Journal of CO2 Utilization 68 (2023) 102345

Contents lists available at ScienceDirect

Journal of CO2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Renewable methanol production from green hydrogen and captured CO_2: A techno-economic assessment

Stefano Sollai [a], Andrea Porcu [a], Vittorio Tola [b], Francesca Ferrara [a], Alberto Pettinau [a,*]

[a] Sotacarbo S.p.A., Grande Miniera di Serbariu, 09013 Carbonia, Italy
[b] University of Cagliari, Dept. of Mechanical, Chemical and Materials Engineering, via Marengo 2, 09123 Cagliari, Italy

ARTICLE INFO

Keywords:
Power-to-methanol
CO_2 hydrogenation
Renewable methanol
Techno-economic assessment

ABSTRACT

This paper aims to present a pre-feasibility study of a power-to-fuel plant configuration designed for the production of 500 kg/h of renewable methanol (e-methanol) from green hydrogen and captured carbon dioxide. Hydrogen is obtained by water electrolysis employing the overproduction of renewable electricity. Carbon dioxide is assumed to be separated from the flue gas of a conventional power station by means of an amine-based CO_2 absorption system. A comprehensive process model has been developed with the support of Aspen Plus tool to simulate all the plant sections and the overall system. After the process optimization, a detailed economic analysis – based on capital and operating costs derived from commercial-scale experience and assuming a 20-year lifetime – has been performed to calculate a levelized cost of methanol (LCoM) of 960 €/t (about 175 €/MWh). The analysis confirms that, today, the technology is still not competitive from the economic point of view, being LCoM more than double than the current methanol price in the international market (450 €/t). However, it indicates that the process is expected to become competitive in a mid-term future, as a consequence of the new European policies. The study also reveals that LCoM is mainly affected by the electricity price and the electrolyser capital cost, as well as the capacity factor of the plant.

1. Introduction

Methanol (CH_3OH, conventionally indicated as MeOH) is today one of the most important building blocks in the chemical and pharmaceutical industry and in the production of synthetic hydrocarbons [1]. The worldwide methanol production is about 90 Mt/yr.: most of it (about 65 %) comes from natural gas by means of steam methane reforming, while the remainder (35 %) comes from coal through gasification processes [2,3]. However, the ever more urgent need for low carbon fuels for the energy transition is leading to a growing interest toward methanol production from renewable energy sources, as proposed in 2005 by Nobel prize laureate George A. Olah [4]. Currently, worldwide renewable (green) methanol production is neglectable – less than 0.2 Mt/yr. (some 0.2 % of the total production) – and it mainly comes from biomass gasification [2]. Several advanced processes and technologies have been recently proposed for renewable methanol production from municipal solid waste, sludge, *etc.* [5,6]. But the increasing deployment of intermittent renewable energy sources (*i.e.* sun and wind) and the need of sustainable fuels for the decarbonization of the so-called "hard-to-abate" sectors (mainly industry and heavy transport) is making more and more interesting the possibility to produce methanol from renewable electricity (e-methanol) and captured carbon dioxide. CO_2 hydrogenation – typically operated in fixed-bed catalytic reactor at 250–300 °C and 50–00 bar – is currently the technology with the largest development perspective at commercial scale [7,8]. Conceptually, renewable electricity is used to produce green hydrogen by water electrolysis, whereas CO_2 can be captured from concentrated sources (*e.g.* flue gas from power generation or industrial plants) or directly from air.

The power-to-methanol approach has a double advantage: it allows to store renewable electricity in chemical form and at the same time to

Abbreviations: BEC, bare erected cost; CoM, cost of methanol; CRI, Carbon Recycling International Ltd; EBIT, earnings before interest and taxes; EBITDA, earnings before interest, taxes, depreciation and amortization; EPCC, engineering, procurement and construction cost; ETS, European emissions trading system; G&A, general & administrative cost; GME, Italian power exchange management company; IRAP, regional tax on productive activity; IRES, Italian tax on company income; LCA, life cycle assessment; LCoM, levelized cost of methanol; MEA, monoethanolamine; MeOH, methanol; NPV, net present value; PEM, polymer electrolyte membrane; TASC, total as-spent cost; TEA, techno-economic assessment; TOC, total overnight cost; TPC, total plant cost.

* Corresponding author.
E-mail address: alberto.pettinau@sotacarbo.it (A. Pettinau).

https://doi.org/10.1016/j.jcou.2022.102345
Received 17 September 2022; Received in revised form 17 November 2022; Accepted 28 November 2022
Available online 5 December 2022

produce a fully renewable product that can replace the fossil-derived one. E-methanol and its derivatives are attractive fuels for the transport sector, being extremely clean and able to use the same distribution and storage infrastructures of the conventional oil-derived transport fuels [9–11]. A LCA study of methanol production reports that CO_2 hydrogenation could reduce the greenhouse gas emissions by 59 %, in comparison to the conventional processes [12].

CO_2 hydrogenation technology for e-methanol production has been successfully demonstrated in the George Olah Renewable Methanol Plant, owned by Carbon Recycling International (CRI) and operating since 2012 in Iceland: it allows to recycle 5500 t/yr. of CO_2 from natural sources to produce 4000 t/yr. of e-methanol [13]. Moreover, a new commercial scale plant based on CRI technology – the Shunli CO_2-to--methanol plant in China (Henan province) – has been commissioned at the end of 2022 [13]. In parallel, one of the most relevant applications of e-methanol as transport fuel is given by the Swedish shipping company Stena Line, that retrofitted the "Stena Germanica" ferry with methanol engines [14]. These industrial applications of e-methanol technologies, despite being successful, still represent peculiar situations in which, only thanks to specific conditions, the production cost is competitive in the international market. But, in general, e-methanol is, by far, more expensive than fossil-derived one. A detailed study by the International Energy Agency [15] indicates a near-term e-methanol production cost between 120 and 210 USD/MWh; however, in the long-term, the cost is expected to decrease to 55–70 USD/MWh, becoming competitive with the current production cost from fossil fuels (that, in turn, should increase significantly as a consequence of CO_2 emissions restrictions). The long-term decrease of e-methanol production cost is due to a decrease of electricity price (that accounts for 40–70 % of the whole production cost) [15]. But a key role is also expected by the optimization of the conversion chain – this is the reason why several studies are focused on the development of advanced copper/zinc-based catalysts, specifically optimised for CO_2 hydrogenation [16,17] – and especially by the economy of scale generated by the diffusion of advanced electrolysers.

For this reason, several studies on techno-economic assessments (TEA) and life cycle assessment (LCA) of e-methanol production processes have been recently published. Lee et al. (2020) [18] propose several options to make e-methanol economically feasible, assessing the effects of key parameters (*i.e.* gas hourly space velocity, temperature, and H_2/CO_2 ratio) on process performance and presenting an estimation of e-methanol costs based on two plant sizes: 0.27 and 100 t per day. Su et al. (2022) [19] present a techno-economic assessment, based on Aspen Hysys model, of a 100,000 t/yr. e-methanol plant compared with conventional fossil-based processes, providing the internal rate of return of the investment in three different future scenarios, defined as "optimistic", "realistic" and "pessimistic". Yousaf et al. (2022) [20] report a very detailed Aspen Plus-based simulation of CO_2 hydrogenation units, under different operating conditions, with some discussion of e-methanol production cost. Harris et al. (2021) [21] compare three different approaches for methanol synthesis – *i.e.* from syngas from either biomass gasification or dry reforming of CO_2, and direct CO_2-to-methanol *via* hydrogenation – with an estimation of current and future methanol production cost. Del Pozo et al. (2022) [1] compare different renewable and non-renewable methanol synthesis technologies, considering direct air capture as one of the potential options for capturing CO_2. Moreover, considering that the economic assessments are typically site sensitive, several relevant studies have been published on renewable methanol production in several countries, such as China [22] and Germany [23]. A specific focus on hydrogen and methanol transport costs is provided by Schorn et al. (2021) [24]. Finally, several different plant configurations and sizes are economically assessed by Bellotti et al. [23,25] and Rivarolo et al. [26], focusing the attention on the flexibility of e-methanol production.

The distinction of this work is a focus on the techno-economic assessment – which combines a process simulation with Aspen Plus and a detailed economic model based on industrial data – of commercial scale (500 kg/h, corresponding to about 4000 t/yr.) modular e-methanol production units, designed to chemically store the overproduction of renewable and intermittent electricity. In particular, the study considers the full process, including CO_2 capture and hydrogen production units. As a case study, the plant is assumed to be operated on Sardinia island (Italy). The Sardinian electric grid is currently semi-independent, being connected with the mainland through two high voltage direct current (HVDC) links called SAPEI and SACOI, characterized by a maximum power of 1000 MW and 300 MW, respectively. Therefore, together with electrochemical energy storage, the production of e-methanol represents a promising solution for assuring the stability of the electric grid (in terms of frequency control and system resiliency), in view of the growth in power generation from sun and wind to replace fossil fuel (coal and heavy oil) electricity plants.

The economic analysis is based on capital and operating costs derived from current commercial-scale applications (considering that most of the components are already available in the market) and it is focused on the assessment of the so-called levelized cost of methanol (LCoM).

2. Plant configuration

The system configuration investigated in this work consists of a commercial-scale plant for e-methanol production from hydrogen and captured CO_2. In particular, green hydrogen is assumed to be produced by water electrolysis powered by wind or solar electricity, whereas carbon dioxide is separated from flue gas produced in a conventional thermoelectric power station or in an industrial plant through an amine-based CO_2 capture system. Fig. 1 presents a simplified scheme of the studied power-to-methanol system and its subdivision in three main sections: (i) water splitting into hydrogen and oxygen through a polymer electrolyte membrane (PEM) electrolyser, (ii) carbon capture with amine-based solvents, and (iii) synthesis and purification of e-methanol through direct CO_2 hydrogenation.

As mentioned above, the economic performance of this application is site specific, being affected by parameters such as the cost of renewable electricity, the availability of concentrated CO_2 sources, *etc.* Therefore, Sardinia has been considered as a case study for the whole economic analysis. This assumption is conservative in the short period (the electricity price in Sardinia is currently higher than the Italian and European mean price), but it can make the technology more competitive in the years to come, due to the expected growth of renewable energy production.

The conventional technologies commercially available for methanol production by steam methane reforming have limited their size, for economic reasons, to a daily production of around 2500 t of methanol, even though the continuous development of catalysts has recently allowed to reach the size of 5000 t per day [27]. Being renewable power generation plants typically distributed in the territory, the plants for e-methanol production would find their best application on a territorial-distributed model based on the local feedstock availability (mainly CO_2 and renewable electricity). In other words, small and distributed e-methanol units closely integrated with renewable power generation plants can contribute to the stability of the electric grid. For this reason, as mentioned, this study considers a system designed to produce 500 kg/h, corresponding to 12 t per day and, considering a capacity factor of 0.9, an annual production of 4000 t. It is basically the same size of the CRI's George Olah Renewable Methanol Plant in Iceland.

Since the main focus of this study is the economic analysis of methanol production from green hydrogen and captured CO_2, this chapter only shows a general description of the overall process and a brief introduction of the models developed to analyse the processes of hydrogen production, CO_2 capture, and methanol synthesis. Detailed descriptions of these models are presented in previous works [28–31].

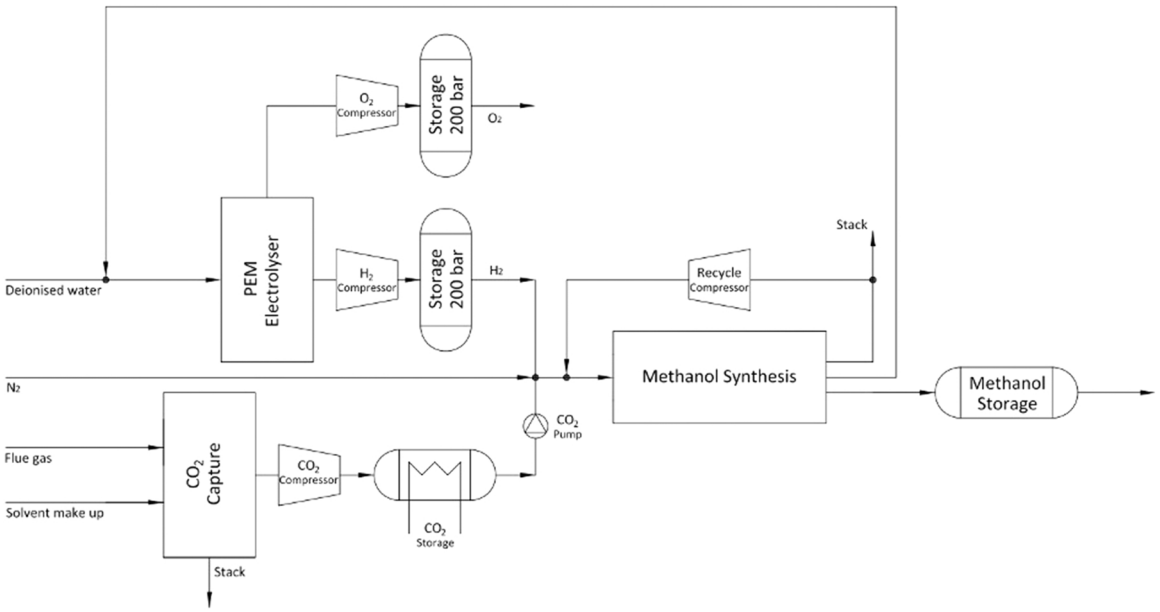

Fig. 1. Simplified plant lay-out.

2.1. Green hydrogen production

Green hydrogen needed for the catalytic hydrogenation of CO_2 to e-methanol is assumed to be obtained by water electrolysis with a PEM electrolyser. The main advantages of this kind of technology, as compared to the more conventional alkaline systems, are given by a faster cold start-up, a higher flexibility and, consequently, a better coupling with dynamic and intermittent power generation systems, like renewable energy sources such as sun and wind. PEM electrolysers can be reversible devices and, with respect to conventional alkaline units, are able to operate at lower cell voltages, higher current densities, and higher temperatures and pressures leading to higher efficiencies [32]. On the other hand, this technology is currently less mature than the alkaline one and still presents higher costs and a limited lifetime [33]: 60,000 h at most, after which the electrolytic cell stacks need to be gradually replaced due to their degradation [34].

The power consumption for a megawatt scale electrolysis plant varies between 4.5 and 7.5 kWh per cubic meter of hydrogen produced [35], equivalent to 50–80 kWh/kg_{H2}. For the environmental impact of the process to be the lowest possible and for the products to be considered renewable, the electrolyser needs to be powered with electricity generated with renewable energy sources. As mentioned, in this study the electrolyser is considered to be powered with the over-generation of electricity in Sardinia, *i.e.* the share of power production from renewable sources which exceeds the internal needs of Sardinia, which is currently exported. The electricity exported from Sardinia in 2018 was about 3 TWh [36], about 1.7 TWh of which can be considered from renewable sources overgeneration. This energy is much higher than the power requirements of the system in study; however, its actual availability in the course of the year is widely variable and this issue can influence a continuous production with high capacity factor. Therefore, the adoption of a temporary hydrogen storage system operating at 200 bar has been considered in this study, in order to allow to disconnect the production of hydrogen from its subsequent use in the e-methanol synthesis section. The storage system has been sized – as a result of a preliminary optimization – to assure hydrogen availability even when renewable electricity is unavailable for several hours. This introduces higher capital and operating costs. No oxygen storage has been considered (oxygen is supposed to be compressed in cylinders and sold).

To simulate the PEM electrolysis process, a dedicated model has been developed in Aspen-Plus environment, adapting it from the one developed by Zhao and Brouwer [37]. The deionized water is pumped and heated up to the PEM operating pressure and temperature. The water electrolysis reaction is simulated with a RStoic type reactor. The products of the process – hydrogen and oxygen – are then separated and stored. The main characteristics of the hydrogen production system are reported in Table 1. A technology evolution of PEM electrolysers has also been considered. At the end of their lifetime, the stacks are supposed to be replaced with new ones characterized by better performance [38]. Moreover, considering that stack performance deteriorates over time, stack is oversized to assure the required hydrogen production until the end of its life. The energy and material flows of the system are reported in Table 2.

Globally, more than a thousand of kilograms per hour of deionized water are required to obtain the desired hydrogen flow rate equal to 104 kg/h, leading also to an oxygen production of about 820 kg/h. Such a hydrogen production requires a PEM electrolyser with a power capacity slightly lower than 6 MW, since the specific power consumption is equal to 55.8 kWh/kg_{H2}. In a future perspective, the stack power consumption is considered reduced by about 5 %, leading to a specific power consumption of 47.8 kWh/kg_{H2}, that corresponds to a total power consumption (including balance of plant) equal to 53.2 kWh/kg_{H2}.

Table 1
Main characteristics of the hydrogen production system (elaboration from [38]).

Stack		
Year of installation	present	future
Number of cells in any stack	150	150
Active area	700 cm^2	700 cm^2
Current density	2 A/cm^2	3 A/cm^2
Voltage	1.9 V/cell	1.8 V/cell
Degradation rate	1.5 mV/1000 h	1.0 mV/1000 h
Stack lifetime	60,000 h	85,000 h
Stack over-sizing to consider degradation	13 %	13 %
PEM electrolyser		
Water conversion efficiency	90 %	90 %
Number of stacks	15	10
Hydrogen production pressure	30 bar	30 bar
Operating temperature	80 °C	80 °C

Table 2
Energy and material flows of the hydrogen production system.

Specific stack power consumption	50.4 kWh/kg_{H2}
Specific balance of plant power consumption	5.4 kWh/kg_{H2}
Specific total power consumption	55.8 kWh/kg_{H2}
Deionized water flow rate	1037 kg/h
Mean hydrogen flow rate	104 kg/h
Mean oxygen flow rate	821 kg/h
Unconverted water flow rate	110 kg/h
Electrolyser power	5906 kW

2.2. CO2 capture

In this study, CO_2 capture is assumed to be performed by chemical absorption using amine-based solvents. The performance assessment of the CO_2 capture section has been carried out by using a simulation model implemented through Aspen-Plus. A stream of flue gas produced in a conventional coal-fired power plant – with a CO_2 concentration of 15 % dry vol. [39,40] – has been considered as reference CO_2 source (but the process can also be applied in integration with several industrial processes). The CO_2 capture section has been sized for providing the CO_2 flow required by the methanol synthesis process (723 kg/h). A CO_2 capture efficiency of 90 % has been set, as in typical CO_2 capture section based on chemical absorption. Assuming a 90 % removal efficiency from a capture system with 30 % monoethanolamine (MEA) solution [41], without further process optimization, the energy needed for the amine regeneration – typically between 3 and 5 MJ for each kg of CO_2 desorbed [42,43] – is calculated equal to 3.46 MJ/kg_{CO2}. The heat required at the reboiler (operating at 1.2 bar) is provided by steam at about 120 °C, tapped from the power plant that provides the flue gas to be treated. This corresponds to a missed power generation of about 0.161 kWh/kg_{CO2}. The analysis of the CO_2 removal system has been carried out under equilibrium conditions, leading to slightly more optimistic results, since in the real absorber the process is governed by kinetics. Globally, differences are almost negligible, so the equilibrium assumption can be considered an acceptable approximation for the aim of this study [44].

Moreover, during the operation of the adsorption system, new adsorbing solution needs to be introduced periodically, to compensate for the solution deterioration. The solvent consumption is usually in the range of 0.5 – 3.0 kg per tonne of CO_2 adsorbed [45]. A make-up value of 1.5 kg/t_{CO2} has been used in this study [46].

The main characteristics of the CO_2 capture system are reported in Table 3, whereas the energy and material flows are reported in Table 4. The carbon dioxide exiting the system is considered to be temporarily stocked in liquid phase at −24 °C and 20 bar in a 16.5 m^3 tank. These conditions allow an autonomy of about 24 h of independent operation of the capture section from the rest of the plant.

2.3. E-methanol production

Nowadays, methanol is mainly produced from syngas using Cu/ZnO/Al_2O_3-type heterogeneous catalysts requiring high temperature (200–300 °C) and pressure (50–100 bar) [47,48].

Table 3
Main characteristics of the CO_2 capture system.

Gas to be treated	
CO_2 concentration	15%vol 21.8%wt
Solvent	
Type of solvent	MEA
Concentration in aqueous solution	30%wt
Column of adsorption	
Liquid/gas ratio	4.53 kg/kg
CO_2 removal efficiency	90 %
Solvent make-up	1.5 kg/t_{CO2}
Regeneration column	
Thermal vector	steam
CO_2 output pressure	1.2 bar

Table 4
Energy and material flows in the CO_2 capture system.

Flue gas flow rate	3846 kg/h
Separated CO_2 flow rate	723 kg/h
Solvent consumption	1.09 kg/h
Electric power required	6.9 kW
Specific thermal consumption for solvent regeneration	3.46 MJ/kg_{CO2}
Thermal power for the regeneration	697.3 kW_{th}
Equivalent missed electric power	116.4 kW

E-methanol is produced by means of CO_2 catalytic hydrogenation using an adiabatic fixed-bed catalytic reactor. Cu and Zn are reported to be the main components of the catalysts, along with different additives like Al, Zr, Cr, Si, B, Ga, *etc.* [49]. Pre-heated hydrogen and carbon dioxide are catalytically converted into methanol by means of the CO_2 hydrogenation (1), reverse water-gas shift (2), and CO hydrogenation (3) reactions [20]:

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

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (3)$$

The process conventionally operates within a temperature range between 250 and 300 °C and a pressure between 50 and 100 bar, typically using Cu/Zn/Al-based catalysts [4,50,51]. The conversion efficiency is maximized when the reaction operates with an optimal stoichiometric ratio $M = 2$, where M is defined as [1]:

$$M = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} \quad (4)$$

The exit stream is then cooled to condense the liquid product (mainly methanol and water), which is subsequently sent to a distillation column for methanol purification; the unreacted gas (mainly H_2 and CO) is recirculated to the reactor, in order to improve the whole conversion efficiency. Methanol is then temporarily stored in liquid phase at atmospheric pressure and sold to the local utilities as sustainable fuel or chemical reactant.

The process has been modelled in Aspen Plus environment [52], according to the flowsheet reported in Fig. 2. The main blocks of the methanol synthesis section are the reactor and the distillation column, which are implemented in Aspen Plus through the blocks RPlug reactor and RadFrac column, respectively. Hydrogen coming from the electrolyser (stream 1 M) and carbon dioxide coming from the capture Section (3M) are compressed to 65 bar, which is the pressure required by the hydrogenation reactor, and mixed with the recirculation of the unconverted gas coming from the reactor (23 M). This mixture (6 M) is heated with heat recovered from the process products exiting the reactor (8 M). The latter is further cooled, then the unconverted gas is separated from the liquid phase through two flashes. The unconverted gas (18 M and 21 M), mainly made up of hydrogen and CO_2 with traces of methanol, water, and CO, are recirculated back to the reactor. Just a minor portion of about 1 % is purged and flared (19 M) to reduce the accumulation of inert and undesired gas in the circuit. This purge flow slightly increases the CO_2 emissions, but its contribution (about 20 kg/h) can be assumed almost negligible, since it is around 3 % of the overall CO_2 captured from the flue gas.

The raw methanol (12 M) exiting the separators, still containing water and traces of CO_2, is heated up to the operating temperature of the distillation column. Here, water is condensed and collected in the bottom (16 M). The process optimization, by means of the heat recovered from the process gas in a number of heat exchangers, makes the system thermally self-sufficient during operation.

The main parameters of the reactor, of the liquid-vapor separators,

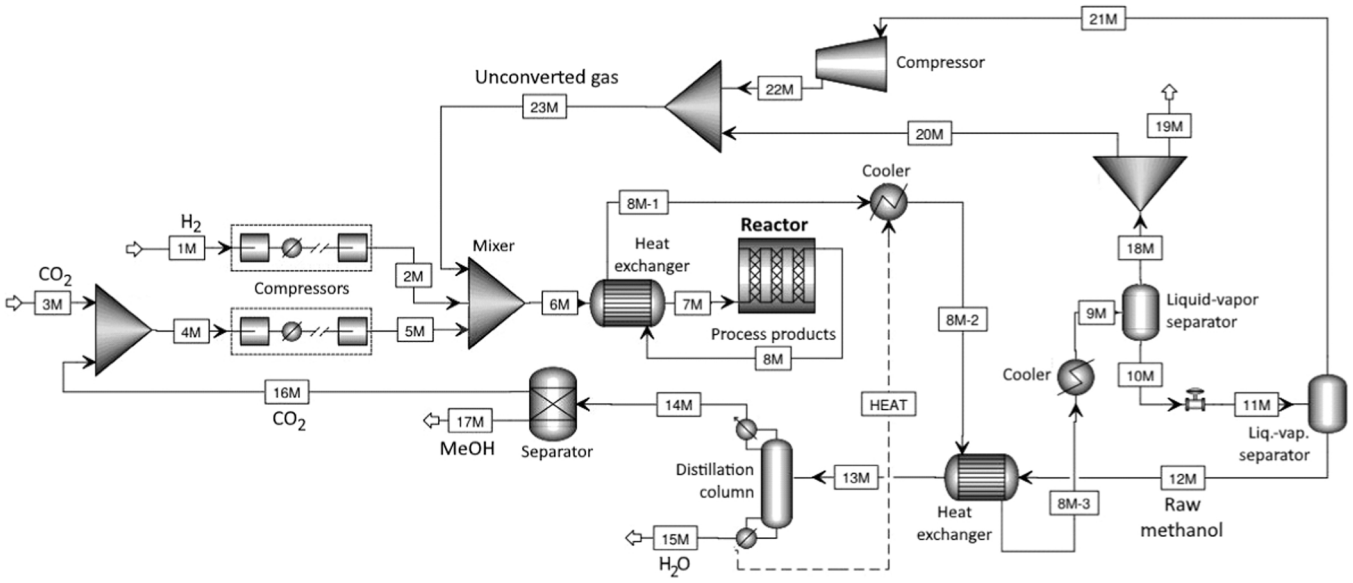

Fig. 2. Simplified flowsheet of the methanol synthesis section modelled in Aspen Plus.

and of the distillation column are reported in Table 5, whereas Table 6 reports the energy and material flows of the section. The catalyst considered is of industrial type: for this kind of catalysts an average lifetime of at least 4 years has been verified, with 8 years observed in some cases [53]. In this study a catalyst lifetime of 4 years has been adopted.

2.4. Process parameters and performance

The main process parameters – whose evaluation is essential for the economic assessment – are summarized in Table 7. The consumption of electricity reported in the table is for the first year of operation. The electrolyser is subject to degradation, so the stack functionality decreases over time. To take that into account, an over-sizing of the electrolyser has been considered, with a gradual increase of power consumption to offset stack degradation to keep hydrogen (and therefore methanol) production constant until the stack is replaced at the end of its lifetime. In particular, the degradation considered corresponds to an increase of energy consumption of 360 Wh/kg_{H2} per each year of life for the starting stacks, and of 239 Wh/kg_{H2} per year of life for the replaced stacks, on the basis of the values previously reported in Table 1.

Table 5
Main process parameters for the methanol synthesis section.

Reactor	
Number of tubes	34
Length of the tubes	12.2 m
Inner diameter of each tube	37.5 mm
Void fraction	0.4
Reactor volume	0.458 m^3
Type of catalyst	Cu/Zn/Al
Catalyst density	1775 kg/m^3
Catalyst lifetime	4 years
Operating pressure	65 bar
Inlet temperature	210 °C
Outlet temperature	290 °C
Liquid-vapor separators	
Operating conditions of the first separator	50 °C 65 bar
Operating conditions of the second separator	22 °C 1.2 bar
Raw methanol composition out of the second separator	48.7%v MeOH 49.4%v H_2O
Distillation column	
Operating pressure	1.01 bar
Operating temperature	80 °C
Composition of distillate	96.4%v MeOH 3.6%v CO_2

Table 6
Energy and material flows in the methanol synthesis section.

Inlet hydrogen flow rate	104 kg/h
Inlet CO_2 flow rate	723 kg/h
Recirculation flow rate	1960 kg/h
Produced methanol flow rate	500 kg/h
Outlet CO_2 flow rate	25 kg/h
Cooling water flow rate	285 kg/h
Amount of catalyst into the reactor	292.4 kg
Power absorption: hydrogen compressor	39.2 kW
Power absorption: CO_2 compressors	49.5 kW
Power absorption: recirculation compressor	14.7 kW

Table 7
Process parameters.

Capacity factor	0.9
Annual operating hours	7884 h/yr.
Nominal size (methanol)	500 kg/h
Plant productivity (methanol)	3942 t/yr.
Oxygen production	6473 t/yr.
Captured carbon dioxide	5703 t/yr.
Hydrogen production	820 t/yr.
Power consumption (PEM, excl. degradation)	45,622 MWh/yr.
Power consumption (other users)	2971 MWh/yr
Industrial water consumption (PEM)	8176 t/yr.
Water consumption (excl. recirculation)	5929 t/yr.
Solvent consumption (CO_2 capture)	8555 kg/yr.
Catalyst consumption (reactor)	73 kg/yr.
Nitrogen consumption	7884 kg/yr.

3. Economic assessment

An economic analysis of the plant depends on a number of key factors, *e.g.* the size and the technology of each component. All the plant costs (capital and operation) have been evaluated from commercial plant data available in literature, adjusted, where needed, to consider inflation, assumed at an annual rate of 1.33 %, as the mean value in Europe for the period 2015–2019 [54], assuming that the most recent data are not significant due to the Covid-19 pandemic effects. All costs

are expressed in Euros (€), considering – when original values were in U. S. dollars ($) – an exchange rate of 0.82 €/$ (mean monthly value in January 2021) [55].

3.1. Capital costs

Capital costs have been mainly taken from the literature in terms of specific costs or actual costs. The latter have been adapted to the plant size considered in this paper by means of the well-known equation:

$$C = C_0 \left(\frac{P}{P_0}\right)^f \quad (5)$$

where C and C_0 represent the cost of the component for the plant assessed in this study and for the reference plant discussed in the literature, respectively. P and P_0 are the comparison parameters for those plants (the nature of which depends on the type and size of plant), and f is a dimensionless scaling factor [23].

The calculation of capital costs follows the classification proposed by the U.S. National Energy Technology Laboratory [56]. In particular, bare erected cost (BEC) considers the process equipment and the supporting facilities (material cost), as well as direct and indirect labour for plant installation; engineering, procurement and construction cost (EPCC) also considers the costs for EPC contractor services; total plant cost (TPC) also includes process and project contingencies; the addition of pre-production costs, inventory capital, financing costs and other owner's costs indicates the so-called total overnight cost (TOC); finally, total as-spent cost (TASC) includes TOC and the additional costs derived from escalation and interest on debt during capital expenditure period.

3.1.1. Cost estimation

A specific material cost of 542.05 €/kW (of which 309.48 for the stack, and 123.07 and 109.49 for mechanical and electrical balance of plant, respectively) has been assumed for the PEM electrolyser's equipment, with a 12 % surcharge to consider direct and indirect labour for plant installation [38]. Overall, the bare erected cost of the PEM electrolyser is 5486 k€, with additional 440 k€ required to replace the stack in 2030 and further 126 k€ to refurbish the stack on the 18th year (this further investment is required to make the electrolyser available until the end of the plant operating lifetime).

The material cost of CO_2 capture and methanol synthesis systems have been adapted from Bellotti et al. (2017) [23], using a scaling factor (f, see Eq. 5) of 0.65 [23].

As for H_2, CO_2 (up to 20 bar) and O_2 compressors (oxygen is compressed and stored in pressurized bottles for selling), the following formula has been used to determine their equipment cost:

$$C = C_0 \bullet (\dot{m} \bullet \ln\beta)^{0.65} \quad (6)$$

where C is the cost of each compressor, C_0 is a base parameter which depends on the type of gas processed by the compressor (equal to 36,856, 2651, and 2327 for H_2, CO_2 and O_2, respectively), $\dot{m}$ is the mass flow rate (kg/h) elaborated by the machine, and β is the compression ratio (6.5 for H_2 and O_2 and 4.47 for CO_2) [57]. CO_2 is stored in liquid phase at 20 bar, but a further compression up to 65 bar is carried out by a pump to reach the pressure required by the methanol synthesis system. The cost of the pump is calculated as [58]:

$$C = 1.417 \bullet 10^6 \bullet (W_P / 1000) + 0.09 \bullet 10^6 \quad (7)$$

where C is the pump cost and W_p is the pump power (in kW). A 10 % surcharge has been considered for all the equipment costs for compression and pumping to consider direct and indirect labour for the installation of the machines.

As for H_2 and CO_2 temporary storage systems (as mentioned, oxygen is directly stored in bottles for selling), the specific costs have been derived from Van Leeuwen (2018) [59] and summarises in Table 8.

Table 8
Specific costs of the storage systems.

Gas	Pressure	State	Volume	Specific cost
H_2 storage	200 bar	gaseous	23.0 m^3	45 €/Nm^3
CO_2 storage	20 bar	liquid	16.5 m^3	8500 €/m^3

Finally, indirect capital costs have been calculated as a percentage of BEC: 8 % for engineering, procurement and construction, 15 % for project and process contingencies, 2 % for site preparation and 15 % for permit fees [60].

3.1.2. Total overnight cost

With reference to the previously described plant configuration, TOC is summarised in Table 9, whereas a detail of BEC is shown in Fig. 3.

As Fig. 3 shows, more than 50 % of BEC is due to the electrolyser – confirming what reported in several studies [20,23,26] – whereas the methanol synthesis section accounts for just 12 %.

3.1.3. Investments during the operation phase

Some further investments during plant life have also been considered, related to the scheduled replacements of the electrolyser stacks (initially characterized by an operating lifetime of about 60,000 h) and of the gas compressors (with a lifetime of 10 years). While the compressors are based on a mature technology that is not subjected to any expected future performance and cost improvement, PEM electrolysers technology is evolving rapidly. For this reason, for the replaced stacks, operating parameters and costs differ from those of the starting year. In particular, a future specific stack cost of 117.21 €/kW and a total specific system cost of 311.48 €/kW have been assumed, with an additional 15 % of total PEM cost accounted for the new stack, and a higher expected life (*i.e.* 85,000 h) [38]. A last stack replacement (4.29 % of the total PEM cost [38]) during the 18th year of plant life has been assumed.

3.1.4. Financial assumptions

Table 10 summarises the main financial assumptions considered for this study, that considers one year (2023) for plant construction and 20 years of operation.

A depreciation plan with a rate of 10 % (10 yearly constant undiscounted instalments) is considered, applied to all the plant, except for the stack of the PEM electrolyser. As mentioned, the stack is characterized by an initial depreciation period estimated in 7 years (60,000 h), whereas the new and more mature stack expected to be installed in 2030 is assumed to have a longer life (85,000 h, with a depreciation of 10 years). A further depreciation period of 10 years is still considered when the original compressors will be replaced at the end of their lives.

The starting investment for the plant construction is considered covered for 75 % with a bank loan (senior debt), with a 10-year refunding period with constant interest rate of 6.14 % [61]. This assumption involves significant financing costs (financing fees, interests

Table 9
Overnight cost estimation.

	Cost (k€)
- PEM electrolyser	*5486*
- CO_2 capture section	*1361*
- Gas compression systems	*2191*
- Gas storage systems	*348*
- Methanol synthesis system	*1230*
Bare erected cost (BEC)	10,615
- Engineering, procurement and construction	*849*
Engineering, procurement and construction cost (EPCC)	11,465
- Project and process contingencies	*1592*
Total plant cost (TPC)	13,057
- Site preparation	*212*
- Permit fees	*1592*
Total overnight cost (TOC)	14,861

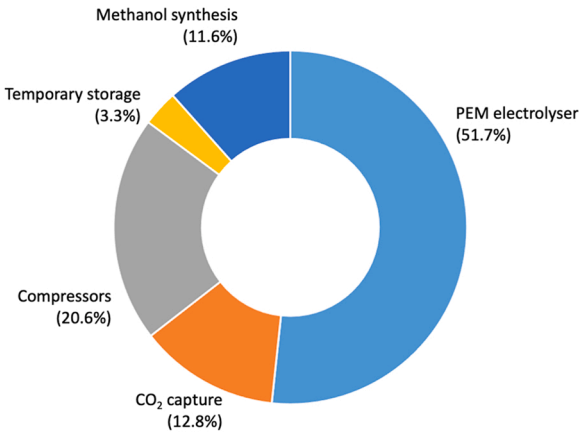

Fig. 3. Bare erected cost.

Table 10
Main financial assumptions.

Plant construction time	1 year (2023)
Plant operating lifetime	20 years
Inflation rate	1.33 %
Discount rate	8 %
Depreciation time (electrolyser stack)	7 years
Depreciation time (rest of plant)	10 years
Senior debt refunding period	10 years
Plant value at end of lifetime	0 €
Financing loan amount	75 % of TPC
Interest rate of loan	6.14 %

and so on) that have a significant impact on the project's operating performance; however, it makes this study closer to actual industrial projects [62].

Finally, an annual discount rate of 8 % (representing the typical value for investments in the energy intensive industry sector) has been assumed to convert the expected future value of costs and profits in its current value [63]. The discount rate is not applied to the bank loan interests.

3.2. Operation and maintenance costs

The operation and maintenance (O&M) costs have been calculated year by year from literature data, adjusting the yearly values with inflation. The main variable operating cost is given by electricity: its value has been estimated on the basis of the mean zone price of Sardinia in 2018 (the last period for which aggregated data are available). The plant is assumed to operate 7884 h/yr. (corresponding to a capacity factor of 0.9).

The main specific variable costs are reported in Table 11 [50,64–66], as well as the actual costs referred to the first year of plant operation.

Apart from the variable operating costs, some fixed O&M costs are also to be considered, as listed in Table 12, again with reference to the first year of operation.

In particular, personnel cost has been assessed considering 3 plant operators with an annual cost of about 70,000 €/yr. (1760 working hours per year at a hourly cost of 40 €). General and administrative (G&A) expenses are assumed as 20 % of personnel cost [67], whereas property tax and insurance are assumed 2 % of TOC [68]. Finally, maintenance cost is assumed as 2 % of TOC for the compressors [59] and 3 % of TOC for all the other equipment [50].

Fig. 4 represents both variable (a) and fixed (b) O&M costs of the project.

Taxes are also considered within the operating costs. They are applied every year of operation to income, decreased by depreciation and bank loan interests. In Italy taxes are represented by IRES (national tax on company income, with a rate of 24 %) and IRAP (regional tax on productive activity, assumed 2.93 % of the income). A total rate of 26.93 % has been used for taxes [69].

Table 11
Variable operating costs.

	Specific cost	Annual cost	Reference
Electricity	57.8 €/MWh	2809 k€/yr.	[64]
Deionized water	10 €/m^3	59 k€/yr.	[65]
Solvent (MEA)	1.90 €/kg	16 k€/yr.	[66]
Catalyst	95.24 €/kg	7 k€/yr.	[50]
Nitrogen	0.2783 €/kg	2 k€/yr.	[65]

Table 12
Fixed O&M costs.

	Annual cost
Labour	211 k€/yr.
General and administrative	42 k€/yr.
Property taxes and insurance	297 k€/yr.
Maintenance (excluding compressors)	253 k€/yr.
Maintenance (compressors)	88 k€/yr.

3.3. Revenues

The main source of revenues for the plant is from e-methanol sales. The current market value for fossil-derived methanol is around 450 €/t [70], which is used to calculate the project's cash flow, although it should be noted that methanol prices have strongly increased in recent years.

Apart from e-methanol, the oxygen obtained during water electrolysis is also a product with a market value. In this study, it is considered to be compressed to 200 bar, stocked in cylinders and sold at 150 €/t, representing a typical market value for these volumes of industrial oxygen without storage and transport [57]. The market price of CO_2, determined by the European Union's emissions trading system (ETS) is also considered. It represents an important cost for conventional plants without CO_2 capture systems. In the plant configuration analysed in this study, CO_2 is captured from the flue gas of a conventional power plant, which would otherwise need to purchase emission credits to cover the CO_2 emitted. Consequently, the emission credit value has been considered positively in the evaluation of the plant profitability. An emission credit value of 80 €/t_{CO2} has been assumed in the starting year of operation (corresponding to the average ETS value in the first half of 2022) [71]. In consideration of the growing restrictions on emissions in future years, this starting value has been assumed to increase with time to a value of about 129 €/t_{CO2} in 2030 (with an annual increasing rate from today's value of 7.05 %) and 212 €/t_{CO2} in 2040 (annual increasing rate from 2030 of 5.10 %) [72].

The expected revenues from oxygen and e-methanol sales (the latter calculated with reference to the current market price) and from the CO_2 emission credits are summarized in Table 13 with reference to the first year of operation.

3.4. Economic performance indicators

The analysis here reported follows two complementary approaches, *i.e.* the investment profitability approach, where the project's net present value (NPV) is calculated by the annual cash flow, having fixed the market price at which methanol is sold, and the levelized cost of methanol (LCoM) approach, where the selling price of methanol is calculated in order to achieve a NPV equal to zero. In other words, LCoM is the price at which methanol should be sold to reach break-even at the end of plant lifetime. In particular, with reference to the whole life of the project (including construction and operation), cost of methanol (CoM)

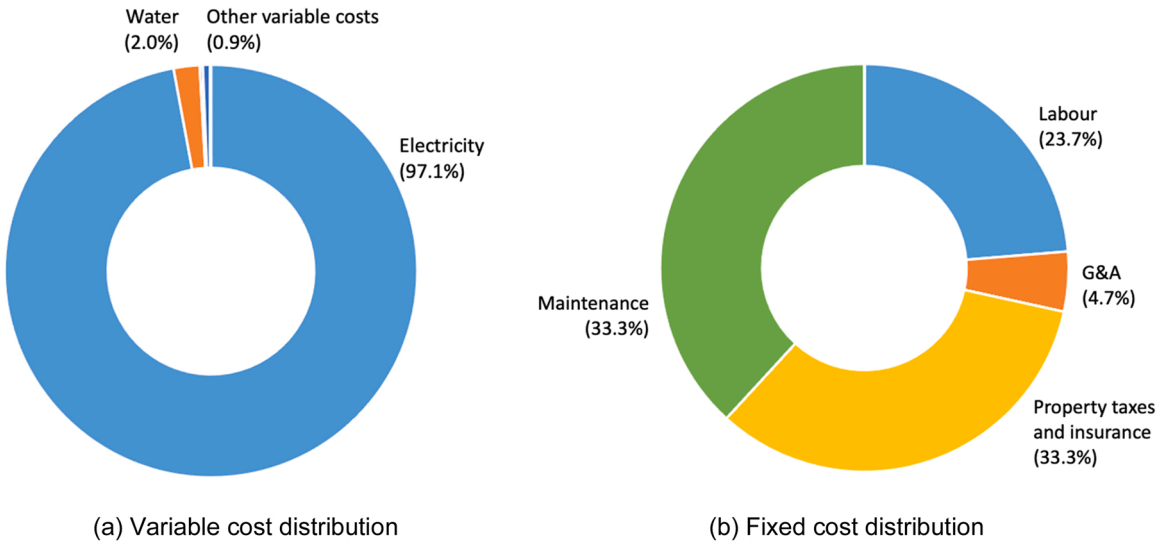

Fig. 4. Variable and fixed O&M costs.

Table 13
Revenues in the first year.

Oxygen	971 k€/yr.
Methanol	1774 k€/yr.
CO_2 emission credits	456 k€/yr.
Total	3202 k€/yr.

is the algebraic sum of all the cost (capital and operating) and revenues of the plant, divided by the whole amount of methanol produced. However, in order to take into account the depreciation (a discount rate of 8 % has been assumed in this study), the analysis considers LCoM, conceptually similar to CoM, but based on the present values of costs and revenues, instead of the future values. LCoM can be calculated by means of the following equation:

$$LCoM = \frac{\sum_{t=0}^{20} \frac{(CC_t + OC_t) - (RO_t + E_t)}{(1+r)^t}}{\sum_{t=0}^{20} \frac{P_t}{(1+r)^t}} \quad (7)$$

where, for year t ($t = 0$ during construction period and $1 \leq t \leq 20$ during the operation period), CC is the actual investment for the year (corresponding to TASC for $t = 0$ and to the investments during operation for $t > 0$), OC is the total (variable and fixed) operating cost, RO is the revenue from oxygen selling, E is the cost saving from CO_2 emissions credits, P is the annual methanol production and r is the discount rate.

4. Results and discussion

As mentioned, the economic performance has been assessed on the basis of both investment profitability and LCoM approaches. The first indicates the conventional profitability of the investment. The second indicates how the market should evolve to make the technology feasible from the economic point of view.

4.1. Investment profitability

Having fixed the e-methanol selling price (450 €/t), it is possible to calculate the annual cash flow, shown in Fig. 5 with reference to the present values (with a discount rate of 8 %). For each year of plant life, the algebraic sum of income (e-methanol and oxygen sales) decreased by the capital and operating costs determines the so-called earnings before interest, taxes, depreciation and amortization (EBITDA), from which the so-called earnings before interest and taxes (EBIT) is obtained after depreciation is deducted. Taxes are therefore calculated from EBIT decreased by the bank loan interests, but only applied if this value is positive. The fiscal year result is finally obtained subtracting the taxes and the mortgage capital instalment.

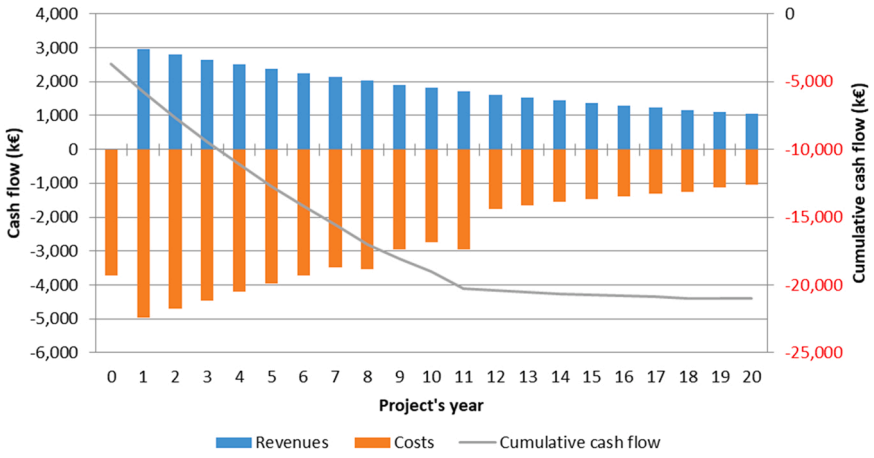

Fig. 5. Cash flow (present values).

During the first 10 years of plant operation, the annual cash flow is negative and decreasing, mainly due to the loan instalments. Starting from the eleventh years, profits slightly exceed costs, making the cumulative cash flow almost constant. What it is important to notice it that the net present value (NPV) – *i.e.* the cumulated sum of the discounted cash flow of each year – is − 21,000 k€. Such a negative value clearly indicates that the technology is still far from competitiveness, in particular if e-methanol is sold at the same market price of fossil-derived methanol.

NPV is significantly affected by the behaviour of the market, in particular of methanol and CO_2, the latter-assumed to be governed by the European ETS, whereas e-methanol is assumed to be sold at the same price of the fossil-derived methanol. Fig. 6 shows the combined effect of both these prices on NPV, which is positive only for very high prices of methanol and CO_2. The price of CO_2 here refers to its initial value, with the same growth rates discussed above).

This outcome fully confirms the general results of other studies [15], that indicate that e-methanol is still far from being competitive with the fossil-derived one, so this kind of investment is currently not profitable.

4.2. Levelised cost of methanol

The previously discussed cash flow analysis is based on the assumption that e-methanol is sold at the current market price of fossil-derived methanol. A complementary analysis involves the levelized cost of methanol (LCoE), defined above by Eq. (7), which is the price at which methanol should be sold to get a null NPV at the end of the plant lifetime, as shown in Fig. 7.

Keeping unchanged all the other parameters, the LCoM is 960 €/t. This value is more than double the current market value for methanol (450 €/t), confirming that power-to-methanol is not yet competitive for industrial-scale production of renewable fuels from captured carbon dioxide, compared to a traditional system. However, it should be noted that the methanol market is continuously growing and increasing demand may support a higher price in the future. A further price increase of fossil-derived methanol is also expected due to an increase in the cost of CO_2 emission credits. On the other hand, a decrease in e-methanol price could occur as a consequence of the development and diffusion of commercial-scale units (in particular for the electrolysers). According to the comprehensive study on CO_2 utilization published in 2019 by the International Energy Agency (IEA) [15], e-methanol price should decrease from 530 to 950 €/t in the near-term (100–170 €/MWh, where the range depends on the cost for capturing CO_2 used as a feedstock) – which is in line with LCoM value reported above – to 250–310 €/t (45–60 €/MWh), to be compared with the current methanol marked price of 450 €/t (82 €/MWh) considered in this paper.

The assessment of the investment and operation costs considered in this study is based on reliable data (most derived from commercial experience), for all the main plant's components. However, as the system of this study is a complex plant with limited industrial maturity, and especially considering the quick change of the market for low-carbon products, some uncertainty may persist on some of the parameters. A sensitivity analysis has therefore been considered in order to evaluate the effect of possible variations of those parameters on the economic performance of the plant.

Fig. 8 shows the main results of the sensitivity analysis, where a variation of a number of parameters in a range of ± 10 % of their reference values has been applied. The parameters considered in this analysis are: (i) the e-methanol selling price, (ii) the oxygen selling price, (iii) the electricity price, (iv) the value of ETS CO_2 emission credits, (v) the total capital cost, (vi) the fixed operating costs, and (vii) the plant capacity factor (number of hours of annual operation). In order to simplify the reading of the results, this analysis has been carried out fixing the e-methanol price at 960 €/t, which is the LCoM for which NPV is equal to zero; then, NPV variation have been determined consequently.

As Fig. 8 shows, the e-methanol selling price, the electricity cost and the plant capacity factor are the parameters which have, by far, the most impact on the investment profitability. And it is important to underline that, considering the quick evolution of the energy market, the electricity price is one of the most uncertain variables for this kind of project. A decreasing of capital investment can be expected in the following years due to the growing commercial maturity of the electrolysers that, as shown in Fig. 3, accounts for more than 50 % on the whole investment. Just a minor impact is expected from oxygen selling price, fixed operating costs, and the price of ETS credits. As a matter of fact, even if the direct impact of ETS credits on NPV is lower than that of other variables, the upward trend in their price will raise the cost of fossil-

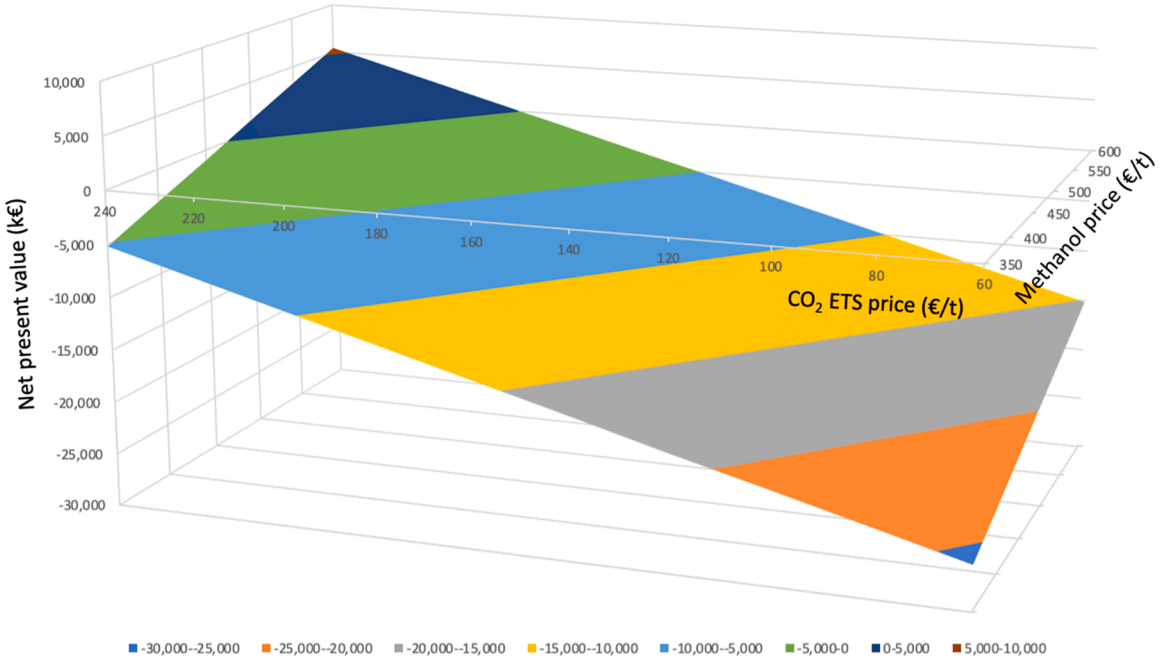

Fig. 6. Effects of methanol and CO_2 price on NPV.

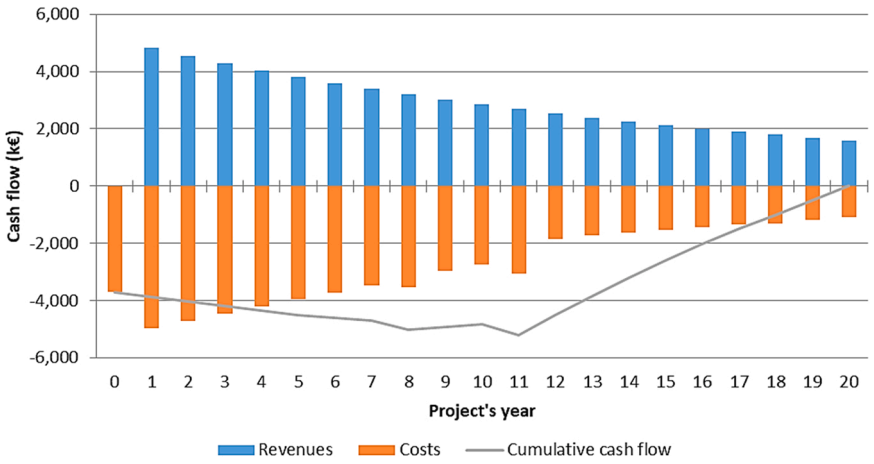

Fig. 7. Cash flow (present values) to achieve NPV = 0.

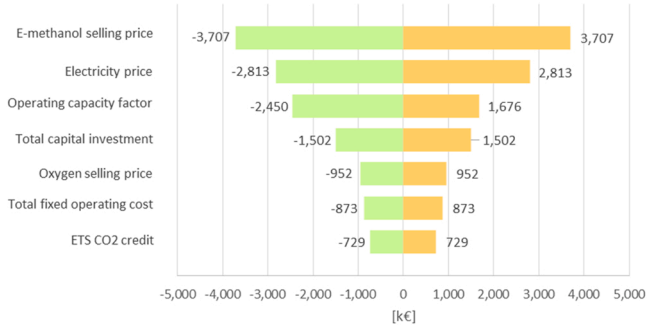

Fig. 8. NPV variation (in k€) corresponding to a ± 10 % variation of some parameters.

derived methanol, making e-methanol (and, in general, e-fuels) more competitive with the corresponding fossil-derived fuels.

The LCoM value corresponding to a variation of the number of hours of plant operation, and the resulting mean electricity cost, have also been estimated. The average electricity cost has been calculated cross-checking the 2018 hourly district electricity price for Sardinia supplied by GME (the Italian power exchange management company) [73] with the Sardinian electricity production provided by Terna (the Italian transmission system operator) [74]. The results are shown in Fig. 9.

With the increase of plant operation, the average electricity cost increases and the LCoM decreases with a nearly linear trend above 4000 h/yr. In particular, with the considered capacity factor of 0.9 (to which corresponds an operation of 7884 h/yr.) and an electricity price of 58 €/MWh, a LCoM of 960 €/t is obtained. It also results that, if the plant is operated only when electricity is at low cost (lower than 40 €/MWh), the number of operating hours would be limited to 2000 at most, with a corresponding LCoM greater than 2000 €/t.

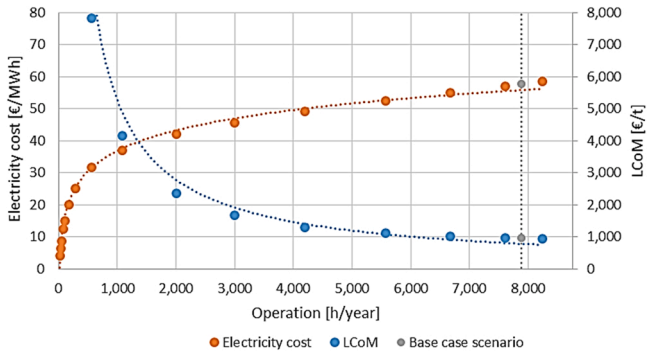

Fig. 9. LCoM variation with plant operation and electricity cost.

5. Conclusions

The combined need to chemically store renewable electricity – with the aim of enabling a wide deployment of intermittent energy sources – and to improve the production of sustainable fuels for the decarbonization of "hard-to-abate" sectors is making the power-to-fuels concept one of the most promising approaches to support energy transition towards carbon neutrality. Among the electrically-derived fuels (e-fuels) e-methanol is particularly interesting for the wide variety of its potential use, directly as a fuel or as a building block for a number of chemical processes.

The comprehensive approach followed in this techno-economic assessment – which starts from the Aspen Plus modelling of the whole plant (including green hydrogen production and carbon capture) to provide process parameters to set a detailed economic analysis based on commercial data – allows to quantify the economic performance of the integrated system.

From the technical point of view, the plant has been sized to produce 4000 t/yr. (500 kg/h, with a capacity factor of 0.9) of e-methanol and 6500 t/yr. of oxygen as by-product, using 820 t/yr. of green hydrogen (produced from about 46 GWh/yr. of renewable electricity) and avoiding the emission of about 5700 t/yr. of carbon dioxide.

Such a plant requires an initial investment of about 15 M€, more than a half (52 %) of which is due to the electrolyser (PEM – polymer electrolyte membrane – technology) for green hydrogen production. Similarly, the cost of electricity accounts for about 75 % of operating costs.

Under current market conditions, e-methanol production is far from being competitive with the conventional methanol production from fossil fuels (*i.e.* natural gas and coal), that today costs about 450 €/t. Assuming that e-methanol is sold at this price, the investment is not profitable, with a negative net present value (NPV) of about 21 M€. On the other hand, a levelized cost of methanol (LCoE, representing the price at which e-methanol should be sold to have NPV equal to zero) of 960 €/t has been calculated, more than double of the current market price for fossil-derived methanol.

A sensitivity analysis has been performed to underline the effect of several key parameters on the economic performance of the investment. Apart from methanol price (the most impacting parameter), the price of electricity and the operating capacity factor are particularly relevant in terms of economic impact on the technology.

Finally, the application of the proposed technology can be expected to become profitable in a mid-term timeframe (2030–2035) thanks to the combined effect of (i) commercial price increasing of renewable

methanol (boosted as a consequence of the new European policies and then decoupled by the price of fossil-derived methanol), (ii) reduction of the investment for the electrolysers (the sole component still far from commercial maturity) as a consequence of the diffusion and optimization of the technology, (iii) the expected increasing of CO_2 ETS price (using captured carbon dioxide means higher CO_2 credits), and especially (iv) a reduction of renewable electricity cost due to the expected wider deployment of renewable energy sources. Considering a renewable methanol selling price 25 % higher than the current market price and a 15% reduction of the electrolyser's capital cost, a 25–30 % decreasing in the average electricity price (which can be considered as a conservative assumption in a future scenario characterized by a high share of intermittent renewable electricity) should be sufficient to make renewable methanol production profitable.

This confirms the increasing interest for this kind of technology, that promises to become one of the key pathways for decarbonising sectors as heavy transport and industry in view of the energy transition towards net zero greenhouse gas emissions.

CRediT authorship contribution statement

Stefano Sollai: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Andrea Porcu**: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Vittorio Tola**: Methodology, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Francesca Ferrara**: Conceptualization, Writing – review & editing, Supervision, Project administration. **Alberto Pettinau**: Conceptualization, Methodology, Writing – review & editing, 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.

Acknowledgements

This work has been funded by the Italian Ministry of Ecologic Transition in the framework of the Research on Electric System Programme, research plan 2019–2021 (CUP: I34I19005780001). The authors are grateful to Dr. Mauro Mureddu (Sotacarbo) for his very useful support.

References

[1] C.A. del Pozo, S. Cloete, A.J. Álvaro, Techno-economic assessment of long-term methanol production from natural gas and renewables, Energy Convers. Manag. 266 (2022), 115785, https://doi.org/10.1016/j.enconman.2022.115785.
[2] International Renewable Energy Agency (IRENA), Innovation outlook: renewable methanol, 2021, https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2021/Jan/IRENA_Innovation_Renewable_Methanol_2021.pdf [accessed 21 June 2022].
[3] D. Wang, W. Meng, H. Zhou, Y. Yang, J. Xie, S. Yang, G. Li, Novel coal-to-methanol process with near-zero carbon emission: pulverized coal gasification-integrated green hydrogen process, J. Clean. Prod. 339 (2022), 130500, https://doi.org/10.1016/j.jclepro.2022.130500.
[4] G.A. Olah, Beyond oil and gas: the methanol economy, Angew. Chem. Int Ed. 44 (2005) 2636–2639, https://doi.org/10.1002/anie.200462121.
[5] Y. Sun, Z. Qin, Y. Tang, C. Liao, Y. Liu, X. Ma, Techno-environmental-economic assessment on municipal solid waste to methanol coupling with/without solid oxygen electrolysis cell unit, Process Saf. Environ. Prot. 161 (2022) 611–628, https://doi.org/10.1016/j.psep.2022.03.060.
[6] T. Shi, Y. Liu, A. Yang, S. Sun, W. Shen, J. Ren, Developing a novel gasification-based sludge-to-methanol utilization process and exergy-economic-environmental (3E) analysis, Energy Convers. Manag. 260 (2022), 115600, https://doi.org/10.1016/j.enconman.2022.115600.
[7] A. Wilk, L. Więcław-Solny, T. Speitz, A. Tatarczuk, CO_2-to-Methanol conversion – an alternative energy storage solution, Chemik 70 (2016) 626–633.
[8] J. Kotowicz, D. Węcel, M. Brzęczek, Analysis of the work of a "renewable" methanol production installation based ON H_2 from electrolysis and CO_2 from power plants, Energy 221 (2021), 119538, https://doi.org/10.1016/j.energy.2020.119538.
[9] S. Verhelst, J.W. Turner, L. Sileghem, J. Vancoillie, Methanol as a fuel for internal combustion engines, Prog. Energy Combust. Sci. 70 (2019) 43–88, https://doi.org/10.1016/j.pecs.2018.10.001.
[10] N. de Fournas, M. Wei, Techno-economic assessment of renewable methanol from biomass gasification and PEM electrolysis for decarbonization of the maritime sector in California, Energy Convers. Manag. 257 (2022), 115440, https://doi.org/10.1016/j.enconman.2022.115440.
[11] L. Luo, H. Wang, C. Li, Y. Hu, Life cycle assessment of methanol vehicles from energy, environmental and economic perspectives, Energy Rep. 8 (2022) 5487–5500, https://doi.org/10.1016/j.egyr.2022.04.009.
[12] N. Von Der Assen, J. Jung, A. Bardow, Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls, Energy Environ. Sci. 6 (2013) 2721–2734, https://doi.org/10.1039/C3EE41151F.
[13] Carbon Recycling International (CRI), 2022. www.carbonrecycling.is [accessed 22 June 2022].
[14] H. Valera, D. Kumar, A. Kumar Agarwal, Evaluating the effect of variable methanol injection timings in a novel co-axial fuel injection system equipped locomotive engine, J. Clean. Prod. 349 (2022), 131452, https://doi.org/10.1016/j.jclepro.2022.131452.
[15] International Energy Agency (IEA), 2019. Putting CO2to use, Paris, France, 2019, https://iea.blob.core.windows.net/assets/50652405-26db-4c41-82dc-c23657893059/Putting_CO2_to_Use.pdf.
[16] M. Mureddu, F. Ferrara, A. Pettinau, Highly efficient CuO/ZnO/ZrO_2@SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO_2, Appl. Catal. B: Environ. 258 (2019), 117941, https://doi.org/10.1016/j.apcatb.2019.117941.
[17] D.M. Saad, R.A. Bilbeisi, S.Y. Alnouri, Optimizing network pathways of CO_2 conversion processes, J. CO_2 Util. 45 (2021), 101433, https://doi.org/10.1016/j.jcou.2020.101433.
[18] B. Lee, H. Lee, D. Lim, B. Brigljevĭc, W. Cho, H.S. Cho, C.H. Kim, H. Lim, Renewable methanol synthesis from renewable H_2 and captured CO_2: How can power-to-liquid technology be economically feasible, Appl. Energy 279 (2020), 115827, https://doi.org/10.1016/j.apenergy.2020.115827.
[19] C. Su, H. Wei, Z. Wang, H. Ayed, A. Mouldi, A.A. Shayesteh, Economic accounting and high-tech strategy for sustainable production: A case study of methanol production from CO2 hydrogenation, International Journal of Hydrogen Energy, IN PRESS, https://doi.org/10.1016/j.ijhydene.2022.01.124.
[20] M. Yousaf, A. Mahmood, A. Elkamel, M. Rizwan, M. Zaman, Techno-economic analysis of integrated hydrogen and methanol production process by CO_2 hydrogenation, Int. J. Greenh. Gas. Control 115 (2022), 103615, https://doi.org/10.1016/j.ijggc.2022.103615.
[21] K. Harris, R.G. Grim, Z. Huang, L. Tao, A comparative techno-economic analysis of renewable methanol synthesis from biomass and CO_2: opportunities and barriers to commercialization, Appl. Energy 303 (2021), 117637, https://doi.org/10.1016/j.apenergy.2021.117637.
[22] Y. Gu, D. Wang, Q. Chen, Z. Tang, Techno-economic analysis of green methanol plant with optimal design of renewable hydrogen production: a case study in China, Int. J. Hydrog. Energy 47 (2022) 5085–5100, https://doi.org/10.1016/j.ijhydene.2021.11.148.
[23] D. Bellotti, M. Rivarolo, L. Magistri, A.F. Massardo, Feasibility study of methanol production plant from hydrogen and captured carbon dioxide, J. CO_2 Util. 21 (2017) 132–138, https://doi.org/10.1016/j.jcou.2017.07.001.
[24] F. Schorn, J.L. Breuer, R.C. Samsun, T. Schnorbus, B. Heuser, R. Peters, D. Stolten, Methanol as a renewable energy carrier: an assessment of production and transportation costs for selected global locations, Adv. Appl. Energy 3 (2021), 100050, https://doi.org/10.1016/j.adapen.2021.100050.
[25] D. Bellotti, L. Cassettari, M. Mosca, L. Magistri, RSM approach for stochastic sensitivity analysis of the economic sustainability of a methanol production plant using renewable energy sources, J. Clean. Prod. 240 (2019), 117947, https://doi.org/10.1016/j.jclepro.2019.117947.
[26] M. Rivarolo, D. Bellotti, L. Magistri, A.F. Massardo, Feasibility study of methanol production from different renewable sources and thermo-economic analysis, Int. J. Hydrog. Energy 41 (2016) 2105–2116, https://doi.org/10.1016/j.ijhydene.2015.12.128.
[27] D. Sheldon, MeOH production – a technical history, Johnson Matthey, Technol. Rev. 61 (2017) 172–182, https://doi.org/10.1595/205651317×695622.
[28] F. Lonis, V. Tola, G. Cau, Renewable methanol production and use through reversible solid oxide cells and recycled CO_2 hydrogenation, Fuel 246 (2019) 500–515, https://doi.org/10.1016/j.fuel.2019.02.108.
[29] F. Lonis, V. Tola, G. Cau, Assessment of integrated energy systems for the production and use of renewable methanol by water electrolysis and CO_2 hydrogenation, Fuel 285 (2021), 119160, https://doi.org/10.1016/j.fuel.2020.119160.
[30] V. Tola, F. Lonis, Low CO_2 emissions chemically recuperated gas turbines fed by renewable methanol, Appl. Energy 298 (2021), 117146, https://doi.org/10.1016/j.apenergy.2021.117146.
[31] G. Cau, V. Tola, C. Bassano, Performance evaluation of high sulphur coal-fired USC plant integrated with SNOX and CO_2 capture sections, Appl. Therm. Eng. 74 (2015) 136–145, https://doi.org/10.1016/j.applthermaleng.2014.03.027.

[32] D.S. Falcão e A.M.F, R. Pinto, A review on PEM electrolyzer modelling: Guidelines for beginners, J. Clean. Prod. 261 (2020), 121184, https://doi.org/10.1016/j.jclepro.2020.121184.

[33] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, Int. J. Hydrog. Energy 38 (2013) 4901–4934, https://doi.org/10.1016/j.ijhydene.2013.01.151.

[34] A. Weiß, A. Siebel, M. Bernt, T.-H. Shen, V. Tileli, H.A. Gasteiger, Impact of intermittent operation on lifetime and performance of a PEM water electrolyzer, J. Electrochem. Soc. 166 (2019) F487–F497, https://doi.org/10.1016/S0378-7753(01)00950-8.

[35] M. Götz, J. Lefebvre, F. Mörs, A. McD. Koch, M. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Power-to-Gas: a technological and economic review, Renew. Energy 85 (2016) 1371–1390, https://doi.org/10.1016/j.renene.2015.07.066.

[36] Terna, Dati statistici sull'energia elettrica in Italia 2018, available at https://download.terna.it/terna/Annuario%20Statistico%202018_8d7595e944c2546.pdf [Italian].

[37] L. Zhao, J. Brouwer, Dynamic operation and feasibility study of a self-sustainable hydrogen fueling station using renewable energy sources, Int. J. Hydrog. Energy 40 (2015) 3822–3837, https://doi.org/10.1016/j.ijhydene.2015.01.044.

[38] D. Peterson, J. Vickers, D. DeSantis, DOE hydrogen and fuel cells program record 19009: Hydrogen production cost from PEM electrolysis-2019, US Department of Energy (2020), available at ⟨https://www.hydrogen.energy.gov/pdfs/19009_h2_production_cost_pem_electrolysis_2019.pdf⟩.

[39] I. Aouini, A. Ledoux, L. Estel, S. Mary, Pilot plant studies for CO_2 capture from waste incinerator flue gas using MEA based solvent, Oil Gas. Sci. Technol. 69 (2014) 1091–1104, https://doi.org/10.2516/ogst/2013205.

[40] R. Zevenhoven, P. Kilpinen, Control of pollutants in flue gases and fuel gases, Helsinki University od Technology Technical Report TKK-ENY-4, Finland (2001), available at ⟨http://www.hut.fi/-rzeveho//gasbook⟩.

[41] B. Xue, Y. Yu, J. Chen, X. Luo, M. Wang, A comparative study of MEA and DEA for post-combustion CO_2 capture with different process configurations, Int. J. Coal Sci. Technol. 4 (2017) 15–24, https://doi.org/10.1007/s40789-016-0149-7.

[42] M.R.M. Abu-Zahra, L.H.J. Schneiders, J.P.M. Niederer, P.H.M. Feron, G. F. Versteeg, CO_2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine, Int. J. Greenh. Gas. Control 1 (2007) 37–46, https://doi.org/10.1016/S1750-5836(06)00007-7.

[43] P. Luis, Use of monoethanolamine (MEA) for CO_2 capture in a global scenario: Consequences and alternatives, Desalination 380 (2016) 93–99, https://doi.org/10.1016/j.desal.2015.08.004.

[44] T. Yokoyama, Analysis of reboiler heat duty in MEA process for CO_2 capture using equilibrium-staged model, Sep. Purif. Technol. 94 (2012) 97–103, https://doi.org/10.1016/j.seppur.2011.12.029.

[45] A.B. Rao, E.S. Rubin, A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control, Environ. Sci. Technol. 36 (2002) 4467–4475, https://doi.org/10.1021/es0158861.

[46] K. Li, W. Leigh, P. Feron, H. Yu, M. Tade, Systematic study of aqueous monoethanolamine (MEA)-based CO_2 capture process: techno-economic assessment of the MEA process and its improvements, Appl. Energy 165 (2016) 648–659, https://doi.org/10.1016/j.apenergy.2015.12.109.

[47] S.S. Araya, V. Liso, X. Cui, N. Li, J. Zhu, S.L. Sahlin, S.H. Jensen, M.P. Nielsen, S. K. Kær, A review of the methanol economy: the fuel cell route, Energies 13 (2020) 596, https://doi.org/10.3390/en13030596.

[48] D. Cocco, A. Pettinau, G. Cau, Energy and economic assessment of IGCC power plants integrated with DME synthesis processes, Proc. Inst. Mech. Eng. Part A: J. Power Energy 220 (2006) 95–102, https://doi.org/10.1243/095765006×76027.

[49] J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, A short review of catalysis for CO_2 conversion, Catal. Today 148 (2009) 221–231, https://doi.org/10.1016/j.cattod.2009.08.015.

[50] P. Battaglia, G. Buffo, D. Ferrero, M. Santarelli, A. Lanzini, Methanol synthesis through CO_2 capture and hydrogenation: thermal integration, energy performance and techno-economic assessment, J. CO_2 Util. 44 (2021), 101407, https://doi.org/10.1016/j.jcou.2020.101407.

[51] S. Meesattham, P. Kim-Lohsoontorn, Low-temperature alcohol-assisted methanol synthesis from CO_2 and H_2: The effect of alcohol type, Int. J. Hydrog. Energy 47 (2022) 22691–22703, https://doi.org/10.1016/j.ijhydene.2022.05.083.

[52] Aspen technology Inc., Aspen Plus Version V8.8 user guide, Cambridge, MA, USA, 2016.

[53] F. Schmidt, N. Ringer, L. Plass, The catalysis of methanol synthesis, in: Methanol: The Basic Chemical and Energy Feedstock of the Future, di Bertau M., Offermanns H., Plass L., Schmidt F., Wernicke H.-J. (Springer, 2014), https://doi.org/10.1007/978–3-642–39709-7.

[54] Inflation E.U., ⟨https://www.inflation.eu/en/⟩ [Accessed 17th March 2022].

[55] Banca d'Italia, ⟨https://tassidicambio.bancaditalia.it/terzevalute-wf-ui-web/averageRates⟩ [Accessed 15th January 2022].

[56] U.S. Department of Energy, Nationan Energy Technology Lab., Cost. Estim. Methodol. NETL Assess. Power Plant Perform., Tech. Rep. DOE/NETL-2011/1 455 (2011 (available at).

[57] D. Bellotti, M. Rivarolo, L. Magistri, Economic feasibility of methanol synthesis as a method for CO_2 reduction and energy storage, Energy Procedia 158 (2019) 4721–4728, https://doi.org/10.1016/j.egypro.2019.01.730.

[58] D.L. McCollum, J.M. Ogden, Techno-economic models for carbon dioxide compression, transport, and storage & correlations for estimating carbon dioxide density and viscosity, University of California, Davis (2006), available at: file:///Users/alberto/Downloads/eScholarship%20UC%20item%201zg00532.pdf.

[59] C. Van Leeuwen, Innovative large-scale energy storage technologies and Power-to-Gas concepts after optimisation, D8.3 Report on the costs involved with PtG technologies and their potentials across the EU (2018), available at: https://cordis.europa.eu/project/id/691797.

[60] B. James, W. Colella, J. Moton, PEM electrolysis H_2A production case study documentation, Prepared for the U.S. Department of Energy, Fuel Cell Technol. Off. (2013) 31 (available at), ⟨https://www.hydrogen.energy.gov/pdfs/h2a_pem_electrolysis_case_study_documentation.pdf⟩.

[61] G. Cau, V. Tola, F. Ferrara, A. Porcu, A. Pettinau, CO_2-free coal-fired power generation by partial oxy-fuel and postcombustion CO_2 capture: techno-economic analysis, Fuel 214 (2018) 423–435, https://doi.org/10.1016/j.fuel.2017.10.023.

[62] A. Pettinau, F. Ferrara, V. Tola, G. Cau, Techno-economic comparison between different technologies for CO_2-free power generation from coal, Appl. Energy 193 (2017) 426–439, https://doi.org/10.1016/j.apenergy.2017.02.056.

[63] L. Mantzos, T. Wiesenthal, F. Neuwahl, M. Rózsai, The POTEnCIA Central scenario: An EU energy outlook to 2050, Publications Office of the European Union, Luxembourg (2019), available at: ⟨https://publications.jrc.ec.europa.eu/repository/handle/JRC118353⟩.

[64] G.M.E., Dati storici MGP, available at https://www.mercatoelettrico.org/it/download/DatiStorici.aspx [Accessed 15th January 2022].

[65] A. Nicita, G. Maggio, A.P.F. Andaloro, G. Squadrito, Green hydrogen as feedstock: Financial analysis of a photovoltaic-powered electrolysis plant, Int. J. Hydrog. Energy 45 (2020) 11395–11408, https://doi.org/10.1016/j.ijhydene.2020.02.062.

[66] K. Li, W. Leigh, P. Feron, H. Yu, M. Tade, Systematic study of aqueous monoethanolamine (MEA)-based CO_2 capture process: techno-economic assessment of the MEA process and its improvements, Appl. Energy 165 (2016) 648–659, https://doi.org/10.1016/j.apenergy.2015.12.109.

[67] S. Szima, C.-C. Cormos, Improving methanol synthesis from carbon-free H_2 and captured CO_2: a techno-economic and environmental evaluation, J. CO_2 Util. 24 (2018) 555–563, https://doi.org/10.1016/j.jcou.2018.02.007.

[68] Energy.gov, Hydrogen program, available at ⟨https://www.hydrogen.energy.gov/h2a_prod_rules.html⟩ [Accessed 15th January 2022].

[69] A. Porcu, S. Sollai, D. Marotto, M. Mureddu, F. Ferrara, A. Pettinau, Techno-economic analysis of a small-scale biomass-to-energy BFB gasification-based system", Energies 12 (2019) 494, https://doi.org/10.3390/en12030494.

[70] The Methanol Institute, ⟨http://www.methanol.org⟩ [Accessed 15th June 2022].

[71] SENDECO2, ⟨https://www.sendeco2.com/it/prezzi-co2⟩ [Accessed 23th June 2022].

[72] R.C. Pietzcker, S. Osorio, R. Rodrigues, Tightening EU ETS targets in line with the European Green Deal: impacts on the decarbonization of the EU power sector, Appl. Energy 293 (2021), 116914, https://doi.org/10.1016/j.apenergy.2021.116914.

[73] GME, Inside Information Platform, available at ⟨https://pip.ipex.it/⟩ [Accessed 15th January 2022].

[74] Terna, Download Center, available at ⟨https://www.terna.it/it/sistema-elettrico/transparency-report/download-center⟩ [Accessed 15th January 2022].