Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment

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Abstract

The purpose of this paper is to assess via techno-economic and environmental metrics the production of methanol (MeOH) using H₂ and captured CO₂ as raw materials. It evaluates the potential of this type of carbon capture and utilisation (CCU) plant on (i) the net reduction of CO₂ emissions and (ii) the cost of production, in comparison with the conventional synthesis process of MeOH Europe. Process flow modelling is used to estimate the operational performance and the total purchased equipment cost; the flowsheet is implemented in CHEMCAD, and the obtained mass and energy flows are utilised as input to calculate the selected key performance indicators (KPIs). CO₂-based metrics are used to assess the environmental impact. The evaluated MeOH plant produces 440 ktMeOH/yr, and its configuration is the result of a heat integration process. Its specific capital cost is lower than for conventional plants. However, raw materials prices, i.e. H₂ and captured CO₂, do not allow such a project to be financially viable. In order to make the CCU plant financially attractive, the price of MeOH should increase in a factor of almost 2, or H₂ costs should decrease almost 2.5 times, or CO₂ should have a value of around 222 €/t, under the assumptions of this work. The MeOH CCU-plant studied can utilise about 21.5% of the CO₂ emissions of a pulvertised coal (PC) power plant that produces 550 MWnet of electricity. The net CO₂ emissions savings represent 8% of the emissions of the PC plant (mainly due to the avoidance of consuming fossil fuels as in the conventional MeOH synthesis process). The results demonstrate that there is a net but small potential for CO₂ emissions reduction; assuming that such CCU plants are constructed in...
1. Introduction

The contribution of fossil fuels to the energy share in Europe will continue to be higher than renewables and nuclear power at short and medium term [1]. Moreover, process industries like cement, iron and steel, aluminium, paper and pulp and refineries, have inherent CO2 emissions as a result of raw material conversion. In this context, carbon capture, utilisation and storage (CCUS) is presented as a medium term alternative to mitigate climate change.

According to the Energy Roadmap 2050 [1], carbon capture and storage (CCS) will have to be present in 7–32% of the fossil fuel power generation contribution by 2050, depending on the scenario considered, to meet a 80–95% greenhouse gas (GHG) emissions reduction by 2050, with 1990 as reference year. The 2030 Climate and Energy Policy Framework [2], proposes the reduction in GHG to at least 40% compared to 1990 by 2030, to meet the 2050 objective. The renewable energy share is targeted at no less than 27%, whilst an indicative target of 27% is set for improving energy efficiency compared to projections of future energy consumption based on the current criteria. The European Commission has recently acknowledged the Energy Union Strategy to face climate change policies that will transform the European energy system. Among the reinforced dimensions (energy security, integration of the European market, energy efficiency, decarbonisation and research, innovation and competitiveness), CCS and CCU in power and industrial sectors are supported as a part of the solutions to reach 2050 climate objectives in a cost-effective way, which need further development [3]. In 2013 the total CO2 emissions in the power sector were of 3400 MtCO2, while the 2030 objective is to reduce these CO2 emissions to 1550 MtCO2, in EU-28 [4]. CO2 management has therefore a main role in these targets.

Carbon capture and utilisation (CCU) represents a new economy for CO2, since captured CO2 can be used as raw material for other processes. This includes the synthesis of chemicals and materials (such as methanol, formic acid, polyols for polyurethanes, carbonates), fuels (like methane or kerosene) and direct use in applications based on CO2 physico-chemical properties (for example in supercritical state) [5]. Additionally, CO2 can be involved in biological conversions, like for instance in a direct photo-conversion of CO2, bacterial CO2 fermentation, or in an algae biorefinery. Carbon dioxide as raw material is involved in synthesis reactions (i) by incorporating the whole CO2 moiety into organic backbones, which are exothermic, or (ii) by incorporating only a portion of it, to other C1 or Cn molecule, which are endothermic. Reactions type (ii) are the most common ones, and can be used to store renewable energy, by using the excess electric energy to integrate CO2 reduction and water splitting, for instance, and converting CO2 into an H2 carrier [6,7]. The consumption of energy in CCU is hence important and has to be taken into account to perform the balance of emissions. CCU is at different levels of development. It ranges from laboratory (like photo-catalysis) to demonstration (like the synthesis of methanol by direct hydrogenation) levels, passing by pilot projects (for instance, the synthesis of syngas) [8,9]. Therefore, the prospects for each CCU alternative are at different time horizons.

CCU may delay carbon emissions to the atmosphere, for different periods depending on the final product: the CO2 used to synthesise the chemical product is released once the CO2-based...
product is used or consumed. Enhanced oil and gas recovery (EOR, EGR), as well as CO₂ mineralisation, result in a permanent storage or in a long-term storage of tens and more years [9], while in the other utilisation cases CO₂ is emitted later in the product chain. This should be taken into account when evaluating the real potential of CCU for CO₂ emissions reduction. In this sense, a life cycle assessment (LCA) is crucial to count for each CCU plant capability to prevent CO₂ emissions. Von der Assen et al. [10] highlight that the amount of utilised CO₂ is not the amount of CO₂ avoided. The total balance should include the different value chain echelons: capture, transport, CO₂ transformation, and CO₂ product consumption. However, the main advantage of a plant which uses captured CO₂, called CCU-plant hereafter, remains on the reduction of the original feedstock consumption (usually a fossil fuel) and the prevention of emissions associated to them, when compared to well-known and conventional pathway(s) to synthesise a specific product. This will possibly offer financial incentives for the deployment of CO₂ capture.

CCU, due to its inherent potential and principally regarding its use to synthesise materials, chemicals and fuels, has to be complementary to geological CO₂ storage if pursuing an important CO₂ emissions reduction impact [11–13]. Nowadays, the existing CO₂ re-used represents 0.4% of the emitted carbon [11]. Future markets for captured CO₂ will have to map and prioritise points of CO₂ emission with utilisation opportunities, promoting tailor-made and local (clusters of sources and sinks) solutions [14].

In this context, there is a need for research and development focused on CCU options with significant CO₂ uptake potential, which may lead into a net reduction of CO₂ emissions in Europe, thus contributing to climate change mitigation. Further, there is a need for detailed analysis regarding the impact that different CCU options can have on the energy system and under which conditions the CCU products can have a sustainable market. The main objective of this study is to evaluate and quantify the abatement of CO₂ through the production of methanol (CH₃OH, MeOH) by direct CO₂ catalytic hydrogenation. This route has been already proved at a pilot scale [15]. Its potential impact as a commercial and well-established process has not been yet evaluated under a European context.

In the current paper we analyse (i) MeOH economic and technical feasibility, by evaluating process conditions, mass and energy flows; (ii) its environmental advantage due to raw material replacement compared to conventional processes; (iii) the total amount of CO₂ that is not emitted and (iv) under which conditions the CCU production of MeOH is competitive with the traditional plants. This work simulates the MeOH plant at a commercial scale (based on an average scale of the already existing MeOH synthesis plants in Europe) in the process modeller CHEMCAD. The retrieved data are used to calculate a selected group of key performance indicators (KPIs). The paper is divided as follows: first, a brief state of the art provides an overview of the CCU context, and in particular, of the MeOH context. Then, the methodology is described, followed by the modelling strategy and performance section, and the results or KPIs evaluation. Finally, the discussion and conclusion parts indicate the main findings of the current work and which are important features to be covered in future work.

1.1. State-of-the-art

CO₂ is already commercialised to synthesise other products. The traded CO₂ usually derives from industrial processes as by-product (i.e. H₂ production by steam reforming of natural gas or ethanol production by fermentation), not from captured CO₂ from flue gas streams. The value chain for captured CO₂ is similar to the one that already exists for the CO₂ by-product: once the CO₂ is obtained, it is liquefied, and liquid CO₂ is transported to end users (nowadays it is usually road transport). Current uses, among others, are in beverage carbonation, food industry, medical applications, rubber/plastics or to mix gases/aerosols [16]. Even though the similarities with current traded CO₂ supply chain, CO₂ capture, transport, storage and use are facing important challenges, as summarised in the following lines.

Li et al. [17] point out that an important number of patents have been published for CO₂ capture techniques (removal and separation) in the last years (2006–2010). Nevertheless, safety, efficiency and economy are still challenges to capture CO₂ from large and stationary sources. Roddy [18] describes the differences between CO₂ capture in industrial and power plants; while power plants afford post-combustion configurations, industrial facilities will usually have to deal with less direct retrofitting layouts, as for pre-combustion and oxy-fuel combustion configurations. The cited work points out the potential benefit and interest of integrated capture-transport networks; including large and smaller sources of CO₂. The size of the networks will depend on future context developments, codes and standards for CO₂ pipelines. A number of studies [19,8,11,6,5,20] highlight the wide range of possibilities for CO₂ use as raw material; with each one at different levels of development, different product scales and market prospects. Catalytic synthesis is the most developed conversion method for enhanced carbon recovery. However, electrochemical and photo-chemical conversion, less developed, may be more efficient and emit less CO₂. Depending on the technology used to synthesise the final product from CO₂, the process is more or less sensitive to impurities in the CO₂ stream, for instance, ranging from formic acid synthesis to mineralisation, which may have significant cost implication. Algae production is an example of an emerging technology for biofuel synthesis, with a probable relevant contribution [21,22]. CCU is attracting attention of policy makers as an alternative to (i) motivate local economies, (ii) arrange CO₂ after capture and (iii) potentially decrease CO₂ emissions. These are the reasons why CCU applications may have different motivating drivers. Reports like the one from the Global CCS Institute (GCCSI) [14], the Carbon Sequestration Leadership Forum (CSLF) [12,13] and the French Environment and Energy Management Agency (ADEME) [9] highlight the potential of existing and future CCU options, their limited but feasible scale contribution, and their competitive advantage.

This work refers to MeOH due to its important potential as fuel. According to Olah [23], (i) hydrogen can be stored in MeOH, (ii) it can be used as a convenient fuel and (iii) as a feedstock to synthesise olefins (which can be used to synthesise hydrocarbons). Hydrogen production from MeOH to be applied in mobile devices is studied for instance in [24]. As fuel, it can be blended with gasoline, it can be further transformed and blended with diesel, and it may be used in fuel cells. Recent studies demonstrate an interest on alcohols use as fuel in sectors like maritime [25] and aviation [26]. The production of MeOH is especially attractive in emerging economies, as a liquid fuel to replace conventional sources of energy. Particularly, the motivation of a “methanol economy” may stimulate its manufacturing, as proposed in China and USA [27]. If using the conventional MeOH synthesis pathways, from natural gas or coal (as mainly in China), the synthesis of MeOH may cause water shortages and increase GHG emissions [28]. Therefore, there is a need to find alternative ways to synthesise MeOH, other than using fossil fuels as raw materials. There exist two catalytic routes to synthesise MeOH from CO₂: direct hydrogenation of CO₂ with H₂ or CO₂ conversion into CO and further hydrogenation of CO [29]. As alternative, MeOH can be also produced electrochemically by CO₂ reduction and H₂O oxidation [30]. The electrochemical conversion of CO₂ can be customised to produce different products by appropriately selecting electrocatalysts, electrolytes and applied potential [31]. Yamamoto et al.
specify that MeOH can be a product of CO₂ reduction and water oxidation in a fuel cell, producing oxygen as by-product. Research is also in the line of considering solar energy as the source for CO₂ reduction with H₂O in a compacted photo-electrochemical cell [32].

Methanol synthesis from captured CO₂ is moving forward: Iceland and Japan have different plants that combine CO₂ and renewable H₂ [6]. Carbon Recycling International (CRI) started the operation of the first commercial demonstration plant in Iceland, in 2011, whose aim is to improve plant economics for larger plants and to gain operation expertise [34]. This plant has as particular advantageous situation its access to very low cost electricity [27]. Its capacity is about 5 Mt MeOH/yr. Moreover, CRI has a pilot plant operating since 2007. CRI is involved in a H2020 project whose aim is to use surplus and intermittent renewable energy sources to produce chemicals and fuels from CO₂ from coal power plants. The study will focus on the deployment of fast response electrolyser [34]. Mitsui Chemicals Inc., in 2008, built a pilot plant to synthesise MeOH from CO₂ and H₂ in Osaka, with a capacity of around 100 t MeOH/yr. The installation uses CO₂ emitted from factories and H₂ obtained from water photolysis. The purpose of the produced MeOH is to produce olefins and aromatics [35]. The presence of these plants allow us to conclude a Technology Readiness Level (TRL) [36] of 6–7 for MeOH from CO₂. As such, research and development is crucial to move towards a competitive CCU-process, from the most fundamental research level (e.g. [37], fundamental research on catalysts) to integrated studies at conceptual design level (e.g. [38], complete plants).

Hydrogen for MeOH production must be provided to the process in a carbon-free way to reduce the life cycle CO₂ emissions: Hydrogen from water electrolysis using a renewable source of electricity is considered as renewable. It may be produced through alkaline or proton exchange membrane electrolysis (PEM), while H₂ from steam electrolysis is produced via a solid oxide electrolyser cell (SOEC). The latter is the most efficient option, but this is currently the less developed [39]. Biomass, solar radiation and wind are the most common renewable sources proposed for electricity supply in water electrolysis [40]; while wind is currently the most cost effective and dominant source among renewables [41].

Summing up, the current CO₂ market is likely to expand with new CO₂ applications, in different sectors. CCU appears as a developing alternative, with an important potential to motivate carbon capture. CCU will not replace geological storage as a tool to reduce anthropogenic emissions and fight against climate change, but its contribution should not be ignored as a local alternative. This works aims at evaluating the potential of MeOH synthesis in Europe using CO₂ as raw material, and under what conditions it results competitive towards its conventional production.

2. Methanol market in Europe

Methanol is a commodity used for several industrial chemicals. The main chemical derivatives produced are formaldehyde, acetic acid, methyl tertiary-butyl ether (MTBE) and dimethyl ether (DME). Its transformation into olefins is an emerging sector. In the so-called “methanol economy”, mentioned in the previous section, the demand of MeOH can increase if its use is encouraged in direct gasoline blending, for production of DME and/or biodiesel [42].

Global MeOH installed production capacity has been growing since 2009 with an average annual rate of about 10%, while the production has been also growing at a slightly smaller rate, around 7%, reaching 58 Mt in 2012, according to the International Energy Agency (IEA) [43] or 60.6 Mt according to the Methanol Market Services Asia (MMMSA) [44]. Concerning nameplate capacity installed worldwide, it was 95.5 Mt in 2012 [44] and 98.3 Mt in 2013, with Europe accounting for 3% [45–47], mostly located in Germany [45] and Norway [46]. China hosts about 50% of the world capacity and consumption [48]. Note that European plants in 2013 had load factors around 82%, when in USA they were around 74% [45]. China is expected to experience significant growth of MeOH capacities, followed by North America, while European production is expected to be constant [49].

China dominates not only the world MeOH capacity, but also the world MeOH consumption [48]. Total MeOH production in 2013 in Europe was about 2.9 Mt, while total consumption is estimated to be about 2.62 times the production, the excess being covered by imports. The main derivative of MeOH is formaldehyde, accounting for 31% of the world MeOH demand in 2012 [44] and 2013 [48]. Use of MeOH in direct fuel applications include MTBE/tert-Amyl methyl ether (TAME), biodiesel, gasoline blending and DME, accounting in total for 37% of the world MeOH demand [44].

The global MeOH demand is driving the growth in production and it depends on the demand for the main derivatives. In the next five years, the global demand for formaldehyde is expected to grow at an average rate just over 5%, but its demand for fuel applications is expected to raise more strongly at a rate of about 6.5% [48]. The demand is driven by China, but it is assumed for the purpose of this paper that Europe will follow similar rates to the global ones, even if no increase in installed capacity is foreseen. This work looks at horizon 2030; it is also supposed that non important change occurs regarding methanol and its use as hydrogen carrier to that date.

2.1. Conventional production of methanol

Methanol is typically produced by the Fischer–Tropsch process, where pressurised synthesis gas (or syngas, a mixture of mainly H₂, CO and CO₂) reacts in the presence of a catalyst, according to Eq. (1):

\[
\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}
\] (1)

The reaction is highly exothermic and a major challenge is the removal of excess heat, in order to shift the equilibrium towards the products and avoid side reactions and catalyst sintering [50]. Syngas can be produced either by steam reforming in the case of light hydrocarbons, such as natural gas or light naphthas, or by partial oxidation, in the case of heavy oils or solid carbonaceous materials. The feedstocks used in the European industry are mainly natural gas and residual fuel oil with ratio 3:7 [45]. Steam reforming consumes (per tonne of product produced) 36.5 GJ/MeOH or 33.4 GJ/MeOH of natural gas, without and with primary reform, respectively. Partial oxidation consumes 37.15 GJ/MeOH of oil [51]. Typical CO₂ emissions from MeOH production range between 0.5 tCO₂eq/MeOH for steam reforming with primary reform and 1.4 tCO₂eq/MeOH for partial oxidation of residual oil [51]. In the case of European plants, due to the use of both technologies, the average CO₂ emissions (direct and indirect) are assumed to be 0.76 tCO₂eq/MeOH [45].

Taking into consideration information provided in source [45] concerning prices for the European industry, and combining them with information from Eurostat about natural gas [52] and electricity [53] costs, the cost of MeOH production can be estimated, as a weighted average among the European facilities. The average feedstock costs (i.e. natural gas and fuel oil) is 345 €/tMeOH, while the average costs for utilities (including electricity, cooling and process water, catalysts and other materials) add up to 15 €/tMeOH, with 86% of it corresponding to electricity needs. See
in Table 4 more specific information about MeOH conventional plants contrasted with the results obtained in the current paper for the MeOH CCU-plant.

3. Methodology

This section summarises the main methods and tools used to evaluate the potential impact of the production of MeOH using CO₂ as raw material. The main goals are to determine (i) the cost of MeOH production via CCU and under which conditions the project is financially viable, and (ii) the net reduction of CO₂ emissions if compared with the conventional synthesis process, at plant level. Process flow modelling is used to calculate the CCU-plant conceptual design operational and cost performances. Mass and energy balances are the input for the KPIs evaluation, which also assesses the performance of the CCU-plant. Specific technical, economic and environmental metrics are compared to the metrics of the weighted average among the MeOH European facilities, related to their production rate.

3.1. Process modelling and cost of purchase

A conceptual design of the MeOH CCU-plant is implemented in CHEMCAD. An estimate of the capital cost is obtained, with an accuracy typically in the range of ±20% (preliminary or feasibility estimate) [54]. A pinch analysis is performed in the CCU-plant to design the heat exchanger network (HEN). The use of CHEMCAD CC-therm module allows the estimation of the cost and the pressure drop of the heat exchangers. The purchased equipment costs are obtained in CHEMCAD. The following hypotheses and conditions are considered for the calculation of the mass and energy balances and the purchase cost of the main equipment:

- The boundaries of the model and the analysis are set on the utilisation plant itself; CO₂ capture and transport, H₂ generation and transport, and further purification steps of the CO₂ stream, are thus outside the scope of this work. Both streams entering into the CCU-plant are assumed to be 100% pure.
- Hydrogen is supplied by an integrated pipeline network. It is generated via a network formed by the most cost efficient centralised and decentralised producers, using a range of different technologies, according to the modelling hypotheses and results of JRC-EU-TIMES model [55]. The JRC-EU-TIMES is a linear optimisation, partial equilibrium, bottom-up technology-rich energy system model generated with the TIMES model generator from Energy Technology Systems Analysis Program (ETNASP) of the IEA [59]. It covers the energy systems of EU28 plus Switzerland, Iceland and Norway, from 2005 to 2050.
- The scale of the MeOH CCU-plant corresponds to an average representative size of conventional plants. The plant produces 440 ktMeOH/yr.
- The plant is built in Western Europe (location factor of 104.3%, to transform the costs from US Gulf Coast basis to Western Europe [45]). Ambient air temperature is 20 °C. Atmospheric pressure is 1.013 bar.
- The currency used is €2014. Currency conversion is performed using Eurostat data [56]. The Chemical Engineering Plant Cost Index (CEPCI) published monthly in the Chemical Engineering Magazine is used to actualise each unit purchase cost, specifically the CEPCI for July 2014 from the Chemical Engineering Research and Design Journal [57].
- The purchased equipment costs estimated in CHEMCAD for a plant built from carbon steel, are adapted to consider the utilisation of 304 stainless steel, by means of a material cost factor of 1.3 [54].
- The electricity needed in the MeOH CCU-plant is provided by a conventional pulverised coal (PC) power plant of 550 MWnet of electricity, as worst case scenario, as all the electricity is supplied by the most carbon intensive power plant. Its CO₂ emissions factor is 803 tCO₂/GW h [58].
- Production time of 8000 h per year (capacity factor of 91.3%).

3.2. Key performance indicators

The MeOH CCU-plant is evaluated through the following technological (or plant performance), economic and environmental metrics. The selected metrics represent different aspects of the process that are relevant to the total CO₂ emissions of the plant. The different indicators are normalised to the tonne (t) of MeOH produced.

3.2.1. Technological metrics

The technological metrics are mainly direct results from the process modelling:

- Mass balance. It evaluates the total amount of principally inlet CO₂ and H₂ to the CCU-plant, and of water and flue gases as by-products or outlet streams to be disposed.
- Energy balance. It quantifies overall electricity, heat and cooling requirements, and integration of needs.
- CO₂ converted. Two metrics evaluate, (i) the CO₂ that is converted in the reactor of the synthesis process, and (ii) the CO₂ that is transformed into MeOH through the whole process, i.e. taking into account the recycling streams. They are expressed as a percentage of the total amount of CO₂ that enters the process as raw material, as in Eqs. (2) and (3).

\[
\text{CO}_2\text{convR} = \left( \frac{\text{CO}_2\text{in} - \text{CO}_2\text{out}}{\text{CO}_2\text{in}} \right)_{\text{Reactor}}
\]

\[
\text{CO}_2\text{convP} = \left( \frac{\text{CO}_2\text{in} - \text{CO}_2\text{out}}{\text{CO}_2\text{in}} \right)_{\text{Process}}
\]

where CO₂in is the inlet flow rate to the reactor or to the whole process, and CO₂out is the outlet flow rate. In the case of the Process metric evaluation, CO₂in is the CO₂ entering the system as raw material.
- CO₂ used (retained, or recycled). It is defined as the total amount of CO₂ that is converted into MeOH. Gross CO₂ used takes into account the difference between the amount of CO₂ raw material and the CO₂ that goes out from the process through flue gas, purge and/or venting streams (i.e. direct CO₂ emission streams from the balance of the CCU-plant). Net CO₂ used incorporates indirect emissions from the generation of electricity used in the MeOH CCU-plant, as in Eq. (4).

\[
\text{NetCO}_2\text{used} = (\text{CO}_2\text{in} - (\text{CO}_2\text{out} + \text{CO}_2\text{indirect}))_{\text{Process}}
\]

where CO₂in is the inlet flow rate (in mass basis) that enters the whole process, CO₂out is the outlet flow rate, and CO₂indirect corresponds to the CO₂ emissions due to electricity consumption.

As part of the technological analysis, the energy balance, electricity and water consumptions from the MeOH CCU-plant are contrasted with the weighted-average MeOH conventional plant values in Europe.

3.2.2. Economic metrics

Breakdown of capital and operating costs are calculated and depicted to identify which items are responsible of the highest contributions. Capital cost, variable cost of production and fixed
cost of production provide the needed information to compare the studied CCU-plant with the weighted-average MeOH conventional plant in Europe.

The approach applied to calculate the installed costs (ISBL) follows the detailed factorial methodology described in Towler and Sinnott [54]. The starting cost value is the purchased equipment cost estimated in CHEMCAD. The total fixed capital cost (TFCC) represents the total cost for designing, constructing and building the plant, as well as the linked modifications to prepare the site. It includes: (i) the inside battery limits (ISBL) investment as the cost of the plant itself, and it is composed by the total purchased equipment costs, equipment erection, piping (including insulation and painting), instrumentation and control systems, electrical (power and lighting) system, civil work and site preparation; (ii) the outside battery limits (OSBL) investment that accounts for the modifications to the site infrastructure; (iii) the engineering costs (between 10% and 30% for large-small projects); and (iv) the contingency charges that represent extra costs added to the estimated budget, with the objective to cover errors and uncertainty (+30% is assumed here).

Except for the purchase cost, all the items that contribute to the TFCC are fractions of the ISBL or of the total purchase cost. The working capital is also evaluated, and it represents the investment of capital to maintain plant operation, such the continuance of inventories. It is assumed that the working capital is recovered at the end of the plant operation.

Variable costs of production (VCP) are proportional to the plant production and include raw materials costs, by-products and waste streams disposal, consumables (in this case, catalyst consumption), and utilities consumption. Fixed costs of production (FCP) take into account those costs that are made independently of the plant operation rate, such as salaries and overheads, maintenance or capital charges. The most important economic evaluation parameters are provided in Appendix A.

Revenues (REV), in this particular case, come from the income gained from selling MeOH. The gross margin (GM) is calculated as in Eq. (5).

\[
GM = REV - RM
\]

(5)

where RM is the cost of buying the raw materials.

The benefit/cost ratio (BCR) is calculated as benefits divided by costs as in Eq. (6). This metric provides information about how much of the costs to make a product is covered by the benefit of selling this product.

\[
BCR = \frac{\text{Total unitary benefit of selling the product}}{\text{Total unitary cost to make the product}}
\]

(6)

3.2.3. Environmental metrics

The environmental indicators take into account direct CO₂ emissions (as a result of the process) and indirect CO₂ emissions (due to electricity consumption). These values are compared with direct, indirect and total emissions of the conventional weighted-average MeOH plant in Europe.

One of the added values of a CCU process, as was mentioned in Section 1, is the potential to yield a net reduction of CO₂ emissions, if compared to the conventional process to synthesize the CCU product. In order to quantify the potential benefit of installing a CCU process instead of a conventional plant, two metrics are defined in Eqs. (7) and (8). While Eq. (7) takes into account the real CO₂ savings, i.e. CO₂ not-produced because of the no-utilisation of fossil fuels as raw material in the chemical process, Eq. (8) refers to the whole amount of CO₂ that is not emitted into the atmosphere (until the MeOH is consumed), i.e. the CO₂ avoided, because (i) there is a certain amount of CO₂ that enters to the CCU-plant to be used as raw material, and (ii) some CO₂ is not produced if compared to the conventional process.

\[
(CO_2)_{\text{not-produced}} = (CO_2)_{\text{conv}} - (CO_2)_{\text{ccu}}
\]

(7)

\[
(CO_2)_{\text{avoided}} = (CO_2)_{\text{not-produced}} + (CO_2)_{\text{in-ccu}}
\]

(8)

where CO₂ for conventional ((CO₂)_{\text{conv}}) and CCU-plants ((CO₂)_{\text{ccu}}) take into account direct and indirect emissions, and (CO₂)_{\text{in-ccu}} is the CO₂ raw material that enters the CCU-plant.

The environmental impact outlook of the MeOH CCU-plant is evaluated by considering that the expected MeOH demand growth is provided by CCU-plants in Europe (according to the market description in Section 2).

3.3. Financial analysis

The MeOH CCU-plant is evaluated from a private investor viewpoint. The main metric considered here is the net present value (NPV). The following assumptions are taken into account:

- The CCU-plant has a life of 20 years, without any further investment.
- The capital expenses occur during the first three years of the project (30%, 60% and 10% of the TFCC).
- Pre-taxation rates are of concern (neither taxes nor depreciation are considered).
- In years 1 and 2 there are no revenues. In years 3, 4 and 5 the plant operates at 30%, 70% and 100% of its average capacity (91.3%), respectively.
- Prices for raw materials, utilities, products and by-products, are estimated for year 2014 (the project starting in year 2015), and are considered constant along the 20 years, except for H₂ and electricity. The price of these two commodities vary in years 2020, 2025 and 2030, along the results of the JRC-EU-TIMES model runs under the scenario “current policies” (CPI).
- The real discount rate is iₙ of 8%.

The competitiveness of the MeOH CCU-plant is studied through four sensitivity analyses, regarding the change of the NPV derived from the variation of investment costs, CO₂, H₂ and MeOH prices. The base case scenario considers that CO₂ has a price of zero.

4. Methanol synthesis evaluation

The MeOH synthesis process can be separated into three different stages, as explained in the Ullmann’s encyclopedia of Industrial Chemistry [60]. In the first process stage, the feed gases are compressed up to the reactor feed pressure, using several compression stages with intercooling. In the second process stage, the pressurised feed is heated up and fed to the reactor. In the third process stage, MeOH is separated from water in a distillation column. Before entering the distillation column, which is operated at ambient pressure, the process stream coming from the reaction section is depressurised. While the main stream is condensed, the unreacted H₂ and CO₂ are purged from a flash vessel. The process is governed by the two main reactions that occur in the reactor, Eqs. (9) and (10).

\[
CO_2 + 3H_2 = CH_3OH + H_2O
\]

(9)

\[
CO_2 + H_2 = CO + H_2O
\]

(10)
While reaction (9) is the one that produces MeOH, the second one is undesired because it consumes the feed meant for MeOH formation. The selectivity is pushed towards the MeOH formation by recycling the formed CO together with unreacted H₂ after the flash separation of MeOH and water. The heat of reaction is partially used to heat feed streams.

4.1. Reference CCU process

The MeOH synthesis route proposed by Van-Dal and Bouallou [50] is the reference process. Their proposed flowsheet has been simulated and optimised using a pinch point analysis (i.e. the integrated CCU process).

Methanol production is 1320 t/day at a purity of \( n_{\text{CH}_3\text{OH}} > 99.9\text{wt}\% \). Therefore, 41,000 std. m\(^3\)/h of CO\(_2\) at ambient pressure and temperature and 123,000 std. m\(^3\)/h of H\(_2\) at 25 bar and ambient temperature are fed. This leads to a stoichiometric mixture, according to reaction (9). The reactor is operated with controlled feed conditions at 76 bar and 210°C. The commercial catalyst Cu/ZnO/Al\(_2\)O\(_3\) is used in this process, due to the available information, even if it is less efficient with only CO\(_2\) than when used with mixtures of CO/CO\(_2\).

**Process description.** The flowsheet of the reference process is depicted in Fig. 1. The CO\(_2\) feed stream 1 is compressed through a four stage compressor with intermediate cooling. It is assumed that the CO\(_2\) enters the system at 1 bar. The compressors 1, 3, 5, and 7 are modelled as adiabatic compressors with an isotropic efficiency of 0.75. The pressure increase of each compressor is approximately \( \frac{P_{\text{out}}}{P_{\text{in}}} \approx 3 \), leading to a final pressure of 78 bar, stream 9. Intermediate cooling in heat exchangers 2, 4, and 6 is performed with water at 28°C, which is heated up until the difference with the temperature of the inlet gas stream is 10°C. Hot water is then used in an organic Rankine cycle (ORC) to generate electricity. The gas stream is cooled down to about 38°C after each cooler.

The H\(_2\) feed stream 8 is compressed with compressor 8 from 30 up to 78 bar. Streams 9 and 10 are mixed with the compressed recycle stream 20 and fed to heat exchanger 10, where they heated up with a fraction of the reactor outlet stream 14, to reach the reactor inlet temperature of 210°C.

Reactor 11 is modelled as an adiabatic ideal plug flow reactor (PFR), according to the kinetics for reactions (9) and (10) as in the paper by Van-Dal and Bouallou [50]. The complex rate equations are directly implemented in CHEMCAD. The amount of catalyst utilised is 44,500 kg of Cu/ZnO/Al\(_2\)O\(_3\) [50]. The obtained fixed bed volume is 42 m\(^3\). As seen in Fig. 2, the equilibrium of reactions (9) and (10) is reached almost half a way through the
reactor. Therefore, a reduction of the mass of catalyst is possible, but this is not further considered here.

Gaseous stream 13 leaves the reactor at 290 °C, with a MeOH content of 4.7 vol %. The conversion of CO₂ to MeOH is around 21%. About 0.4% of the incoming CO₂ is converted to CO due to reaction (10). Stream 13 is divided into two streams. Stream 14, which is used to heat the reactor feed in heat exchanger 10; and stream 32, which is used in reboiler 22 that belongs to the distillation column (unit 21), and to preheat the feed to the column in heat exchanger 20. After this heat integration, the streams are mixed again and cooled down to 35 °C in heat exchanger 14, allowing for the condensation of almost all MeOH and water. Gas and liquid phases are then separated in flash vessel 18. The released heat is transferred to a stream of water, which will be used in the ORC. Gas stream 18, which is mainly composed by H₂ and carbon oxides, is compressed and recycled back to the reactor. About 1% of the recycle stream is purged (stream 35) to avoid the accumulation of inert gases. The condensed liquid 21 is throttled to the pressure of 1.2 bar. The released gas in separated in another flash vessel (unit 19) and purged (stream 36).

Condensate 23 is an almost gas-free mixture of MeOH and water with a MeOH concentration of $\approx 63$ wt%. This mixture is preheated and partially evaporated in heat exchanger 20, using heat from the reactor off-gas. Then, the 2-phase stream is fed to distillation column 21. This unit is modelled with 57 equilibrium stages, seeded at stage 44 (counted from top). A reflux ratio of 1.2 and a reboiler duty of 21.2 MW, are required to reach the design specifications of MeOH purity ($\approx 99.95$ wt %) and MeOH recovery ($\approx 99.95$ wt %) [50]. A distillation process analysis shows that a considerable amount of reboiler duty can be saved by a feed tray optimisation. By feeding the 2-phase stream into stage 38, the required reboiler duty is reduced from 21.2 MW to about 15 MW. A rate-based calculation of the column is performed, using the mass and heat transfer model from Billet and Schultes implemented in CHEMCAD [61], for its sizing. Mellapack 250Y is used as packing in the column. The column is designed to operate at about 60% of its flooding capacity which leads to a diameter of 4.4 m. The calculated height is 25 m of packing, to include the required amount of equilibrium stages. The top gas stream 29, coming from partial condenser 23, is compressed up to 1.2 bar to compensate the pressure drop incurred in the following heat exchanger 25. Here, MeOH is condensed at 35 °C, and the remaining inert gases are purged. The heat released in the condenser (unit 23) is used to heat water for the ORC.

Finally, product liquid MeOH, stream 31, leaves the process. Purge streams 35, 36 and 38 are collected and combusted in furnace 28 with air at 1200 °C. Off-gases are used to produce steam in boiler 30, which can be sold as by-product or used in the upstream carbon capture unit. For further details see [50].

4.2. Integrated CCU process

Fig. 3 depicts the hot and the cold composite curves, arranged for a AT of 10 °C. Fig. 4 represents the hot composite curve utilisation in the reference process. The hot stream coming from the reactor is divided and used in heat exchangers 10, 20 and 22. High temperature differences, as in units 20 and 22, destroy exergy. The heat generated and not integrated along the process, is used to generate electricity in the ORC in the reference process. The low temperature level in the ORC may cause inefficiencies, while producing an amount of 2.2 MW of electricity. The generated electricity is increased in the integrated CCU process, by using 4 ad-hoc expanders (around 8 MW). According to Fig. 3, around 120 MW are available at over 220 °C and can be used for steam generation; in the integrated process, the generated steam is used directly in 4 turbines that replace the electric motors of the 4 CO₂ compressors. The remaining low temperature hot composite is used to heat cycle water that comes from the condenser of a power plant, assuming that the MeOH CCU-plant is integrated into the power plant. By this approach, the CCU-plant saves in cooling water needs and the power plant takes advantage of the heat; 54 m³/h of cycle water can be heated from 20 °C to 133 °C.

Process description. The new approach requires a more complex HEN. The process flow diagram of the integrated process is shown in Fig. 5. Saturated steam at 25 bar is now produced in heat exchanger 13, which is placed directly after the reactor to extract energy at high temperature from the hot composite. Heat exchangers 11 and 18 are added to integrate the heat required for the cold composite. The recycle stream is heated in heat exchanger 18 with hot water coming from the intermediate coolers, the partial condenser of the distillation column and the final condenser 25. The generated steam from boiler 30 at 90 bar and boiler 13 at 25 bar, are expanded in a system of two and two steam turbines (not depicted in Fig. 5). The conditions of each one of the streams depicted in Fig. 5 are detailed in Appendix B.

4.3. Cost estimation

Purchased equipment costs estimation for the reference case MeOH CCU-plant and the integrated process are performed with the cost functions implemented in CHEMCAD. Energy and mass balances and cost evaluation of the integrated process, are utilised to evaluate the KPIs in the current work. Specific details for each simulated and cost-evaluated unit:
Compressors are modelled as belt driven centrifugal compressors. All heat exchangers are sized with the CHEMCAD CC-THERM module. They are assumed to be shell and tube heat exchanger of the TEMA Type AEL (Removable Cover, Single Pass, Fixed Tube Sheet). Flash vessels are sized with the CHEMCAD internal routine based on the work by Watkins [62]. The distillation column is sized by applying Billet and Schultes method implemented in CHEMCAD.

5. Results and discussion

5.1. KPIs evaluation

Tables 1 and 2 summarise the technological evaluation of the MeOH CCU-plant. Concerning Table 1, the mass balance underlines the produced amount of water, considered here as a by-product to disposal. Due to the proposed integrated solution that burns the purge gases and take advantage of their calorific values, there is an amount of air that enters the system, and the consequent flue gases that leave it.

The total electricity consumption results from the needs of compression (CO\textsubscript{2}, H\textsubscript{2} and gas recycling) and water circulation (pumping system), minus the electricity generated by the ad-hoc steam turbines system. Heating and cooling needs expressed in Table 1 correspond to the “external” needs, after heating–cooling integration among the streams of the main MeOH synthesis process (i.e. the needs provided by the ad-hoc pressurised water system described in Section 4). The conversion rate of CO\textsubscript{2} in the catalytic reactor is 22%, while its total conversion in the whole process is 94%. This is reflected in the gross amount of CO\textsubscript{2} used, which is 1.37 t/t\textsubscript{MeOH}, while the total amount of CO\textsubscript{2} entering the system is 1.46 t/t\textsubscript{MeOH}. The final net amount of CO\textsubscript{2} used is less, 1.23 t/t\textsubscript{MeOH}, due to the emissions allocated for electricity consumption. In the

![Fig. 5. Process flow diagram of the integrated process.](image-url)
case that the total amount of electricity was provided by renewables, gross and net CO₂ emissions would have been the same.

As depicted in Table 2, the heat integrated (total amount of heating and cooling needs) in the process is of 1.48 MW h/tMeOH (81 MW), and the heat recovered to the steam expanded in the four turbines is of 0.68 MW h/tMeOH (i.e. 38 MW). The electricity needs are reduced by 46% when comparing reference and integrated configurations.

A comparison of costs for reference and integrated CCU processes, shows that the integrated process has around 28% lower purchase costs than the reference process. The breakdown of the purchased equipment costs and operating costs are depicted in Fig. 6. From Fig. 6(a), the most expensive unit in the plant is the compression system, followed by the HEN. The total equipment purchase cost is 27 M€.

The price of H₂ is 3090 €/t, and in years 2020, 2025 and 2030 decreases 4.7% and increases a 5.25% and a 5%, respectively, in relation to the value in 2015. The price of electricity is 95.1 €/MW h in year 2015, and decreases to 94.5 €/MW h in year 2020, while it increases to 107.7 €/MW h and 121 €/MW h in years 2025 and 2030, respectively [55]. The price of water is 0.03 €/t [45] (mainly water from the pressurised water system derived from the power plant) and the price of the catalyst is 95.24 €/kg [63]. A market price of 400 €/t is assumed for MeOH [64]. See in Table 3 the main economic indicators. Fig. 6(b) highlights that the salary and overheads are the largest fraction of the FCP. VCP are dominated by the raw material cost, i.e. the cost of H₂.

The GM of the MeOH plant is −95 Me/t yr, as H₂ purchase surpasses the revenues obtained by selling MeOH. The BCR is 0.6. This emphasises the need to compensate the high production costs: the total cost of production is almost 1.7 times the expected revenue.

The CO₂ emissions indicators underline the positive CO₂ balance for the CCU process. The direct and indirect emissions of the CCU process are 0.1 Mt/yr, while the conventional plant to synthesise MeOH emits 1.17 Mt/yr [45]. See in Table 4 the comparison of energy consumption, costs and emissions of CCU and conventional plants. Mainly due to the relatively high price of H₂, the variable costs for the CCU-plant are higher than variable costs for the conventional plant. Capital cost for the CCU-plant is lower than for the conventional plant. According to Hansen et al. [65], the syngas production step in a conventional plant, which normally uses natural gas as raw material (including oxygen production and compression) may account for at least 60% of the investment. This step in a conventional plant (steam reforming of natural gas or fuel oil) also increases the consumption of water. Lower capital cost and water consumption for the CCU plant are expected, as the syngas synthesis step is missing (while the rest of the plant, MeOH synthesis and purification, remain similar). Whereas the CCU-plant consumes more electricity than the conventional plant, the final balance of CO₂ emissions shows a clear advantage for the CCU-plant. The CO₂ not-produced is 0.54 t/tMeOH and the CO₂ avoided is 2 t/tMeOH.

5.1.1. Water electrolysis to produce H₂

In the current work, it is assumed that the needed H₂ to synthesise MeOH is provided by an hypothetical H₂ network. Since the selected boundaries do not take into account H₂ generation, this echelon does not contribute to the global balance of CO₂ emissions. The inclusion of the electrolyser within the boundaries of the CCU plant allows the evaluation of its impact on (i) investment costs and (ii) emissions. Moreover, water is needed as raw material and oxygen is produced as by-product. The electrolyser contributes by increasing costs, electricity needs and decreasing net CO₂ used until negative values if for instance the European electric grid is taken as reference. Note that such a CO₂ emissions increase will not provide any advantage in terms of CO₂ savings regarding the conventional process of MeOH synthesis. Thus, it is mandatory to use a renewable source like wind, where it can be assumed that electricity is obtained at zero emissions [10,66].

![Fig. 6. Distribution of the purchased equipment costs and the operating costs for the MeOH CCU-plant.](image-url)
5.2. Financial analysis

The NPV of the base case configuration is negative, thus at the assumed prices and conditions, the MeOH CCU-plant is not an attractive investment at an 8% of cost of capital. The value of the NPV is −1036.2 M€ for a project of 20 years.

The following sensitivity analyses (i) explore the effect of the TFCC uncertainty (varied between ±30%) on the profitability of the project, and (ii) demonstrates under which CO2, H2 and MeOH prices the NPV is zero. According to the slopes of each sensitivity analysis, a price variation of H2 has the highest impact on NPV, followed by CO2 and MeOH. See in Fig. 7 the sensitivity analyses performed and in Table 5 the values that make NPV = 0. From Fig. 7(b), uncertainty in TFCC cannot reach a positive NPV. The calculated values in Table 5 allow for an increase in revenues of around 143 M€/yr. The negative CO2 value indicates that the plant would receive 222 € for each tonne of consumed CO2. As a matter of comparison, the tonne of CO2 in the European Emissions Allowance market is at 7.5 €/t [67]. Hydrogen price decrease (2.13 times) may be triggered by learning by doing and/or the use of cheaper and newer technologies. The price of MeOH should be higher (1.8 times) as its current price, reaching levels that has not been historically reached [64].

![Figure 7](image-url)

(a) Sensitivity analysis for CO2 value (negative values mean that the MeOH plant receives a revenue for using captured CO2).

(b) Sensitivity analysis for H2, MeOH and investment costs, represented in relative increments/decrements to their base case values.

Fig. 7. Sensitivity analysis of the main variables in a MeOH CCU-plant.

Table 5

<table>
<thead>
<tr>
<th></th>
<th>Breakeven value (€/t)</th>
<th>Base case price (€/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>−221.7</td>
<td>0</td>
</tr>
<tr>
<td>H2</td>
<td>1453.3</td>
<td>3090</td>
</tr>
<tr>
<td>MeOH</td>
<td>723.6</td>
<td>400</td>
</tr>
</tbody>
</table>

5.3. Perspective

According to the market description reported in Section 2, the global demand of MeOH is expected to grow up to 2018. The study of the environmental KPIs in the current paper demonstrates that there exists a potential amount of CO2 avoided, 2 t/t\(_{\text{MeOH}}\) and 0.54 t/t\(_{\text{MeOH}}\) of CO2 not-produced. The global demand of MeOH is expected to increase a 5% for formaldehydes and a 6.5% for fuel applications per year. The demand of MeOH in Europe is around 7.6 Mt/yr; with 38% of it being provided by European plants. Assuming (i) that the European market grows as the global industry, and (ii) that the needed production increase, including imports, is provided by CCU technology, the following results are presented:

- The total increase of MeOH demand in Europe is 300,580 t/t\(_{\text{MeOH}}\). One MeOH CCU-plant with the same capacity as the plant simulated in this work would be needed, working at 68%, to provide one year of growth of demand.
- Regarding the European MeOH imports, the demand is of 4.7 Mt/t\(_{\text{MeOH}}\). This value is equivalent to 10 CCU-plants working at full capacity, and one CCU-plant working at 65% of capacity.
- One MeOH CCU-plant needs 0.644 MtCO2/t\(_{\text{MeOH}}\) (1.46 tCO2/t\(_{\text{MeOH}}\)) as raw material, that come from capture.
- One MeOH CCU-plant involves a total amount of CO2 used, or retained in MeOH, of 0.54 tCO2/t.
- If compared to conventional MeOH plants, the amount of CO2 avoided is 0.883 tCO2/t, which means 0.239 CO2 not-produced.
- Taking into account that 143 MeOH plants per year are needed to make it profitable (in form of CO2 value, H2 price decrease, or MeOH price increase), the cost of the tonne of CO2 not-produced is about 600 €/tCO2.
- As a matter of comparison, a conventional PC power plant that generates 550 MW\(_{\text{ac}}\) of electricity produces around 3 MtCO2/yr of CO2 [58]. Compared to the needs of one MeOH CCU-plant, this plant would ask for 21.5% of the total CO2 emissions of the power plant. Taking into account the amount of CO2 not-produced, 8% of the total amount of CO2 emitted in the power plant represents net emissions savings, i.e. derives into CO2 which is not produced in the downstream CCU-plant. Note that the MeOH CCU-plant needs around 9.5 MW per year.
- Overall, the above mentioned 11 CCU-plants (10 plants at full capacity and 2 more plants at 68% and 65% of capacity), can theoretically reach a net CO2 emissions reduction of 2.71 MtCO2/yr (CO2 not-produced). This is comparable to the CO2 emissions of one PC power plant.

5.4. Discussion

This work has evaluated an integrated MeOH CCU-plant to assess its techno-economic performance while accounting for its potential benefits as a CO2 emissions reduction alternative. The integrated CCU-plant shows a clear benefit in costs and electricity consumption, in comparison with a less integrated configuration. The CCU plant uses conventional units. However, mainly due to the price of the raw materials, CO2 and H2, such a project is not financially feasible, even if the capital cost is lower than that of the conventional technology. In the evaluation of the water electrolyser, it has been highlighted that the high price of H2 is linked to the still emerging technology used to synthesise it. An analogous situation can be depicted for CO2 capture technologies. Therefore, the economic feasibility of MeOH synthesis from CO2 and H2 is linked to the evolution of the technologies used to synthesise its feeding streams.
The different CO\textsubscript{2} metrics defined and analysed in this paper, reveal the complexity (and possible subjectivity) of the problem when defining “CO\textsubscript{2} emissions reduction”. As was pointed out in Section 1, the synthesised products that use CO\textsubscript{2} as raw material, (i) represent a recycling pathway for CO\textsubscript{2}, where CO\textsubscript{2} may be not permanently removed from the atmosphere and, (ii) avoid the use of fossil fuels. This implies a net reduction of CO\textsubscript{2} emissions, which is lower than the total CO\textsubscript{2} used as raw material. As such, the MeOH CCU-plant can be considered as a small scale contributor in CO\textsubscript{2} avoidance. An analysis of the plant, taking into account the whole value chain (LCA), will be needed to evaluate all the CO\textsubscript{2} emissions linked to the CCU system, from CO\textsubscript{2} origins, up to the use of the CCU product.

The market outlook shows that there is place for a number of MeOH CCU-plants in Europe (at the production scale assumed in this work) which can cover the predicted annual demand increase and reduce imports for formaldehyde and fuel applications, under the hypotheses of complete coverage of demand growth, and a rising demand supposed identical in Europe than in the overall global market. There is place for more than 11 CCU plants, meaning a net emission reduction of about 2.71 MtCO\textsubscript{2}/yr (CO\textsubscript{2} not-produced).

### Table A.6
Costs breakdown and assumed parameters [54].

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<tr>
<th>Category</th>
<th>Description</th>
<th>Assumptions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total fixed capital cost (TFCC)</td>
<td>ISBL capital costs</td>
<td>Factorial methodology</td>
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<td></td>
<td>OSBL capital costs</td>
<td>35% of ISBL</td>
</tr>
<tr>
<td></td>
<td>Engineering costs</td>
<td>20% of ISBL and OSBL</td>
</tr>
<tr>
<td></td>
<td>Contingency</td>
<td>30% of ISBL and OSBL</td>
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<tr>
<td></td>
<td>Working capital</td>
<td>15% of ISBL and OSBL</td>
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<td>CAPEX</td>
<td>TFCC + Working capital</td>
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<tr>
<td>Variable costs of production (VCP)</td>
<td>Raw materials costs</td>
<td>Market price and model results</td>
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<td></td>
<td>By-products disposal</td>
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<tr>
<td></td>
<td>Catalyst consumption</td>
<td>[50]</td>
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<td></td>
<td>Utilities consumption</td>
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<td>Fixed costs of production (FCP)</td>
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<td>Interest</td>
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<td>Royalties</td>
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### Table B.7
Stream's conditions for the integrated CCU process (Fig. 5) (1/3).

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Mass flow (t/h)</th>
<th>Temp (°C)</th>
<th>Pres (bar a)</th>
<th>Vapor fraction</th>
<th>Composition (wt%)</th>
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<td>1</td>
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<td>CO\textsubscript{2} inlet</td>
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### Table B.8
Stream's conditions for the integrated CCU process (Fig. 5) (2/3).

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<th>Stream No.</th>
<th>Mass flow (t/h)</th>
<th>Temp (°C)</th>
<th>Pres (bar a)</th>
<th>Vapor fraction</th>
<th>Composition (wt%)</th>
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<td>28</td>
<td>54.9</td>
<td>64</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>29</td>
<td>55.2</td>
<td>79</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
</tbody>
</table>

### Table B.8
Stream's conditions for the integrated CCU process (Fig. 5) (3/3).

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Mass flow (t/h)</th>
<th>Temp (°C)</th>
<th>Pres (bar a)</th>
<th>Vapor fraction</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>467.6</td>
<td>135</td>
<td>75.70</td>
<td>0.98</td>
<td>MeOH inlet</td>
</tr>
<tr>
<td>31</td>
<td>467.7</td>
<td>35</td>
<td>75.56</td>
<td>0.98</td>
<td>H\textsubscript{2}O inlet</td>
</tr>
<tr>
<td>32</td>
<td>379.9</td>
<td>35</td>
<td>74.30</td>
<td>0.98</td>
<td>H\textsubscript{2} inlet</td>
</tr>
<tr>
<td>33</td>
<td>376.2</td>
<td>41</td>
<td>78.50</td>
<td>0.98</td>
<td>CO\textsubscript{2} inlet</td>
</tr>
<tr>
<td>34</td>
<td>376.2</td>
<td>62</td>
<td>78.30</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>35</td>
<td>87.8</td>
<td>35</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>36</td>
<td>86.8</td>
<td>35</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>37</td>
<td>86.6</td>
<td>80</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>38</td>
<td>56.4</td>
<td>99</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>39</td>
<td>56.4</td>
<td>101</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>40</td>
<td>112.0</td>
<td>67</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>41</td>
<td>57.1</td>
<td>64</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>42</td>
<td>54.9</td>
<td>64</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
<tr>
<td>43</td>
<td>55.2</td>
<td>79</td>
<td>1.20</td>
<td>0.98</td>
<td>CO inlet</td>
</tr>
</tbody>
</table>
Table B.9 Stream’s conditions for the integrated CCU process (Fig. 5) (3/3).

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Name</th>
<th>Mass flow (t/h)</th>
<th>Temp (°C)</th>
<th>Pres (bar a)</th>
<th>Vapor fraction (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>MeOH</td>
<td>55.1</td>
<td>40</td>
<td>1.05</td>
<td>0.00</td>
</tr>
<tr>
<td>32</td>
<td>Purge 1</td>
<td>467.7</td>
<td>118</td>
<td>75.70</td>
<td>0.95</td>
</tr>
<tr>
<td>33</td>
<td>Purge 2</td>
<td>129.1</td>
<td>81</td>
<td>75.66</td>
<td>0.92</td>
</tr>
<tr>
<td>34</td>
<td>Purge 3</td>
<td>467.7</td>
<td>76</td>
<td>75.56</td>
<td>0.92</td>
</tr>
<tr>
<td>35</td>
<td>Water</td>
<td>3.8</td>
<td>35</td>
<td>74.30</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The results obtained in this paper, exclusively focused on the CCU-plant, are closer to a real project situation as long as the transport step is avoided (i.e., there exists a power plant in the vicinity, that supplies electricity, cycle water and CO₂ to the CCU-plant), and the CO₂ entering into the CCU-plant is pure or it is further purified at no cost for the CCU-plant. Taking into account that the project has a negative NPV in the base case situation, this promotes the incorporation of the CCU plants near the plants that produce/release and capture CO₂, to avoid further costs (and emissions). The project can result financially attractive if the H₂ price decreases, maybe driven by research and development in the sector, or if the MeOH price is higher than what has been the tendency of the market, or if CO₂ has a value of at least 222 €/t.

6. Conclusions

The analysis presented in this work considers a promising CCU technology. MeOH production with CO₂ and H₂ as raw materials. Its conceptual design, at a commercial scale, has been simulated in CHEMCAD in order to obtain the needed mass and energy balances to evaluate the technological, economic and environmental metrics. An integrated flowsheet has been conceived and evaluated in the selected techno-economic and environmental criteria. The total amount of electricity needed is decreased by the utilisation of four expanders that take advantage of the caloric value of the purge gases, and fully covers the electricity demand of the CO₂ compressor.

The conversion of CO₂ in the catalytic reactor is 22%, while the total amount of CO₂ converted in the process is 94%. The amount of CO₂ needed in the process is 1.46 t/tMeOH. Whereas the net amount of CO₂ used (retained in the product) is 1.23 t/tMeOH. If taking into account the direct and indirect emissions of the MeOH CCU-plant. The most expensive unit in the CCU-plant is the compression system, followed by the heat exchangers network. The total equipment purchase cost is 27 M€. The total fixed capital cost is 200 M€. Variable operating costs are dominated by the cost of H₂, while, the CO₂, in the base case scenario, is obtained at no cost. The total cost of production is almost 295 M€/yr, which is greater than the expected revenue in 117 M€/yr; the BCR of 0.6 emphasises the need to compensate a production cost that is almost 1.7 times the expected revenue. Compared to a conventional MeOH plant, the CCU-plant has lower capital cost (when the electrolyser is outside the boundaries of the plant), whereas variable costs are higher. The CCU-plant presents net CO₂ emissions reduction: CO₂ not-produced is 0.54 t/tMeOH and CO₂ avoided is 2 t/tMeOH.

At current conditions, the MeOH CCU-plant is not financially viable. In order to make the CCU-plant financially attractive, four sensitivity analyses have been performed by varying capital costs, CO₂, H₂ and MeOH prices. The uncertainty assumed in the estimation of the investment, cannot make the NPV positive. The break-even values that make NPV equal to zero are: a MeOH price increased in almost 2 times (1.8), or a H₂ price decreased in almost 2.5 times (2.13), or a CO₂ value of around 222 €/t.

The MeOH CCU-plant studied, can utilise 21.5% of the emissions emitted from a PC coal power plant that generates 550 MWₑ net of electricity, meaning net CO₂ emissions savings of 8%. The results obtained in this paper are closer to a real project situation as long as the transport step is avoided, and as long as the CO₂ released/obtained is pure or further purified at no cost for the CCU-plant. The results demonstrate that there is a net but small potential for CO₂ emissions reduction. Assuming that such CCU-plants are constructed in Europe to meet the MeOH demand growth and the quantities that are currently imported, the net CO₂ emissions reduction is of 2.71 MtCO₂/yr.

The paper has presented and demonstrated the validity of the methodology to estimate the potential benefit of a CCU-plant, at a plant level, and the potential prices that make the project financially attractive, at the conditions and hypotheses of the analysis.

As future work, the same methodology will be applied to other CCU technologies in order to address their European potential, i.e. urea yield boosting, formic acid synthesis, polyols for polyurethanes synthesis and mineralisation. The boundaries of the study will be enlarged, to include a more exhaustive study of the purification of CO₂ step, the production of H₂ from electrolysis using renewable electricity, and a complete LCA.

Acknowledgments

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Appendix A. Economic evaluation parameters

See Table A.6.

Appendix B. Modelling characteristics


References

ener/files/documents/roadmap2050_ia_20120430_en_0.pdf> [last accessed January 2015].


