

Assessment of CO₂ Utilization Technologies into Valuable C₁ Organic Chemicals: a Modelling and Simulation Analysis

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The concentration of carbon dioxide (CO₂) within the atmosphere reached unprecedented levels mainly due to population and industrial growth, both of them requiring high energy consumption. Strategies such as the use of renewable energy sources, multiple actions aiming to improve the energy efficiency, or the integration of Carbon Capture Utilization and Storage (CCUS) technologies are currently investigated to mitigate the greenhouse emissions. The utilization of CO₂ to produce value-added chemical compounds / energy carriers is of major importance to meet the emission targets set by the European Union. The current research is focused on the conversion and valorisation of captured CO₂, through CO₂ hydrogenation, to produce green C₁ high-priced chemicals such as: i) substitute natural gas (SNG), ii) formic acid (FA), and iii) methanol (MeOH). Water electrolysis is considered for H₂ production with the employ of renewable energy sources, as for example solar, wind, or hydro power, with the purpose of developing a green and sustainable technology. A thermal output of 100 MW was assumed in the case of SNG production, whilst considering an annual productivity of 10,000 t of formic acid and 50,000 t of methanol. Aspen Plus simulator software was used to model the SNG production, and ChemCAD process simulation software was used for the FA and MeOH production processes. The integrated mass and energy balance data were afterwards used to evaluate all considered cases from a technical perspective. The evaluated designs were validated based on data from the scientific literature. As the results show, the proposed CO₂ utilization technologies are very promising in terms of high energy efficiency (50 – 60 % range) as well as high CO₂ conversion yields (>90 %).

1. Introduction

One of the key objectives of nowadays society consists in the greenhouse gas reduction and climate change mitigation by shifting the energy sector from fossil-based fuels towards sustainable alternatives (Cipoletta et al., 2020). Taking into account that the availability of renewable electric sources (RES) is heavily influenced by the geographic characteristics (Cormos et al., 2021), the employment of CCUS technologies is the most appropriate choice on a mid-term to meet the goals set within the Paris agreement (Chen et al., 2021). A lot of attention moved in the direction of Carbon Capture and Utilization (CCU) topic as the captured CO₂ might be employed in the production of chemicals used either as green fuels or energy storage media (Abad et al., 2021), known as power-to-gas strategy (PtG). This concept is meant to eventually increase the competitiveness of the CCUS technology from an economic perspective (Lin et al., 2022), while also exhibiting a positive social impact. Methanol is among the major CO₂ hydrogenation products due to its large utilizations either as a feedstock in the production of valuable chemicals such as dimethyl ether, formaldehyde or dimethyl carbonate, or as a green fuel alternative (Yousaf et al., 2022). The CO₂-to-MeOH through the hydrogenation process reached a Technology Readiness Level (TRL) of 8-9, with the “George Olah” plant located in Svartsengi, Iceland, approaching a commercial scale (CRI, 2022). SNG represents another PtG product that could possibly reduce and curb the CO₂ emissions through either direct injection into the grid distribution or storage, achieving deep decarbonisation (Yin et al., 2022). Despite the advantages of the CO₂ methanation over other conversion processes, for example higher selectivity and energy efficiency, as well lower cost (Sun et al., 2022), the TRL

is slightly lower compared to the MeOH production (Chauvy et al., 2019). Recently, numerous investigations were carried out towards FA production via CO₂ hydrogenation (Chatterjee et al., 2021). Formic acid gained a lot of consideration as an energy carrier based on the FA catalytic decomposition to produce H₂ and CO₂, with the possibility of converting back the CO₂ into FA, in the presence of H₂ (Verma et al., 2021). The European Green Deal strategy identifies great opportunities in lowering the industrial greenhouse gas emissions and generating sustainable products, strengthening the level of interest, over short to medium-term, towards the CCUS systems (European Commission, 2019). The present research is focused on the technical evaluation of green C₁ chemicals production in the framework of the CO₂ utilization topic. The key novelty aspects brought by the current study relate to the in-depth technical evaluation of the CO₂ conversion into added-value green C₁ chemicals through the CO₂ hydrogenation technology. The assessment methodology considers relevant evaluation tools such as modelling and simulation, validation, mass and energy integration, quantification of overall performances etc. The C₁ molecules selection was based on high industrial interest exhibited towards SNG and MeOH, as the first could be injected in the gas grid as a natural gas substitute, whereas the latter is an intermediate key component or may be used as a green fuel (Chauvy et al., 2019). Formic acid was considered based on its promising results obtained when used as a fuel in the direct formic acid fuel cells.

2. Plant configuration and models assumptions

The following cases were investigated in the current study:

Case 1: Green SNG production from renewable H₂ and CO₂ through the CO₂ hydrogenation process;

Case 2: Green formic acid production starting from electrolytic H₂ and CO₂ by means of CO₂ hydrogenation technology;

Case 3: Green methanol production using renewable H₂ and CO₂ through the CO₂ hydrogenation technology.

As presented before, Cases 1-3 convert the captured CO₂ and renewable H₂ through the CO₂ hydrogenation technology into valuable chemicals. The CO₂ reach stream is considered as being acquired from a CCS system coming from a carbon intensive process such as cement, iron and steel or ammonia production. Hydrogen is typically produced starting from fossil fuels, mostly natural gas, through the steam methane reforming process. However, to achieve the environmental targets set by various regulations, to approach near-zero CO₂ emissions, alternative processes such as biomass gasification or water electrolysis have to be considered (Pérez-Fortes et al., 2016). The current research assumed H₂ production through water electrolysis. The employment of RES as for example photovoltaics, wind or hydropower is of high importance in order to achieve a proper environmental performance. The process flow diagrams for the above-described processes are further presented in Figures 1-3. Figure 1 depicts the CO₂ methanation process. Peng-Robinson was chosen as thermodynamic package due to the employment of light hydrocarbons. The raw-materials, captured CO₂ and electrolytic H₂, are brought to the working conditions. The feed-streams are compressed in a single-step compression unit to 10 bar, after which being preheated to 350 °C before entering the first reactor. The reaction section consists of four adiabatic reactors to maximize the CO₂ conversion. The reactions occurring in the CO₂ methanation process are:

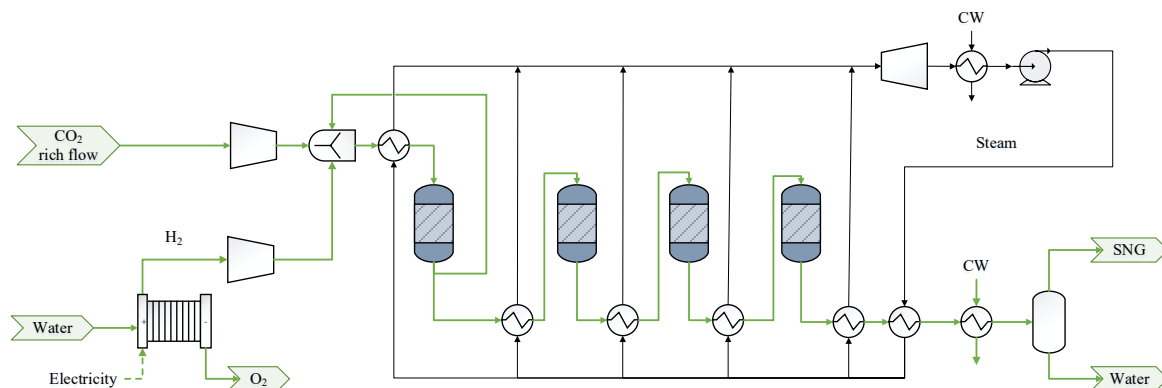


Figure 1: Process flow diagram for the SNG production by means of the CO₂ methanation process

The outlet of the first reactor is divided into two streams, the first one is recycled to the reactor inlet to keep the temperature below 650 °C and avoid catalyst deactivation. To achieve high CO₂ yield, the reaction mixture of each unit is fed to a heat exchanger to cool down the temperature to 350 °C. The outlet of the fourth reactor is cooled down to 25 °C, condensing and removing the water vapour from the main product to obtain the desired outlet specifications. Process' configuration and operational parameters was such established to prevent the formation of CO and carbon deposition.

Figure 2 illustrates the FA production through the CO₂ hydrogenation technology. Based on the operational conditions (i.e., high pressures) and employed chemical compounds, Predictive Soave-Redlich-Kwong (PSRK) thermodynamic model was used. As observed, the process can be divided into three different sections. To assume the worst possible case, it is presumed that the CO₂ reach flow enters the system at both ambient temperature and pressure, for this reason the CO₂ stream follows a compression stage with intermediate cooling to reach the reaction conditions. Hydrogen is produced through electrolysis. Besides the H₂ stream obtained at high pressure, oxygen (O₂) is also produced and may be further used within other sections or processes. Even if H₂ comes at a high pressure, 30 bar, a further compression with intermediate cooling is needed to achieve the reaction conditions. Formic acid is produced through CO₂ hydrogenation at 123 °C and 60 bar. The reaction occurring in the hydrogenation reactor is as follow:



Further, a flash unit is used to separate the FA from the CO₂ and H₂ mixture, considering a 95 % efficiency and recycling the gaseous phase at the inlet of the reactor.

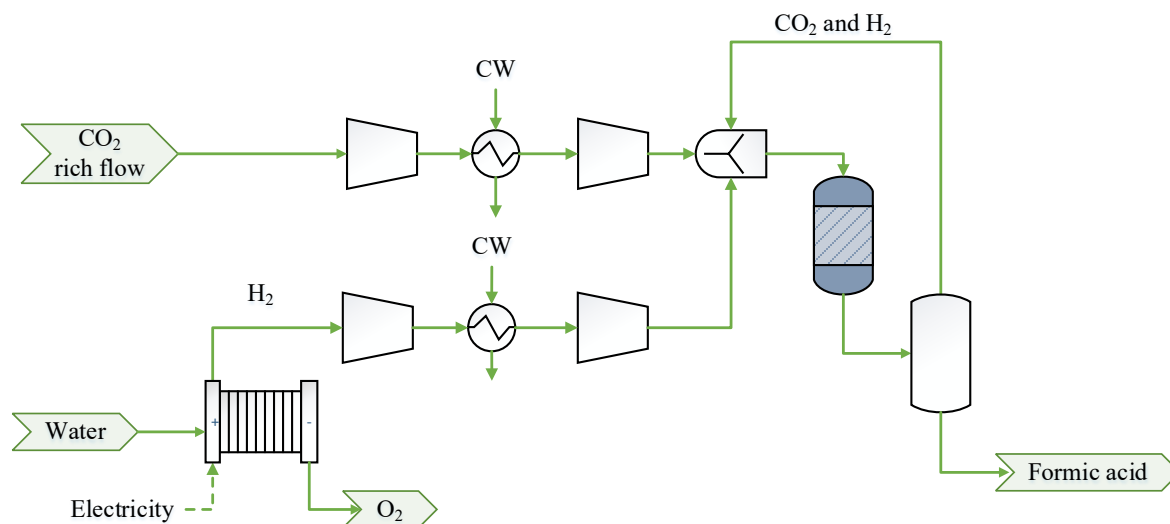


Figure 2: Process flow diagram for the FA production by means of the CO₂ hydrogenation process

The process flow diagram for MeOH production starting from CO₂ and green H₂ as raw-materials is shown in Figure 3. The Universal Functional Group Activity Coefficient (UNIFAC) was chosen as thermodynamic model for the MeOH production process, based on the involved chemical substances and operating conditions. As in the previously presented cases, both CO₂ and H₂ feed-streams are compressed up to 78 bar in a four-stage, and one-stage compression unit to reach the working pressure. The compression section is performed with intermediate cooling by using cooling water (CW) at 15 °C. After being compressed, the raw materials are mixed with a recycle stream, fed to a heat exchanger where the mixture is preheated to reach the reaction temperature, 210 °C and further sent to the reactor. The reactor is modelled as a plug flow reactor with the following two main reactions taking place, R5 and R6.



The reaction mixture is used to perform heat integration, a fraction of the reactor outlet preheats the reactor inlet, while the rest is used to preheat the column feed. The reaction mixture is sent to a heat exchanger to lower the temperature to around 30 °C, followed by a gas-liquid separation to almost completely remove the gaseous

phase from the water-MeOH mixture. A distillation column is used to separate the water from the liquid MeOH, obtained at the top of the column with a purity higher than 99 %.

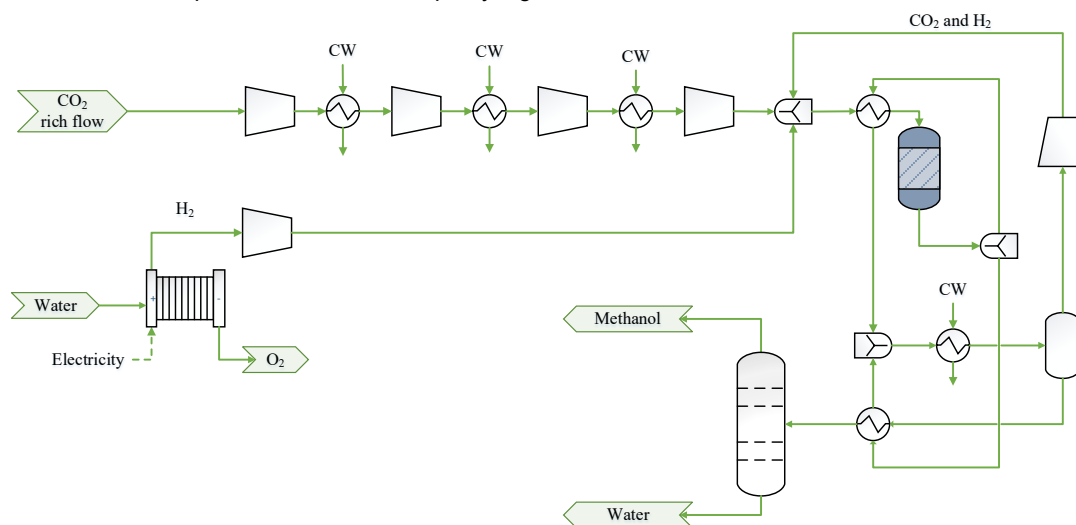


Figure 3: Process flow diagram for MeOH production through CO₂ hydrogenation technology

The main assumptions considered in the process modelling section performed within the current study are summarized in Table 1.

Table 1: Main design assumptions for the considered case studies

Case name	Process modelling and simulation design assumptions
Case 1	Raw-materials: CO ₂ , H ₂ , water; Main product: SNG; Thermodynamic package used: PENG-ROBINSON; Reactor: Number: 4; Adiabatic thermal mode; Inlet temperature: 350 °C; Pressure: 10 bar; 52 % CO ₂ conversion rate per reactor; Cooling water temperature: 15 °C; Heat exchanger: $\Delta T_{\min.}$: 10 °C; Pressure drop: 2-5 %; Pump: 85 % efficiency;
Case 2	Raw-materials: CO ₂ , H ₂ , water; Main product: FA; Thermodynamic package used: PSRK; Reactor: Isothermal mode: 123 °C; Pressure: 60 bar; 19 % CO ₂ conversion rate per reactor; Flash separator; Top product pressure: 15 bar; Bottom product temperature: 180 °C; Cooling water temperature: 15 °C; Heat exchanger: $\Delta T_{\min.}$: 10 °C; Pressure drop: 2-5 %; Pump: 85 % efficiency;
Case 3	Raw-materials: CO ₂ , H ₂ , air and water; Main product: MeOH; Thermodynamic package used: UNIFAC; Reactor: Isothermal mode: 215 °C; Pressure: 78 bar; 22 % CO ₂ conversion rate per reactor; Distillation column: 58 stages; Reflux ratio: 1.2; Bottom component recovery: 0.25 % MeOH; Cooling water temperature: 15 °C; Heat exchanger: $\Delta T_{\min.}$: 10 °C; Pressure drop: 2-5 %; Pump: 85 % efficiency;

3. Results and discussion

The evaluated scenarios include water electrolysis, to obtain the required amount of H₂, together with the CO₂ conversion processes through the CO₂ hydrogenation technology. A program built in MATLAB software was used to perform the simulation for the water electrolysis process. The results were validated based on the research published by Bolat and Thiel (2014). The CO₂ conversion processes were performed using ChemCAD, version 7, and Aspen Plus process simulation software, version 11. The CO₂ methanation process was performed as according to the study made by Chauvy et al. (2021). The results for the CO₂-to-SNG production process are in line with those obtained in the scientific literature, being further scaled up to the desired productivity. The results for the FA production process were validated based on the study performed by Mardini and Bicer (2021). The results for the MeOH production process are in good agreement with those obtained by

Pérez-Fortes et al. (2016). The mass and energy balance data acquired from the process modelling and simulation section were then used to estimate the key performance indicators shown in Table 2.

Table 2: Technical key performance indicators for the evaluated scenarios

Parameter	Units	Case 1	Case 2	Case 3
Water flowrate	kg/t	4,860.00	2,132.28	2,030.64
H ₂ flowrate	kg/t	540.00	236.92	225.63
O ₂ flowrate	kg/t	4,320.00	1,895.36	1,805.01
CO ₂ flowrate	kg/t	2,903.75	5,172.87	1,650.90
CO ₂ conversion per process	%	94.51	95.23	93.38
Energy consumption	MW _e /t	33.42	16.32	15.07
Product rate	kg/h	1,000.00	1,000.00	1,000.00
Main product purity	wt. %	82.69	98.61	99.96

As can be noticed from Table 2, the results are expressed as specific consumptions per 1 t of product to allow an easier comparison between the alternative cases, even though the annual production is different depending on the conversion scenario. By comparing the amount of raw materials used to produce 1 t of desired product, it can be observed that a higher amount of H₂ (e.g., 540.00 kg/h) is required in the first scenario, SNG production. Similar values are needed for the FA production (e.g., 236.92 kg/h) and MeOH production processes (e.g., 225.63 kg/h). As considering that water electrolysis is employed for H₂ generation, the highest amount of water is required in Case 1 (e.g., 4,860.00 kg/h) since the H₂ flowrate is at least 2.3 times higher in Case 1 as compared to Case 2 (i.e., FA production) and Case 3 (i.e., MeOH production). Oxygen is released as a by-product of the electrolysis process. The high quantities released in Case 1 might be seen as an advantage over the other conversion scenarios when considering either a technical perspective (O₂ is ready to be used within other section of the process) or economic point of view (the amount of O₂ produced can be sold as a by-product). The amount of CO₂ needed could be brought from a CCS system integrated within a carbon intensive process as for example cement, iron and steel, or ammonia industry. The highest quantity of CO₂ is needed for the FA production process, Case 2, 5,172.87 kg/h, which also relates to the lowest CO₂ conversion rate per reactor, 19 %. As in contrast to Case 2, an approximately 1.8 times lower CO₂ flowrate is required in Case 1 (e.g., 2,903.75 kg/h) and a roughly 3 times lower value for the MeOH production process (e.g., 1,650.90 kg/h). The highest CO₂ conversion rate per reactor is achieved in Case 1, around 52 %, being followed by the CO₂-to-MeOH process with 22 %. However, as presented in Table 2, each hydrogenation scenario displays CO₂ conversion rate higher than 90 % (for the whole process). The energy requirements are strongly related to the amount of H₂ used due to the fact that H₂ is produced through water electrolysis process. As shown in Table 2, the largest energy consumption is registered in Case 1 (e.g., 33.42 MW_e), which, as already mentioned, requires the highest quantities of H₂. In comparison with Case 1, FA production process (i.e., Case 2) demands a 2 times lower amount of energy per 1 t of product (e.g., 16.32 MW_e), while a 2.2 times lower value (e.g., 15.07 MW_e) is needed for MeOH production. The highest purity is achieved in the CO₂-to-MeOH scenario, 99.96 wt. % purity, followed by the FA production with 98.61 wt. %, and 82.69 wt. % achieved in the SNG case.

4. Conclusions

The atmospheric CO₂ concentration have reached its highest levels in history. The current study evaluates the CO₂ conversion and valorisation through the CO₂ hydrogenation technology to produce green C₁ valuable chemicals as for example SNG, FA, and MeOH. The technical results show that the CO₂-to-MeOH process requires the lowest amount of raw materials, CO₂ and H₂, whilst leading to the highest purity for the main product (e.g., 99.96 wt. %). In terms of purities, the second highest is achieved in the CO₂ hydrogenation to FA production, whilst SNG production records the lowest, 82.69 wt. %. The much-needed H₂ is produced through water electrolysis. The energy consumption is strongly related to the H₂ flowrate. Carbon dioxide to SNG presents the highest energy requirements among the three conversion scenarios, followed by the FA, and MeOH production process. Consequently, as the technical results suggest, the CO₂-to-MeOH conversion scenario represents the best alternative in regard to the CO₂ utilization technologies, that being validated by the high TRL, the process slowly approaching a commercial scale.

Nomenclature

CCUS – Carbon Capture Utilization and Storage

SNG – Substitute Natural Gas

CCU – Carbon Capture and Utilization

TRL – Technology Readiness Level
 RES – Renewable Electric Sources
 PtG – Power-to-Gas
 MeOH – Methanol
 FA – Formic acid
 CW – Cooling water
 PSRK – Predictive Soave-Redlich-Kwong equation of Gmehling
 UNIFAC – Universal Functional Group Activity Coefficient

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