit

Parameter	1G	1G2G		2G
		harvest	off-season	
Operation (h)	4800	4800	3120	7920
Inputs				
CO_2 (t/h)	55.3	72.4	16.1	15.8
Hydrogen (t/h)	10.8	14.5	3.1	3.1
Outputs				
Methanol (t/h)	36.6	47.9	10.6	10.5
CO_2 (t/h)	5.5	7.2	1.6	1.6
Total CO_2 captured (Mt/year)	0.239	0.358		0.113
Total methanol production(Mt/year)	0.176	0.262		0.083
Duties				
CHP available power (MW)	155	42	15	15
CO_2 compression (MW)	5.0	6.5	1.4	1.4
Methanol unit (MW)	1.5	1.9	0.4	0.4
Heating demand (MW_{th})	16	21	5	4
Surplus electricity(kWh/t feedstock)	178	50		220

Table 3. Economic performance results

Parameter	1G	1G2G	2G
CAPEX / t of methanol produced (€/t)	8.44	9.91	18.35
OPEX / t of methanol produced (€/t)	3,379	3,380	3,385
MSP of methanol (€/t)	432.2	436.6	434.5

In general, the MSP of the methanol for each biorefinery scenario indicated it as a competitive product since the methanol market was established in the range of 330 to 375 €/t in 2019 [16]. On the other hand, the methanol unit process achieved a conversion efficiency of 52.6%. These facts could represent a window of opportunity to improve the product portfolio of the Brazilian ethanol and sugar industry.

4.2. LCA results

In all the cases, the sugarcane ethanol produced in Brazil, with or without an additional methanol production, could provide, at least, 72% of the GHG reduction in comparison with fossil gasoline (87.4 gCO_{2e}/MJ) [14].

According to Figure 3a, the GHG emissions associated with ethanol, when a combined methanol production is considered, ranges from 3% lower to and 24% higher than the baseline (conventional ethanol production without methanol production). The lowest value (19.1 gCO_{2e}/MJ) is related to the scenario based on 2G ethanol production, mostly because the GHG emissions from feedstock procurement were disregarded. On the other hand, the highest value was estimated for the 1G scenario (24.2 gCO_{2e}/MJ), when the sugarcane crop corresponds to around 45% of the total emissions. The higher ethanol yield obtained in the 1G2G scenario (124 $L/t_{sugarcane}$) in comparison with the 1G scenario (85 $L/t_{sugarcane}$) justifies the bit lower value estimated for the former (24.0 gCO_{2e}/MJ).

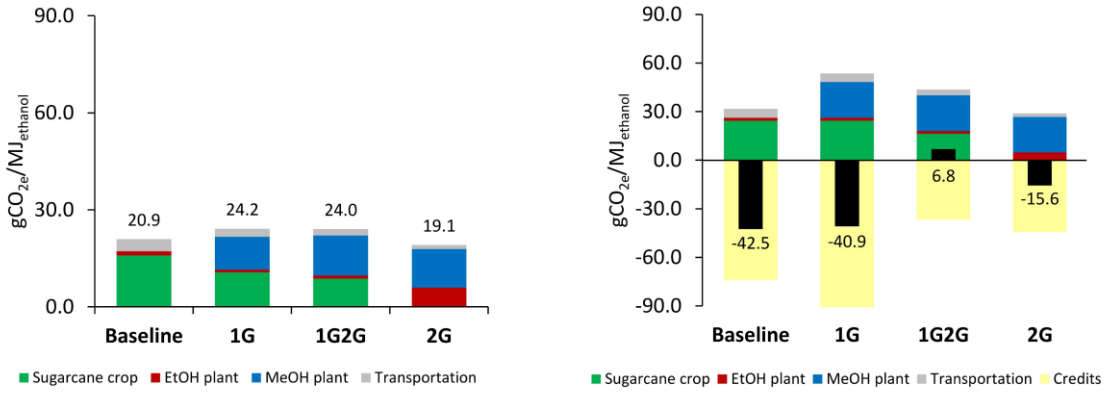

Figure 3.

(a) GHG emissions related to ethanol production on the life cycle basis, assuming energy allocation for the multiple products

(b) GHG emissions related to ethanol production on the life cycle basis, assuming system expansion for the multiple products

The contribution of the sugarcane crop to the overall emissions decreases in the scenarios with the combined methanol production in comparison to baseline, since in these cases, the reference product, i.e., ethanol, divides the environmental burden of the upstream process also with methanol; while in the baseline, the total GHG emissions are allocated only between ethanol and the power surplus.

On the other hand, the methanol production corresponds from 42% (1G scenario) to 63% (2G scenario) of the total emissions, mostly due to hydrogen input, which was assumed to be produced off-site from natural gas. The internal hydrogen production using the power surplus, via electrolysis, from the ethanol mill could improve the environmental performance of these scenarios. However, in all the cases, the power surplus would not be enough for the hydrogen demand for methanol production. In 1G scenario, the power surplus – after its use for CO_2 capture/compression and in the methanol plant – would correspond only to 30% of the power demand to supply the total hydrogen requested for the methanol production, *i.e.*, around 0.20 $kg_{H2}/kg_{methanol}$ or 420 - 430 $kWh/MJ_{ethanol}$ from the inventories assumed here. In 1G2G and 2G

scenarios, the power surplus would supply 5% to 9% of the power demand for the hydrogen requested, respectively.

It is widely recognized that how multiple product systems are evaluated in the LCA perspective could support quite different interpretations [12]. For example, assuming the system expansion approach (see Figure 3b), the environmental performance of the conventional ethanol process (baseline) could provide higher GHG mitigation (-42.5 gCO_{2e}/MJ) than when a combined methanol production is considered, mostly because of the credits related to power surplus. However, in the other scenarios, mainly in 1G2G and 2G, the credits related to alternative methanol production even summed to the power surplus, has their mitigation effect decreased by the relevant emissions associated to the methanol plant.

Indeed, the methanol production in these three scenarios, and consequently the credits, are quite similar (30 $g_{methanol}/MJ_{ethanol}$). The difference is in the power surplus, which goes from 121 Wh/ $MJ_{ethanol}$ (1G scenario) to 23 Wh/ $MJ_{ethanol}$ (1G2G scenario).

There is not a single answer for what approach (energy allocation or system expansion) is the correct one. In a policy context, it depends on what question the LCA intends to answer or what kind of process the policy wants to support. While RenovaBio uses the energy allocation, the Renewable Fuel Standard (USA) [17] assumes system expansion.

5. CONCLUSION

The environmental and economic performance of methanol production from CO_2 released in the fermentation process was evaluated in Brazilian conditions since the relevant dimension of the ethanol industry in Brazil. Three different designs were considered: *i) conventional ethanol production (1G); ii) integrated ethanol production (1G2G); iii) ethanol production from lignocellulosic material (2G).*

The techno-economic assessment applied exclusively on the methanol unit showed that the production could be competitive (around 430 €/ton) with the current methanol price (approximately 330 - 375 €/ton). Therefore, according to the assumptions for this analysis, the CAPEX corresponded to lower than 5% of the total costs. At the same time, the operational expenditures (OPEX), led mainly by hydrogen input, are responsible for the most significant share of the total costs. Therefore, the scaling difference between the three scenarios was not relevant to the total costs.

In turn, the environmental performance of the ethanol assuming a combined production of methanol presented close values (19.1 - 24.2 gCO_{2e}/MJ) to the conventional ethanol processing (20.9 gCO_{2e}/MJ). If credits were assumed for co-products, such as power surplus and methanol, the GHG emissions related to ethanol could range between 6.8 to (-40.9 gCO_{2e}/MJ), mostly led by the credits related to the power surplus.

In general, the hydrogen input for methanol production was considered the bottleneck for economic and environmental performance. Using the power surplus to produce the hydrogen requirement internally could, eventually, improve some indicators, but it was estimated that the amount of the power surplus would not be enough.

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NOMENCLATURE

BECCS	Biomass energy carbon capture storage	GWP	Global warming potential
CAPEX	Capital expenditures	H_2	Hydrogen
CCUS	Carbon capture utilization and storage	LCA	Life cycle assessment
CEST	Condensing-extraction steam-turbine	LCM	Lignocellulosic material
CHP	Combined heat and power	LUC	Land-use change
CO_2	Carbon dioxide	MSP	Minimum selling price
GHG	Greenhouse gas	OPEX	Operational expenditures

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