

Integrated CO₂ capture and conversion into methanol units: Assessing techno-economic and environmental aspects compared to CO₂ into SNG alternative

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ABSTRACT

Using carbon dioxide (CO₂) as a raw-material to produce value-added chemicals has a strategic role to play in the decarbonization of energy resources and the transition to a climate-neutral economy. E-methanol, Synthetic Natural Gas (SNG) and e-kerosene are one of the most promising pathways to convert CO₂. In this context, the aim of this work is to propose an optimized and integrated CO₂ to methanol process and then to compare it to the CO₂ to SNG process from economic and environmental points of views. An optimized reactor configuration in the CO₂ to methanol conversion unit has been successfully implemented in Aspen Plus® and leads to a thermal energy self-sufficiency of this unit. A heat integration with an advanced capture unit has been performed where 5 % of the heat requirement could be provided from the conversion unit while 95 % come from external steam source. Techno-economic assessment of the optimized process showed that methanol is more profitable when it is used as a raw material to synthesize other chemicals. As an energy carrier, SNG is more interesting. Compared to the reference scenario, a net CO₂ emission reduction of 70 % in the CO₂ to SNG route and of 60 % in the CO₂ to methanol route were obtained. Concerning the fossil depletion impact, in both cases, a reduction of more than 60 % was noticed (ca. 75 % in CO₂ to SNG route and 61 % in CO₂ to methanol case).

1. Introduction

Anthropogenic greenhouse gases (GHG) emissions resulting from human activities are causing global warming and accelerating the earth's climate change faster than it ever has during human history [1]. Carbon dioxide (CO₂) emissions from energy combustion and industrial process accounted for 89 % of energy-related greenhouse gas emissions in 2022. CO₂ is the primary GHG emitted in 2022 with 321 Mt coming from energy and industrial sector and reaching a new record of 36.8 Gt [2]. The cement industry ranks as the third-largest emitter of CO₂ worldwide, following power plants and the steel industry, contributing approximately 5–8 % of global CO₂ emissions [3]. Unlike other

industrial processes where CO₂ emissions primarily come from the need of energy, the CO₂ emissions from production processes are generated by the chemical process itself (the decarbonation step) rather than the combustion of hydrocarbons to produce energy. For the best available technologies (BAT) used in cement plants, less than 40 % of total CO₂ emissions are the consequence of fossil fuel combustion and the rest is coming from the process itself [4]. The challenge to reduce these unavoidable CO₂ emissions remains large due to the continuous increase in cement production [3,4]. Concrete actions are being discussed, implemented or developed along the entire value chain in order to restrict global warming to 2°C and attain net zero greenhouse gas (GHG) emissions by 2050 aligning with the goals of the Paris Agreement [5]. In

Abbreviations: APEA, Aspen Process Economic Analyzer; AEL, Alkaline Electrolysis; BAT, Best Available Techniques; CAPEX, Capital Expenditure; CAGR, Compound Annual Growth Rate; CEPCI, Chemical Engineering Plant Cost Index; CC, Climate Change; CCUS, Carbon Capture Utilization and Storage; FD, Fossil Depletion; FCI, Fixed Capital Investment; FU, Functional Unit; GHG, Greenhouse Gases; GHSV, Gas Hourly Space velocity; ICA, Inter-Cooled Absorber; LHHW, Langmuir-Hinshelwood-Hougen-Watson; LCoP, Levelized Cost of The Plant; LCA, Life Cycle Assessment; LHV, Lower Heat Value; OPEX, Operating Expense; PtL, Power to Liquid; PtG, Power to Gaz; PEM, Proton exchange membrane; RVC, Rich Vapor Compression; RWGS, Reverse Water Gas Shift; SNG, Synthetic Natural Gas; SOEL, TRL, Technology Readiness Level; WW, Water Wash.

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this context, Carbon Capture Utilization and Storage (CCUS) emerges as a primary technology pivotal for the decarbonization of the cement sector. Recently, substantial research efforts have focused on optimizing CO₂ capture techniques to enhance their efficiency and cost-effectiveness. The captured CO₂ can then be transported to be geologically sequestered or it can be used as feedstock to synthesize high-value chemicals [6,7]. Carbon Capture and Storage (CCS) is known as an effective method to reduce CO₂ emissions, receiving substantial attention from various sectors (e.g. industries, energy and governments). The CO₂ sequestration can pose particular challenges in terms of liability and public acceptance regarding the unknown long-term risks related to this technology [8]. From the other hand, Carbon Capture and Utilization (CCU) is primarily promoted when products derived from CO₂ can viably substitute the fossil-based ones at a comparable price point, all without additional CO₂ emissions. The estimated potential for CO₂ utilization fluctuates in research, with figures ranging between 200 million metric tons to nearly 500 million metric tons per year, as cited in different sources [7,9]. These calculations exclude extensive applications like CO₂-based fuels. Incorporating these alternatives could potentially enable the utilization of up to 10 % of anthropogenic CO₂ [9, 10]. Various alternative methods to convert CO₂ into valuable products are still in their initial phases of development, despite active research efforts. Chauvy et al. [7] investigated the different technologies for chemical conversion of CO₂, they concluded that routes such as formaldehyde and acetic acid are not expected to be industrialized in the near future, specifically within a timeframe shorter than 5–10 years. Some CCU technologies present themselves as highly promising options in the near future (e.g. methanol and synthetic natural gas (SNG)).

During the last years, various studies investigated the concept of power to liquid (PtL) and power to gas (PtG) where converting CO₂ is done using green hydrogen produced from the energy surplus generated by renewable sources [11–15]. Previous works investigated different cases of PtL and PtG combined with different H₂ production technologies [15–23]. It was shown that the H₂ production step is the key element to define the cost of the plant. Harada et al. [11] investigated an integrated system for producing SNG using direct air capture and water electrolysis. Their study highlighted the significant contribution of electricity costs in the water electrolysis process to overall operating expenses. Among the various water electrolysis techniques, the alkaline electrolysis (AEL) stands out as the most mature but this method has its disadvantages such as its low efficiency (60–70 %) in comparison with two other electrolysis techniques, namely Proton Exchange Membrane electrolysis (PEM) and Solid Oxide Electrolysis (SOEL) [24]. Comparing to SOEL, PEM electrolysis is the most advanced technology and is presently available on the commercial market [25]. The highest system efficiency is accorded to the SOEL technology with of 76–81 % (LHV basis) [26]. However, this technology needs high external fuel energy due to the high temperature electrolysis process (~800 °C) which increases the operating costs (2940–5880 €/kW) [27]. The system efficiency of PEM technology is lower with 53–65 % (LHV basis) [28,29] but with lower price (1155–1890€/kW) [30]¹. According to Martsinchyk et al. the prices are projected to decrease by 15–21 % by 2030 and 29–37 % by 2050 [12].

Regarding the CO₂ conversion, methanol produced by catalytic CO₂ hydrogenation has been already confirmed as one of the most promising CO₂ conversion pathways primarily linked to the technology's maturity (TRL 8–9), the market's size and applications ranging from fuels to chemicals [31]. The worldwide methanol market reached a valuation of 34.8 billion euros in 2021 and is anticipated to achieve 53.5 billion euros by 2030. This growth reflects a Compound Annual Growth Rate (CAGR) of 5.06 % from 2022 to 2030 [32]. Various configurations and/or models to simulate the CO₂ to methanol conversion unit have

been proposed generally with a techno-economic study of the global power to methanol process [33–36]. Generally, the typical methanol production unit consists in several steps: feedstocks (H₂ and CO₂) compression, heating, catalytic reaction and methanol purification. Other studies investigated different catalysts for the named reaction but the copper-based catalysts remain the most referenced due to their high efficiency and low cost [33,37–39]. However, although various works investigated the sustainability of the power to methanol system in general, few of them focused on the conversion unit optimization, especially the improvement of the heat recovery and energetic efficiency. A study conducted by Battaglia et al. [39] on a power to methanol system demonstrated that the heat recovery in the conversion unit helps to reduce the heating and cooling demand by 81 % and 47 % respectively. They also showed that the preheating of H₂/CO₂ reactant mixture to the operating temperature of the methanol synthesis reactor corresponds to 97 % of the external energy demand after heat integration. In another work based on PtG technology, it was revealed that optimizing the heat integration between the CO₂ capture and conversion units could not just lower costs, but also mitigate CO₂ emissions resulting from the external heat demand of the process [13].

In this context, the heat integration of the CO₂ to methanol conversion process has been investigated in the first part of this work. An innovative configuration is considered consisting in using two reactor sections: a first adiabatic one allowing the preheating of the H₂/CO₂ mixture (using the energy released by the exothermic reaction) before injection into an isothermal section. This new reactor configuration allows a full energy self-sufficiency of the conversion unit (see comparison with the case of using one isothermal reactor in the [supporting information](#) (SI.1)). The energy excess from the conversion unit is provided to the capture unit as thermal contribution for the solvent regeneration. Secondly, a techno-economic and environmental assessments of the global power to methanol system was performed, especially combining two other units: (1) PEM electrolyzer for H₂ production. This technology was selected regarding its low price, high efficiency and maturity (availability of unit at large scale 5–10 MW), (2) An advanced capture unit by absorption using MDEA + PZ as solvent and based on the work of Dubois and Thomas [40,41]. The obtained results are compared with the process studied by R. Chauvy et al. [42] aiming to convert the CO₂ into SNG. For a meaningful comparison, both the conversion units (CO₂ to methanol and CO₂ to SNG) and the corresponding water electrolyzers have been scaled considering a similar capture unit size.

2. Material and methods

2.1. Description of the CO₂ conversion system into methanol

The power to methanol system investigated in this work is combined with carbon capture and utilization (CCU) chain where a flue gas emitted from a conventional cement plant (see [Fig. 1](#)) is treated. In this chain, three units are included: the water electrolysis unit for the green hydrogen production, the post-combustion CO₂ capture unit, and the CO₂ conversion consisting in a catalytic CO₂ to methanol conversion unit.

These units are detailed hereafter.

2.1.1. Water electrolysis unit

To generate green hydrogen, a polymer electrolyte membrane electrolysis (PEM) is considered in this work due to its high potential for cost reduction, durability, and efficiency improvement [16,43]. It is assumed that a 10 MW PEM stack (biggest single stack scale currently commercialized), linked to a wind park, corresponds to approximately 180 kg/h of hydrogen production (with an associated oxygen production of 8 kg O₂ per kg H₂) [29,42]. It is worth noting that the process for producing H₂ is not within the focus of the current paper. The entire process, including the carbon capture unit, was scaled based on the hydrogen production one.

¹ The costs in dollar from the different references were converted to euro according to 2023 exchange rate (1\$ = 1.05€)

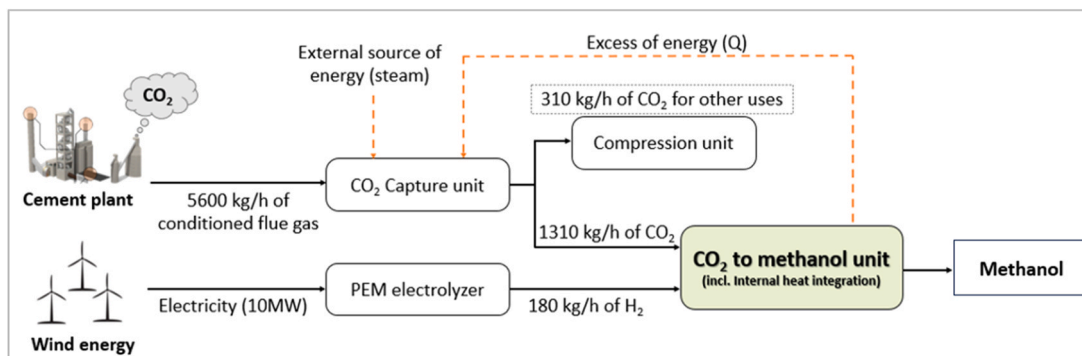


Fig. 1. The conceptual power to methanol system combined with CCU process.

2.1.2. Advanced post-combustion CO₂ capture unit

This paper considers an advanced post-combustion capture unit based on the work outlined by Chauvy et al. [42], as illustrated in Fig. 2 of the presented flowsheet. The unit have been improved and optimized by L. Dubois et al. [40] where they compared different solvents and configurations. The selected solvent is an aqueous blend composed of 10 wt% of methyl diethanolamine (MDEA) and 30 wt% of Piperazine (PZ). The implemented CO₂ capture process includes a Rich Vapor Compression (RVC) process combined with an Inter-Cooled Absorber (ICA) and two Water-Wash (WW) sections, interconnected with a conventional absorption-regeneration process.

In order to compare the CO₂ to methanol process and the CO₂ to SNG one, the size of the capture unit, directly linked to the realistic scale of a single stack (namely 10 MW) for the H₂ production unit, is the same as considered in the work of Chauvy et al. [42]. They verified that the surplus energy reclaimed from the methanation unit is allocated to solvent regeneration within the capture unit, maintaining self-sufficiency in thermal energy within the conversion unit. This results in a possibility to treat 10 % of the global cement plant’s flue gas (5600 kg/h). Considering the Brevik cement plant’s flue gas in Norway as case study, the gas to be treated is injected at 1.2 bar and 146.6°C. Its constituents include N₂, CO₂, O₂, and H₂O at percentages of 64.7, 20.4, 8.6, and 6.3 mol% respectively [44]. It has to be noted that the CO₂ absorption ratio is equal to 90 mol.% resulting in a mass flow rate of 1620 kg of captured CO₂ per hour (with a purity of 98 mol.% at 4.96 bar and 45°C).

The captured CO₂ and green H₂ are sent to the conversion unit with a stoichiometric ratio H₂/CO₂ equal to 3 at the inlet of the installation, which means that 1310 kg/h of CO₂ is used by the process. The residual portion of the captured CO₂ (310 kg/h) undergoes compression up to 110 bar through a three-stage compressor with intercooling down to 40°C. This step is essential for transporting the CO₂ to alternative utilization sites or for storage purposes [45].

2.1.3. CO₂ to methanol conversion unit

The CO₂ conversion unit simulation was conducted utilizing Aspen Plus® software (V12). The Redlich-Kwong equation of state [46] was employed for computing gaseous properties, while the gas-liquid equilibrium calculations within the rectification column were based on the UNIFAC model [47]. The implemented flowsheet of the CO₂ conversion unit is shown in Fig. 3.

The H₂ and CO₂ are fed with a pressure of 30 and 4.96 bar respectively. They are compressed up to 65 bar using one compressor for H₂ and three stages compressor with intermediate intercooling for CO₂. They are then mixed and preheated to 230°C (Heater 1) before entering in a plug-flow reactor comprising a first adiabatic section followed by a second isothermal section operating at 250°C. The model of Graaf has been considered to describe the reaction kinetics [48,49]. This model was established using CuO/ZnO/Al₂O₃ solid catalyst where all reactions are presumed to follow a dual-site Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism [50]. Three reactions are involved: (1) the CO₂ hydrogenation, (2) the Reverse Water Gas Shift

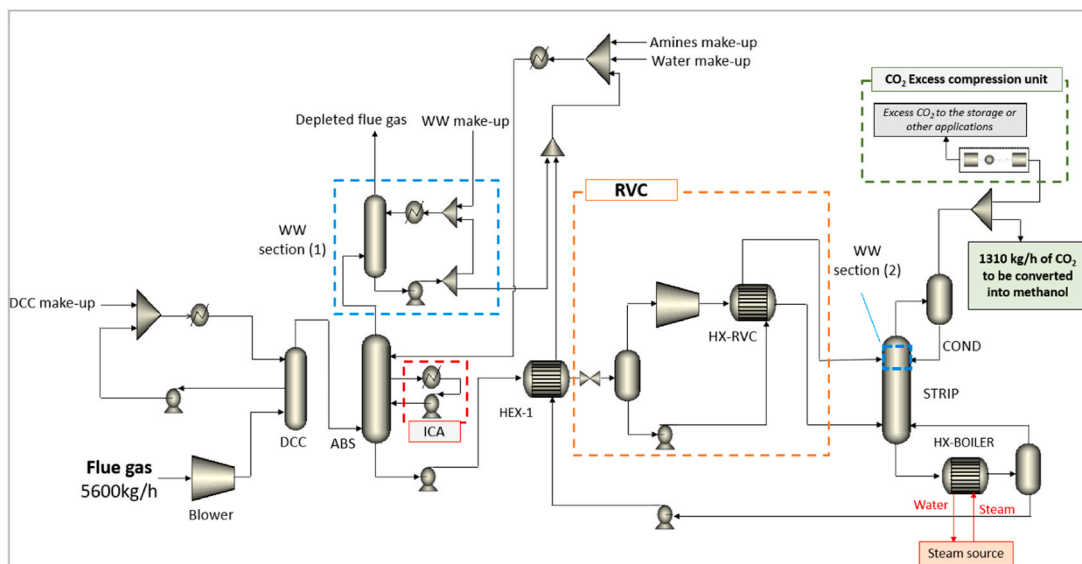


Fig. 2. Post-combustion absorption-regeneration CO₂ capture unit including ICA, WW and RVC.

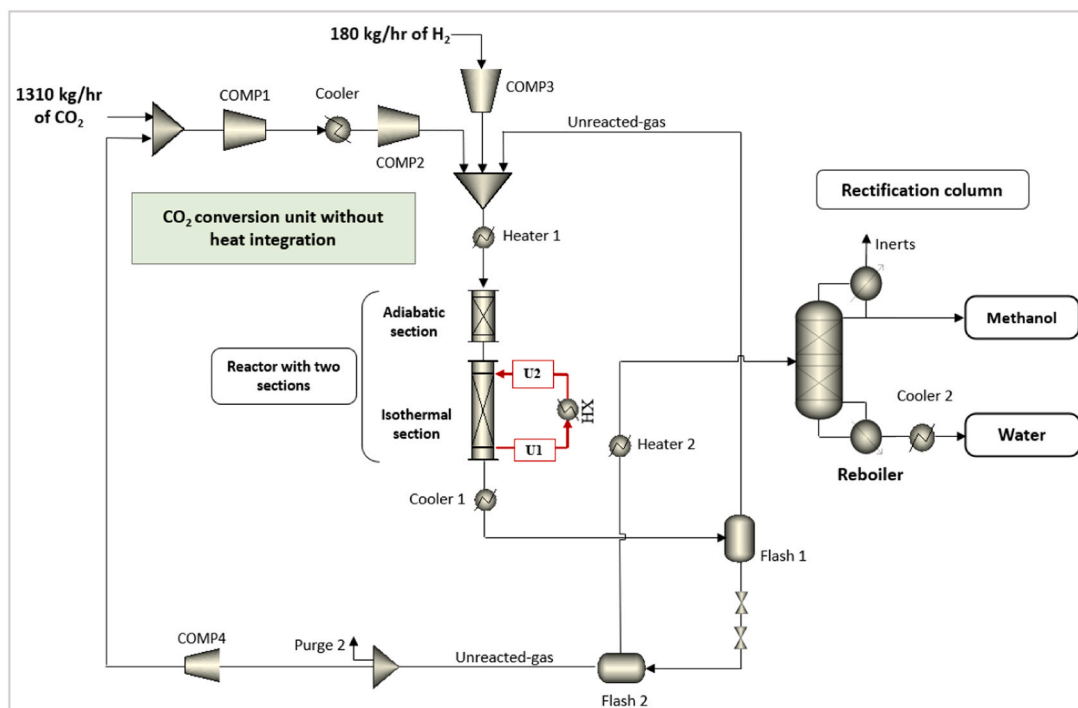


Fig. 3. Flowsheet of the CO₂ conversion unit.

(RWGS) and (3) the hydrogenation of CO. The RWGS reaction is endothermic while the reactions of CO and CO₂ hydrogenation are exothermic.



According to Graaf, the rate for each reaction is expressed as following:

$$r_{(1)} = \frac{k_1 K_{\text{CO}_2} \left(f_{\text{CO}_2} f_{\text{H}_2}^{1.5} - \frac{f_{\text{H}_2\text{O}} f_{\text{CH}_3\text{OH}}}{K_{p,(1)} f_{\text{H}_2}^{1.5}} \right)}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) (f_{\text{H}_2}^{0.5} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{0.5}) f_{\text{H}_2\text{O}})} \quad (4)$$

$$r_{(2)} = \frac{k_2 K_{\text{CO}_2} \left(f_{\text{H}_2} f_{\text{CO}_2} - \frac{f_{\text{H}_2\text{O}} f_{\text{CO}}}{K_{p,(2)}} \right)}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) (f_{\text{H}_2}^{0.5} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{0.5}) f_{\text{H}_2\text{O}})} \quad (5)$$

$$r_{(3)} = \frac{k_3 K_{\text{CO}} \left(f_{\text{CO}} f_{\text{H}_2}^{1.5} - \frac{f_{\text{CH}_3\text{OH}}}{K_{p,(3)} f_{\text{H}_2}^{1.5}} \right)}{(1 + K_{\text{CO}} f_{\text{CO}} + K_{\text{CO}_2} f_{\text{CO}_2}) (f_{\text{H}_2}^{0.5} + (K_{\text{H}_2\text{O}} / K_{\text{H}_2}^{0.5}) f_{\text{H}_2\text{O}})} \quad (6)$$

Here, r_i denotes the rate of reaction i (mol/s kg_{catalyst}), k_i signifies the kinetic constant of reaction i , K_j stands for the adsorption constant of component j , $K_{p,i}$ represents the equilibrium constant of reaction i , and f_j corresponds to the fugacity of component j .

The Gas Hourly Space Velocity (GHSV) can be expressed following (7). Its value has been set at 10000 h⁻¹ as suggested by [18,51].

$$\text{GHSV} = \frac{Q_{v_0} \rho_{\text{catalyst}}}{m_{\text{catalyst}}} \quad (7)$$

Where ρ_{catalyst} represents the apparent density of the bed (measured at 1300 kg/m³), m_{catalyst} (kg) stands for the catalyst mass, and Q_{v_0} (m³/h)

denotes the volumetric flow rate of the gas mixture entering the reactor at standard conditions. The methodology used to size the two-section reactor is detailed in the supporting information (refer to SI. 1). The approach involves establishing the Gas Hourly Space Velocity (GHSV) at 10000 h⁻¹ based on literature [18,51], while ensuring a temperature of 250°C at the exit of the adiabatic section, which corresponds to the operating temperature of the isothermal section.

The product stream leaving the reactor is subsequently cooled to 40°C and directed into a sequence of flashes. These flashes are employed to separate unreacted gases, which are recycled back to the reactor inlet after undergoing compression and preheating. To avoid the inert gases and by-products accumulation within the reaction loop, a portion of the recycled gases is removed (Purges 1 and 2) (1.5 % for each). The liquid phase, consisting of methanol and water, is heated to 90°C and conveyed to a rectification column. This step aims to separate the components, ensuring a high purity level of 99.85 wt% for methanol (adhering to the standard in the methanol market) and 99.9 wt% for water, thus avoiding its post-process treatment. To minimize the energy demand of the rectification column, a parametric optimization has been performed. A Design of Experiments conducted using JMP software and Aspen Plus® simulations was performed to identify the best parameters combination (reflux ratio, reboiler duty, temperature of crude methanol, condenser temperature, number of stages and feed stage number). The aim is to strike a balance, seeking optimal purities for methanol and water while minimizing the energy consumption of the rectification column's reboiler. Additional details are available in the supporting information (see SI. 2).

2.2. Heat integration

To systematically integrate heat between processes (CO₂ capture and conversion) and determine the recoverable surplus energy from the CO₂ conversion unit, a comprehensive pinch analysis was conducted. The methodology consists in collecting the hot and cold streams data, passing through the exchangers (coolers and heaters) to build the hot and cold curves which represent the released and required heat respectively (composite curves). For the evaluated system, a minimum

temperature difference (ΔT_{\min}) has been set at 10 °C [52]. The heat released by the exothermic reactions is recovered from the isothermal reactor using a medium pressure steam (at 174°C and 8 bar) as utility stream, noted U1 and U2 (see Fig. 3). The results of the pinch analysis are used to efficiently integrate the conversion unit in a first stage (internal heat integration) by recovering a maximum energy. Additionally, according to these analysis results, if an excess energy is available, it could be used for the capture unit in a second stage (external heat integration).

2.3. Key indicators definition

2.3.1. Engineering performances

The results of the process modelling using Aspen Plus® software are directly used to calculate the technological indicators including the CO₂ conversion for the reactor (X_{CO_2-Pass}) and for the overall installation ($X_{CO_2-Overall}$) expressed following the (8) and (9) respectively:

$$X_{CO_2-Pass}(\%) = \left(\frac{F_{IN,CO_2} - F_{OUT,CO_2}}{F_{IN,CO_2}} \right)_{\text{reactor}} \quad (8)$$

$$X_{CO_2-Overall}(\%) = \left(\frac{F_{IN,CO_2} - F_{OUT,CO_2}}{F_{IN,CO_2}} \right)_{\text{unit}} \quad (9)$$

where F_{IN,CO_2} and F_{OUT,CO_2} are respectively the inlet and outlet molar flows of CO₂.

The efficiency of the plant η (%) has been calculated according to (10). It is defined as the ratio between the energy output and input and includes the heat and electricity consumption of the system:

$$\eta = \frac{E_{Methanol}}{E_{PEM} + E_{comp} + E_{aux} + E_{heat}} \quad (10)$$

$E_{Methanol}$ is the energy content associated with methanol (MJ), $E_{Methanol} = m_{Methanol} \times LHV_{Methanol}$ where $m_{Methanol}$ is the amount of produced methanol (kg), and $LHV_{Methanol}$ is its lower heating value of methanol (MJ/kg) E_{PEM} represents the electrical energy consumed by the electrolyzer (MJ), E_{comp} and E_{aux} are the energies required for the compression and by the auxiliaries respectively (MJ), E_{heat} is the total required external heat (MJ) considering the surplus heat available from the conversion unit.

2.3.2. Economic performances

Three different indicators have been considered to evaluate the economic performance of the CO₂ to methanol plant: the capital expenditure (CAPEX), the operating costs (OPEX) and the levelized cost of the plant (LCoP). They are defined as following.

2.3.2.1. Capital (CAPEX) and operating expenditures (OPEX).

The CAPEX of the CO₂ capture and conversion units, along with the compression unit for excess captured and non-converted CO₂, was computed using Aspen Process Economic Analyzer (APEA). Integrated Cost Estimation is employed following the completion of the Aspen Plus simulation. Once activated, APEA generates costs using default values for mapping and sizing, drawing insights from the simulation data. For the equipment costing, APEA utilizes comprehensive cost databases containing historical data for various equipment types, regularly updated to reflect current market conditions. It applies scaling laws to adjust costs for equipment sizes different from those in the database. The software employs factorial methods to estimate equipment costs by applying cost factors to base costs, considering design and operational complexities. Additionally, it adjusts costs based on materials of construction, recognizing different cost factors for materials [53]. This tool has been used in several works investigating different processes and technologies where the results were validated by comparison with literature, industrial data and other costing methods [54–56].

The CAPEX comprises direct and indirect costs, such as working

capital. The purchased equipment costs, included in the direct ones, are used to calculate the indirect costs (Involving expenses such as engineering and supervision costs, legal fees, construction expenditures, contractor fees, and contingency funds) by applying a factor of 1.44. The typical working capital cost usually ranges from 10 % to 20 % of the fixed capital investment (FCI), which comprises both direct and indirect expenses. Chauvy et al. [42] considered a value of 15 % for this purpose. It should be noted that all the costs were estimated for the year 2019 (using Aspen Plus software (V12)) and then updated to the year 2023 using the Chemical Engineering Plant Cost Index ($CEPCI_{2019} = 618.7$ for January 2019 and $CEPCI_{2023} = 799.1$ for March 2023) according to (11).

$$CAPEX_{2023} = CAPEX_{2019} \frac{CEPCI_{2023}}{CEPCI_{2019}} \quad (11)$$

The capital expenditure annuity is calculated as follows:

$$CAPEX_{annuity} = CAPEX \frac{i(1+i)^a}{(1+i)^a - 1} \quad (12)$$

where a is the assumed lifetime (year) of the plant and i is the discount rate (%).

The operational expenditures (OPEX) include both variable costs, such as raw material and energy consumption (especially electricity), and fixed costs related to operation and maintenance. The variable costs are calculated considering the increase in energy prices in Europe in 2023. The different assumptions are listed in Table 1. It is important to highlight that the expenses associated with labor, supervisors, laboratory work and patents are excluded from this cost analysis.

2.3.2.2. The levelized cost of the plant LCoP.

Once the investment annuity and operating costs defined, the cost of the CCU chain process can be calculated. The comparison between the CO₂ to SNG and CO₂ to methanol plants from an economic point of view is enabled through LCoP. It is calculated according to (13) [66]:

$$LCoP = \frac{CAPEX_{annuity} + OPEX}{\text{Annual production}} \quad (13)$$

The analysis investigates the impact of parameter variations on the levelized costs of methanol, addressing uncertainties across all cost parameters (sensitivity analysis). The parameters analyzed include electricity expenses, indirect capital costs, operation and maintenance, specific cost associated with the PEM electrolysis, and the discount rate. The sensitivity analysis involves adjusting a single input cost parameter to its upper or lower boundary (refer to Table 1) while maintaining all other parameters at their base values.

Table 1
Cost Parameters: Base Assumptions and Upper/Lower Limits.

Item	Base case	Lower boundary	Upper boundary	Reference
Electricity cost (€/MWh)	115	70	160	[57,58]
PEM Electrolysis specific cost (incl. installation & design costs) (€/kW)	10.38	6.64	15	[42,59]
Steam cost (€/ton)	22.5	10	100	[60]
Catalyst cost ^a (€/kg)	12	-	-	[61,62]
Catalyst lifetime (year)	3	-	-	
Solvent MDEA + PZ (€/kg)	1	-	-	[42,63]
Process water (€/ton)	1	-	-	[64]
Cooling water (€/ton)	0.03	-	-	[64]
Indirect capital costs (ratio)	1.44	1.2	2	[42]
Interest i (%)	6	5	8	
Operation and maintenance (% of CAPEX)	7	5	10	[65]
Plant lifetime a (year)	25	-	-	

^a The cost in dollar was converted to euro according to 2023 exchange rate (1\$ = 1.05 €).

2.3.3. Environmental indicators

A Life Cycle Assessment (LCA) of the integrated CO₂ to methanol process is performed to evaluate the environmental impact of the integrated process and this according to the techno-economic assessment & life cycle assessment guidelines for CO₂ utilization [67]. The outcomes derived from process modeling in Aspen Plus®, coupled with life cycle assessment (LCA) formulation in SimaPro software utilizing the EcoInvent database, serve as the basis for background life cycle inventory and life cycle impact assessment analyses. The standard practice employed is the ReciPe (H) midpoint approach [68]. A cradle-to-gate LCA is envisaged and focused on two environmental impacts: climate change (CC) and fossil resource depletion (FD) taking into account both the direct CO₂ emissions produced by the process and the indirect CO₂ emissions resulting from utilities consumption. The net CO₂ emission is evaluated following (14):

$$netCO_2 = CO_{2Direct} + CO_{2Indirect} - CO_{2Removed} \tag{14}$$

The CO₂ capture and conversion steps are included in the system boundaries along with the hydrogen generation process. Therefore, all processes are accounted for on-site, taking into consideration heat integration, while disregarding the environmental impacts and energy needs associated with transportation and storage. At this stage, infrastructures are not included in the study. The functional unit (FU) is defined as the production of one ton of the product. Two scenarios are defined to get conclusive results regarding the environmental impacts (see Fig. 4):

- **Scenario (A):** this reference scenario includes a cement plant without CO₂ capture nor conversion units. The assessment considers a methanol production unit reliant on fossil resources, while hydrogen production is assumed to utilize surplus renewable energy generated from wind turbines. The BAT cement plant relies on aggregated data obtained from the EcoInvent database and literature sources [69]. Data concerning conventional methanol production from natural gas is sourced from the EcoInvent database.
- **Scenario (B):** an integrated scenario combining CO₂ capture and conversion to methanol, a portion of the captured CO₂ is used onsite to produce methanol, utilizing renewable hydrogen. The rest of the captured CO₂ is compressed for transport to storage or alternative applications. The system also integrates thermal energy between the capture and conversion units.

It should be noted that the environmental assessment results reported by Chauvy et al. [42] and carried out for the CO₂ to SNG case were updated (in terms of calculation methods and data base) in order to highlight the main differences with the CO₂ to methanol case, the same methodology being applied to both cases.

3. Results and discussions

3.1. Engineering performances

The Table 2 presents the different mass flows of the conversion unit simulated in this work. To satisfy the GHSV of 10,000 h⁻¹, a mass of 1732 kg of catalyst is packed in the reactor where 19.6 % is loaded in the adiabatic section and the rest in the isothermal one. This configuration allows the preheating of the flow exiting the adiabatic section from 230°C to 250°C (the operative temperature of the isothermal section) using the energy released by the exothermic reactions. The X_{CO₂-Pass} achieves 5.9 % in the adiabatic section and 17.5 % in the isothermal one which gives a X_{CO₂-Pass} over the two reactor sections of 22.3 %. The CO₂ is converted through the whole installation with X_{CO₂-Overall}(%)= 99.6 %. These values are in coherence with those of the literature [33,37].

Table 2

Key mass flows and energy specifications for the CO₂ capture and conversion units.

Unit	Item	Value
CO ₂ capture	CO ₂ inlet (kg/h)	1800
	CO ₂ captured (kg/h)	1620
	Amines make-up (kg/h)	2.43
	Water make-up (kg/h)	87.83
	Cooling water (m ³ /h)	104.15
	Specific Reboiler duty (MW)	1.03
	Electricity (auxiliaries) (MW)	0.16
CO ₂ compression	CO ₂ inlet (kg/h)	310.36
	Cooling water (m ³ /h)	2.33
	Electricity (MW)	0.03
CO ₂ to methanol conversion	CO ₂ inlet (kg/h)	1310
	H ₂ inlet (kg/h)	180
	Methanol (kg/h)	813
	Water outlet (kg/h)	507
	Reboiler duty (MW)	0.199

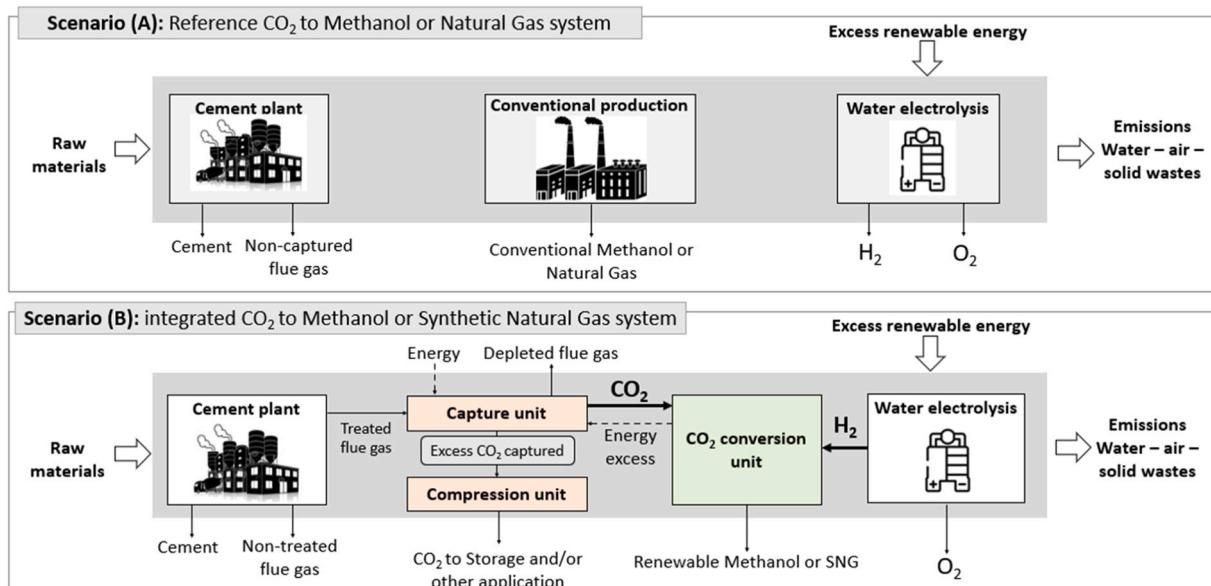


Fig. 4. Environmental Assessment Framework: Defined Scenarios.

The heat demand of the CO₂ capture unit stands at 3.70 GJ/h (1.03 MW), equivalent to 2.28 GJ/tCO₂. It must be noted that a complementary solvent preheating was considered in the CO₂ to SNG case which is not possible for the CO₂ to methanol case due to the lower energy released in this last case (lower exothermicity). Thus, the energy requirement of the capture unit aligns with Chauvy et al.'s estimation [70], which evaluated the regeneration energy at 2.28 GJ per ton of CO₂ without considering additional preheating of the solvent. The overall energy efficiency η of the plant achieves 39.3 % which surpasses the values previously reported in the literature. Values of 35 %, 36 % and 37 % were found by F. Lonis et al. [71], E. Van dal et al. [33] and P. Battaglia et al. [39] respectively.

The composite curves (temperature/ heat load diagram) are presented in Fig. 5. The heat available in the process, between 25 and 250°C, is 2121 kW while the heat demand of the process achieves 2061 kW between 40 and 230°C. The pinch analysis results indicate that the energy demand of the conversion unit could potentially reach 0 kW, thereby negating this requirement. Comparing with the work of P. Battaglia [39] where the preheating of H₂/CO₂ reactant mixture to the operating temperature of the isothermal reactor represents 97.5 % of the external heating demand resulting after thermal integration, in this work, the preheating of reactant H₂/CO₂ is possible using only the hot streams of the process itself thanks to the two-sections reactor configuration. The pinch point is observed between 230°C and 240°C. For the cooling of hot streams with temperature inferior to 80°C, a minimal demand of 441 kW is required.

Taking these informations into account, the CO₂ conversion unit has undergone full thermal integration as follows:

The heat generated in the isothermal section through the exothermic reaction (365 kW) is reclaimed using medium-pressure steam (at 174°C and 8 bar), thereby sustaining the operational temperature at 250°C. This steam serves dual purposes: supplying energy to the reboiler of the rectification column (reducing its duty to 0 kW) and partly preheating the reactant mixture before it enters the adiabatic section (HX1). The products stream leaving the reactor at 250°C provides the energy firstly to produce steam at 185°C and 8 bar using the heat surplus (60 kW) as concluded from the composite curves (HX-EXCESS). Its temperature is decreased to 240°C (hot side of the pinch point). This same stream is used to complete the reactant mixture preheating up to 230°C (cold side of the pinch point) using the exchanger HX2 and then to preheat the liquid phase to be injected into the rectification column (HX3). After that, it is cooled from 80° to 40°C using the cooler 1 (included in the cooling energy demand). The integrated process is presented in Fig. 6.

It is worth noting that unlike the CO₂ to SNG process, the steam produced from the CO₂ to methanol conversion unit provides only 5 %

of the capture unit energy demand against 100 % for methanation unit thanks to the higher exothermicity and the non-separation of raw SNG produced. Consequently, the rest of the energy needed for the solvent regeneration must be provided by an external steam source.

3.2. Economic performances

Table 3 presents the CAPEX costs expressed in M€ and updated to the year 2023 for the integrated CO₂ to methanol plant (without H₂ production). The heat integration costs consider only those related to the external integration (water pump and HX-EXCESS). The conversion unit costs include the internal heat integration costs (corresponding to the exchangers HX1, HX2 and HX3).

The total CAPEX is estimated to achieve 35.64 M€. This value is 1.27 times higher comparing with the CO₂ to SNG plant studied by R. Chauvy et al. [42] (with costs adjusted to the year 2023). This difference is mainly related to the purchased equipment costs achieving 4.83 M€ for the CO₂ to methanol conversion unit against 1.82 M€ for the methanation unit. Please note that the costs associated with the PEM electrolyzer are excluded, totaling 10.1 M€ (updated to 2023).

The breakdown of the CAPEX of each unit and the global equipment costs (9.5 M€) for the integrated CO₂ capture and conversion plant is presented on Fig. 7(a) and Fig. 7(b) respectively. The compressors are the most expensive equipment with 55.5 % of the above-mentioned costs. Reactors, heat exchangers, and columns (absorption, stripping and distillation) are accounted for 2.09 %, 8.76 % and 10.7 % respectively. The RVC unit is the most expensive equipment in the capture unit with a contribution of 10.52 % of the global equipment costs. The expenses related to heat integration account for 0.66 % of the total purchased equipment cost. From a CAPEX perspective, it is worth mentioning that the CO₂-to-methanol process could significantly benefit from economies of scale if larger units were installed. This point is illustrated in the supporting information (see SI. 4).

Table 4 presents the operating costs of the integrated plant. The overall operational expenditure (OPEX) for the plant is projected to reach 3.32 M€ per year, excluding H₂ production costs. The introduction of imported steam results in an additional operational expenditure (OPEX) of 0.32 M€ per year when compared to the CO₂ to SNG plant. This calculation assumes an average price of 22.5 € per ton of steam. In addition, the high pressure needed in the CO₂ to methanol process (65 bar) leads to a high electricity consumption for the compressors (3 times higher than the case of SNG where the pressure of reaction is set at 10 bar). Consequently, the operative costs related to the conversion unit are higher in the current study achieving 0.27 M€ per year (against 0.1 M€ per year for the SNG case). Considering the price of electricity in 2023 (115 € per MWh), the operating costs for PEM electrolyzers and H₂ production have escalated from 4.36 M€ (pre-pandemic and economic crisis, in 2019) to 11.09 M€ per year.

The LCoP of the CO₂ to methanol plant is calculated according to the Eq. (13). On the other hand, the LCoP of the CO₂ to SNG is updated considering the same economic assumptions. Fig. 8(a) and Fig. 8(b) show the costs expressed in (€/ton of product (methanol or SNG)) and (€/GJ) respectively considering three cases:

- Excluding expenses of hydrogen production.
- Incorporating expenses associated with hydrogen production.
- Considering the costs linked to hydrogen production and revenues from oxygen and methanol/SNG selling (87.4 €/ton of O₂ [64], 71.83 €/MWh for natural gas [72] and 510 €/ton of methanol [73]).

It is worth noting that the annual production is assumed to reach 7124 ton of methanol against 3512 ton of SNG per year for each plant. This difference leads to a lower LCoP of the CO₂ to methanol plant when considering the cost per ton of product. Considering the cost of MJ (LHV basis), this trend is reversed and the LCoP of SNG is lower thanks to its higher LHV comparing with methanol. The most attractive option is

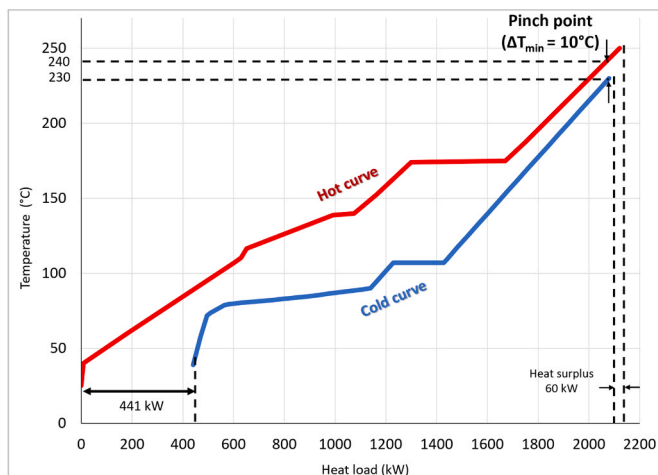


Fig. 5. Composite curves for the CO₂ conversion unit.

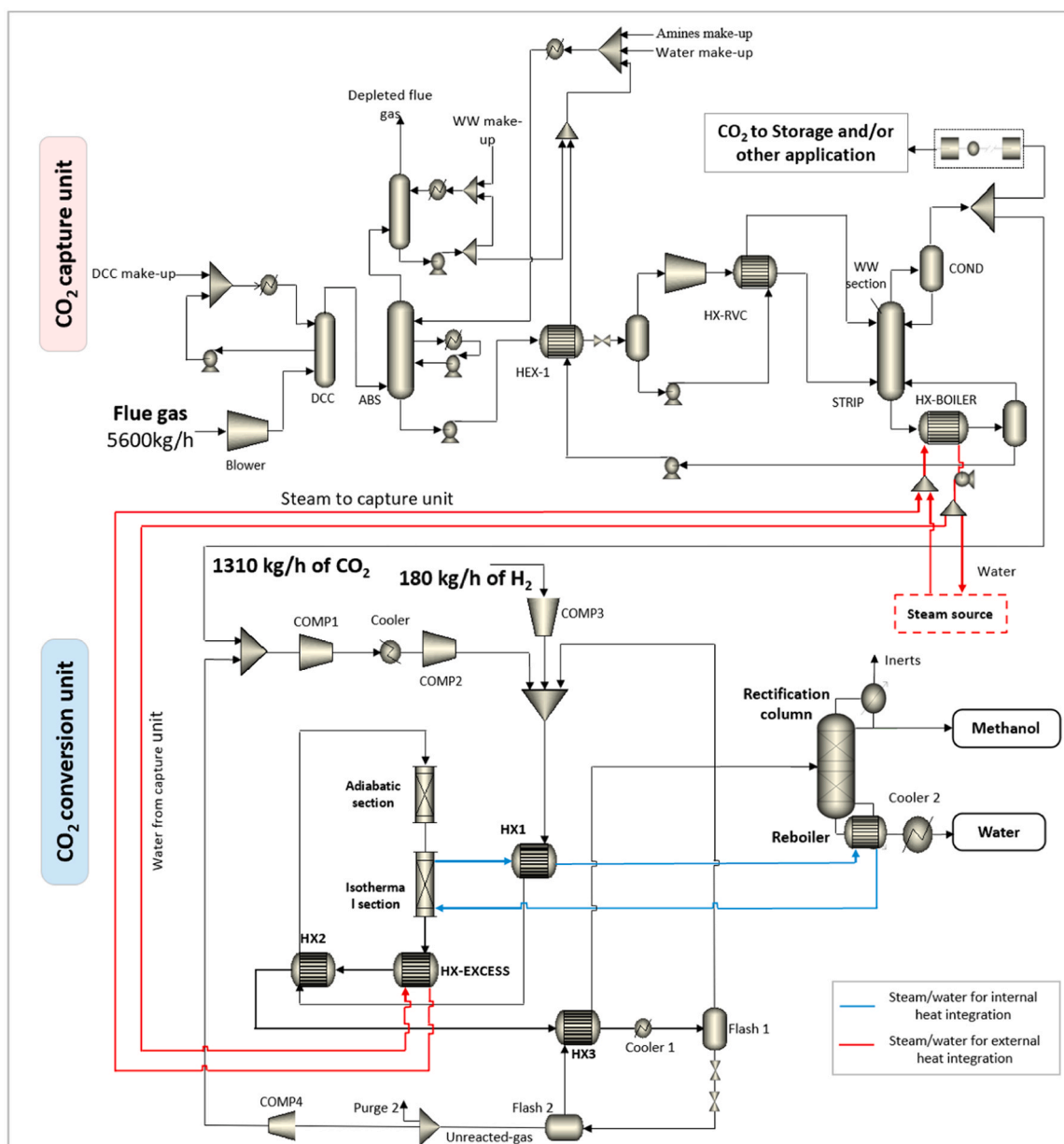


Fig. 6. Integrated CO₂ to methanol process (capture and conversion units).

therefore dependent on the final application of the product. When the costs of H₂ production are considered, the *LCoP* of each plant is increased by 280 % and this highlights the weight of the H₂ production costs on such processes. Even if the revenues are considered, both plants remaining costs are not fully compensated. Note that the results presented per ton of converted CO₂ are provided in the [supporting information](#) (see Fig. SI. 5). The production costs (*LCoP*) of both plants are almost identical when considering the cost per ton of converted CO₂. However, when considering hydrogen production (and the resulting incomes from SNG/methanol such as O₂ selling), the cost of the SNG plant becomes higher than that of the methanol plant (due to the stoichiometry H₂/CO₂ = 3 for methanol case and 4 for the SNG one).

Fig. 9 shows the sensitivity analysis results applied to the *LCoP* of both systems. The major cost driver of the *LCoP* in each case is the electricity price which affects mainly the hydrogen production. Variations in steam price affect the *LCoP* of CO₂ to methanol process especially at the upper boundary. The steam price has no effect on the CO₂ to SNG one (steam generated internally through heat integration). Among

other parameters, the electrolyzer cost (CAPEX PEM) has the most substantial impact on the economic feasibility of both processes.

3.3. Environmental performances

Life Cycle assessment has been performed focusing on two impact factors: Climate Change (CC) and Fossil Depletion (FD). The technological parameters of the CO₂ capture and conversion units standardized to the production of one-ton of methanol are presented in the Fig. 10.

Regarding the climate change impact, a net CO₂ emission reduction by 70 % between scenario (A) and scenario (B) is seen in the CO₂ to SNG route and a reduction by 60 % in the methanol route (Fig. 11 (a) and Fig. 11 (b) respectively). It is worth noting that the global thermal energy required for solvent regeneration in the capture unit is supplied by the heat surplus from the conversion unit. In the CO₂ into methanol case, only a small part, approximately 5 %, of the heat demand for the solvent regeneration is provided. A complete energetic integration can be achieved in the SNG route. This is due to the methanation process being

Table 3
CAPEX costs expressed for the integrated CO₂ conversion and conversion units.

	Capture unit	Conversion unit	Heat integration	Compression unit
Purchased equipment	2.02	4.96	0.02	2.76
Equipment setting	0.03	0.04	0.00	0.02
Piping	0.77	0.72	0.01	0.24
Civil	0.15	0.16	0.00	0.08
Steel	0.08	0.05	0.00	0.03
Others ^a	2.64	2.28	0.03	0.71
Direct costs ^b	5.69	8.21	0.06	3.83
Indirect costs	2.91	7.15	0.03	3.97
Working capital	1.29	2.30	0.01	1.17
CAPEX	9.89	17.66	0.10	8.97

^a Other expenses encompass categories such as instrumentation, electrical work, insulation, and paint.

^b Direct costs compromise the Purchased Equipment, Equipment Setting, Piping, Civil, Steel and others.

significantly more exothermic compared to the CO₂ to methanol process. Therefore, for this latter, the steam required for solvent regeneration must come from an external source. For the environmental performance assessment, a generic data from the EcoInvent database was utilized, which considers the average European fuel mix used in the chemical and petrochemical industry: approximately 57 % natural gas, 14 % coal, 12 % oil, 10 % refinery gas, with the remainder from other sources.

Regarding the fossil depletion impact, results for both scenario in the case of CO₂ to methanol and CO₂ to SNG are presented in Fig. 12 (a) and Fig. 12 (b) respectively. a reduction of more than 60 % was noticed (ca. 75 % in SNG route and 61 % in methanol route). Therefore, the environmental benefits of integrating CO₂ capture and conversion to either SNG or methanol have been demonstrated. This advantage primarily stems from the advanced CO₂ capture process considered, enabling the capture of a significant amount of CO₂ with a fixed energy input. In the case of conversion to SNG, there is an additional benefit from recovering the thermal energy released during the methanation process, leading to higher savings in terms of fossil depletion in comparison with the conversion to methanol where a large quantity of steam must still be provided by an external source.

4. Conclusions

This work focused on the methanol production using CO₂ captured from a cement plant and hydrogen produced from excess renewable

energy. An advanced CO₂ capture process was suggested to handle approximately 10 % of the flue gas emitted by a Best Available Technology (BAT) cement plant. The CO₂ captured and green hydrogen are injected into the conversion unit which has been simulated in Aspen Plus® software. A novel reactor configuration was proposed in order to optimize the heat consumption of the process. The methanol production achieved 0.5 ton per ton of CO₂ captured with high purity of 99.85 %. A pinch analysis has been investigated in order to perform a systematic process-to-process heat integration. A thermal energy self-sufficiency has been achieved for the conversion unit thanks to the reactor configuration. The excess of energy that can be recovered from the CO₂ to methanol conversion unit represents only 5 % of energy requirements of the capture unit. Through heat integration, the system achieved an overall efficiency based on Lower Heating Value (LHV) of 39.3 %, surpassing previously reported literature values that reached up to 37 %.

The economic and environmental aspects of the proposed work have been compared with those of a previous study on the CO₂ to SNG process investigated by R. Chauvy et. al [42]. The aim of this comparison is to highlight the main differences between the two conversion pathways and to highlight an eventual preferred CO₂ conversion route. The results showed that the methanol production plant CAPEX is 1.27 times higher comparing with the CO₂ to SNG plant. This is mainly related to the purchased equipment and in particular the cost of the compressors. It should be noted that the CO₂ to methanol process is carried out under higher pressure, 65 bar against only 10 bar for the CO₂ to SNG process. This also leads to higher OPEX for the methanol case due to higher electricity consumption comparing to the SNG case. In addition, and due to the lower exothermicity of the methanol production, additional steam needs to be provided to the capture unit. This leads to a supplementary OPEX of 0.32 M€ per year comparing with the CO₂ to SNG plant (where the steam is self-produced thanks to the higher exothermicity).

Although the CAPEX and OPEX are higher for methanol case, its

Table 4
Analysis of the OPEX for the integrated CO₂ capture and conversion units.

	Capture unit	Conversion unit	Heat integration	Compression unit
Fixed costs (M€/year)	0.67	1.20	7.35×10^{-3}	0.61
Variable costs (M€/year)	0.53	0.27	1.64×10^{-3}	0.03
OPEX (M€/year)	1.20	1.47	8.99×10^{-3}	0.65
CAPEX _{annuity} (M€/year)	0.67	1.20	7.35×10^{-3}	0.61

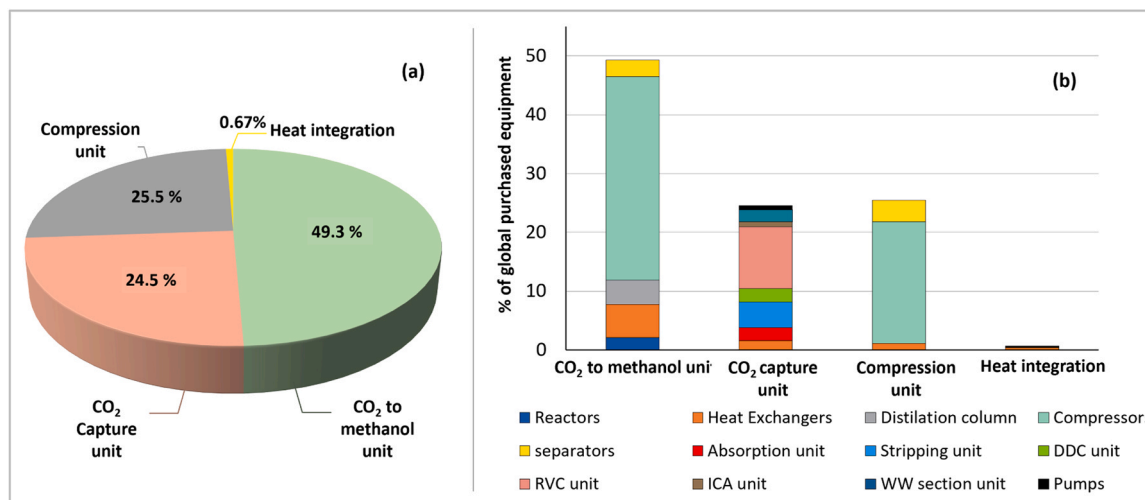


Fig. 7. The breakdown of (a) CAPEX of different units and (b) the purchased equipment costs.

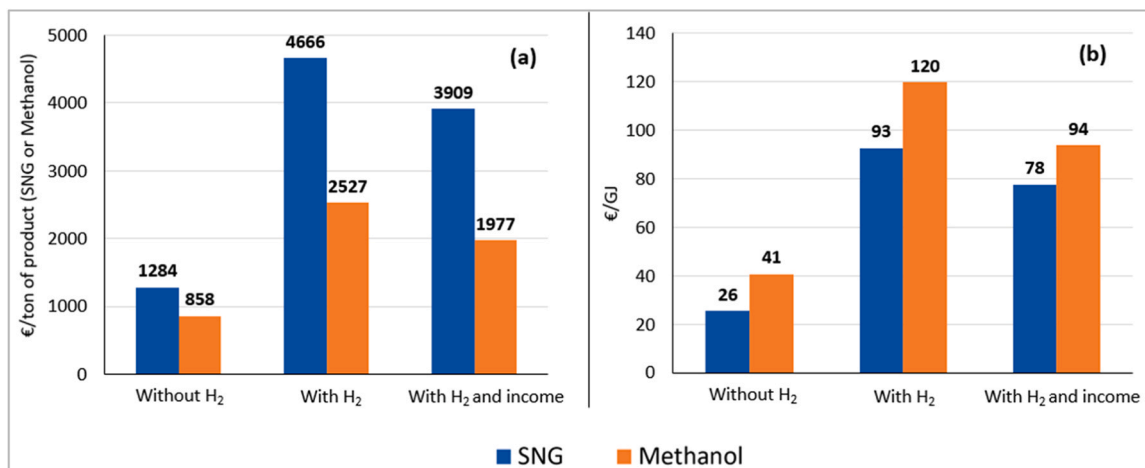


Fig. 8. LCoP related to the CO₂ to SNG and CO₂ to methanol plants expressed in: (a) €/ton of product and (b) €/GJ.

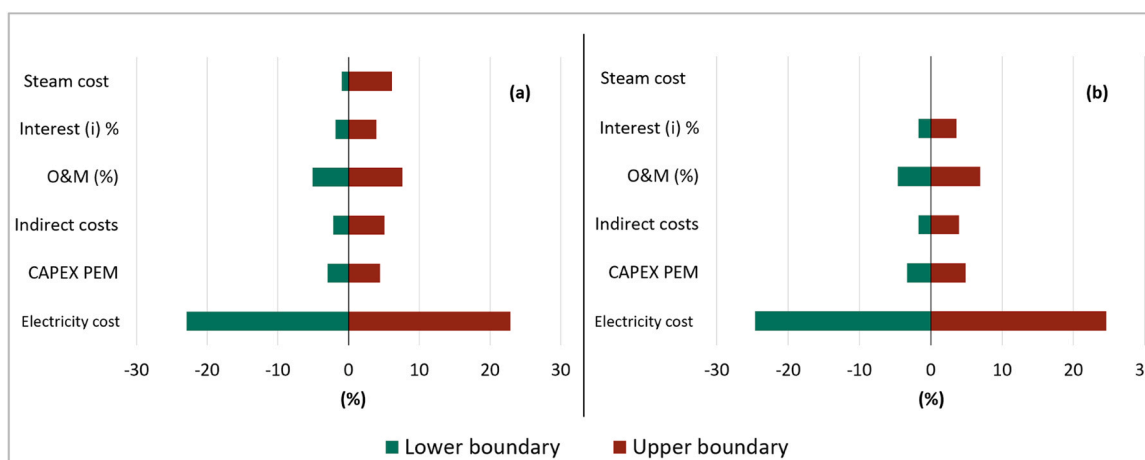


Fig. 9. Sensitivity analysis on the cost of production of methanol (a) and SNG from CO₂ (b).

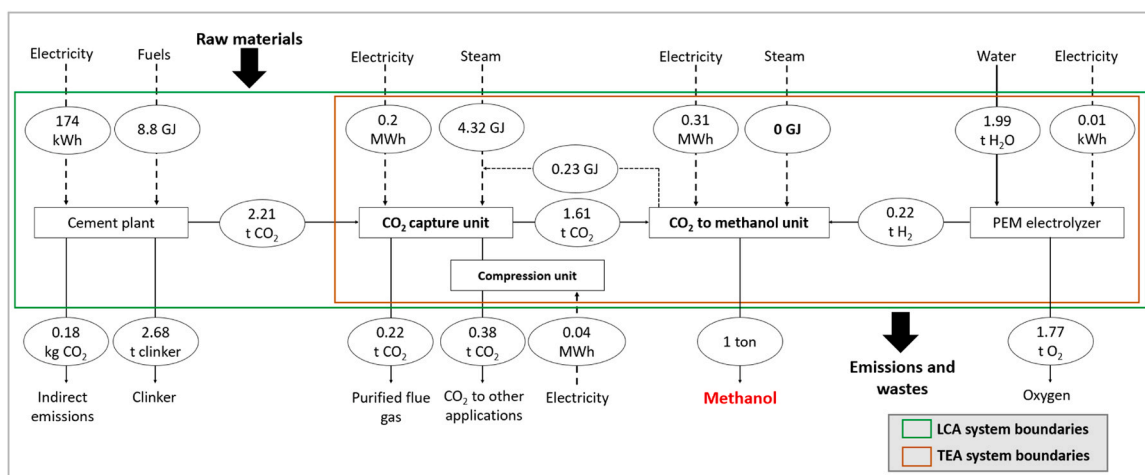


Fig. 10. Parameters of the CO₂ to methanol plant standardized to the production of one-ton methanol (FU).

LCoP is lower comparing to SNG case thanks to the difference of annual production between the two plants, namely 7124 ton of methanol against 3512 ton of SNG per year. This trend is reversed if we consider the two products as fuels. In other words, the LCoP per GJ of methanol is higher than the LCoP per GJ of SNG. The LCoP of each plant is increased

by 280 % when considering the hydrogen production costs that are highly related to the PEM costs but also to the electricity price. Concerning the environmental aspects, two scenarios have been investigated for the two CO₂ conversion pathways. A net CO₂ emission reduction by 70 % between scenario A and scenario B has been observed in the CO₂ to

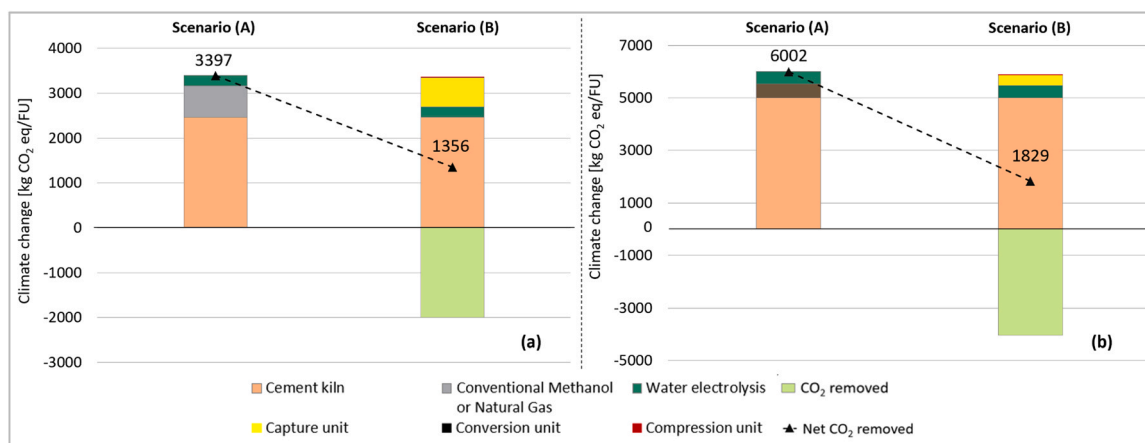


Fig. 11. Climate change impact of both scenarios and routes: (a) CO₂ to methanol and (b) CO₂ to SNG.

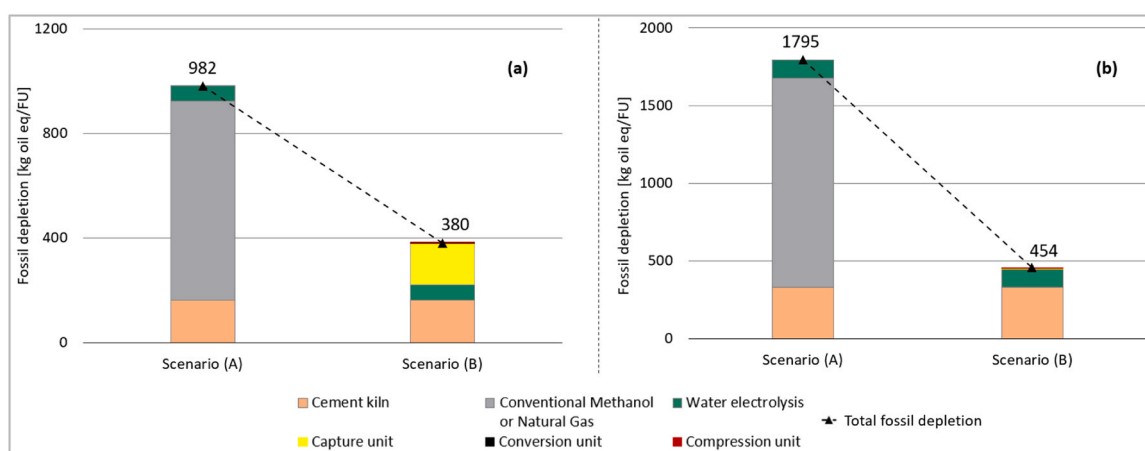


Fig. 12. Fossil depletion impact for both scenarios and routes: (a) CO₂ to methanol and (b) CO₂ to SNG.

SNG case and a reduction by 60 % in the CO₂ methanol one. This difference is mainly related to the energetic integration where no steam is needed to regenerate the solvent (within the capture unit) when considering CO₂ to SNG case. Regarding the fossil depletion impact, the impact reduction is respectively 75 % for the CO₂ to SNG route and 61 % for the CO₂ to methanol route, which is significant in both cases.

As perspectives of this study, other CO₂-based products could be compared using the same methodology (e.g. CO₂ conversion into kerosene). Another CO₂ capture process could be also envisaged, such as purely electrical technologies like membranes, vacuum pressure swing adsorption and (eventually combined with) cryogenics.

CRedit authorship contribution statement

Diane Thomas: Writing – review & editing, Validation, Supervision, Project administration. **Guy De Weireld:** Writing – review & editing, Validation, Supervision, Conceptualization. **Marie-Eve Duprez:** Writing – review & editing, Investigation, Methodology. **Lionel Dubois:** Writing – review & editing, Conceptualization, Investigation, Methodology. **Rania Djettene:** Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Data curation, Conceptualization.

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

More details are provided in the supporting information.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2024.102879](https://doi.org/10.1016/j.jcou.2024.102879).

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