

Feasibility assessment of small-scale methanol production via power-to-X

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ARTICLE INFO

Handling Editor: Kathleen Aviso

Keywords:

Power-to-methanol
Methanol synthesis
Techno-economic analysis
Renewable energy
Small-scale energy storage

ABSTRACT

Decentralized methanol production in the context of energy storage (also called power-to-methanol or PtMeOH) requires the development of new process configurations. This is due to the need to avoid energy-intensive compression stages and to adapt to intermittent H₂ availability. This study aimed at the determination of the techno-economic feasibility of new small-scale PtMeOH process configurations. It was proposed that, in small scale, the pressure should be limited to 30 bar, the standard H₂ delivery pressure of an electrolyzer. This is due to the cost and complexity of a H₂ compressor, unsuitable for small-scale systems. As CO₂ conversion is limited under these conditions, several configurations differing in the valorization strategy of the unreacted stream were assessed. Additionally, the possible coupling with other processes (e.g., biogas upgrading) was considered. It was found that it was not possible to obtain a profit in the production of methanol from renewable H₂ in any configuration at high electricity prices due to the important impact of H₂ cost. The highest electricity price allowing profitable operation was 0.07 USD/kWh for the recycling process. If PtMeOH is coupled with biogas upgrading, the process can also be operated in the cascade configuration with a similar economic performance. Hence, the small-scale PtMeOH process is feasible only under very specific conditions: constant low electricity price or coupled with waste-handling facilities. This study determined the set of parameters with which the PtMeOH process can be economically profitable, highlighting under which conditions cleaner methanol production can be envisaged in the near future.

1. Introduction

Methanol is an important platform molecule to produce several value-added chemicals, such as formaldehyde, acetic acid and dimethyl ether (DME). Methanol can also be used as fuel in combustion engines, in fuel cells or it can be blended with gasoline (Zhong et al., 2020). These important properties of methanol have raised the interest of several researchers towards the development of a 'methanol economy', where renewable methanol plays a key role in the chemical and energy systems (Faber and Paolucci, 2014). However, the advancement of this scenario requires a radical modification of the current methanol production chain, from fossil-based resources to cleaner processes (Rihko-Struckmann et al., 2010). Currently, methanol is produced mainly from natural gas in a three-step process, comprising methane reforming to produce syngas, methanol synthesis from syngas and methanol upgrading to the desired purity (Bozzano and Manenti, 2016). The substitution of this standard process with a renewable energy-based route presents several challenges, linked to the different supply chain of the feedstock and to the altered possibilities of process integration.

This latest point is an important challenge that still needs to be addressed by researchers.

1.1. Studies available on the power-to-methanol process

Several experimental studies showed that, over the industrially-employed Cu/ZnO/Al₂O₃ catalyst, methanol synthesis proceeds from both CO and from CO₂ in the presence of H₂ (Slotboom et al., 2020), even though high pressure is needed (Bansode and Urakawa, 2014). Therefore, a cleaner process to produce methanol from CO₂ and renewable H₂ seems feasible, and it was the object of several studies over the last few years. Pérez-fortes et al. (2016) performed a first techno-economic assessment of the large-scale methanol synthesis from captured CO₂, concluding that an important carbon tax would be needed to make this production route economically feasible. Atsonios et al. (2016) determined the influence of electrolysis costs in the large-scale power-to-methanol (PtMeOH) process and found that electrolyzer capital cost, electricity cost and storage cost play a key role in the economic feasibility of the process. Rivera-Tinoco et al. (2016) assessed the economic performance of a methanol synthesis plant from CO₂ and

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<https://doi.org/10.1016/j.jclepro.2022.132071>

Received 11 March 2021; Received in revised form 24 April 2022; Accepted 29 April 2022

Available online 4 May 2022

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Nomenclature*Abbreviations*

AEL	Alkaline Electrolyser
CAPEX	Capital Expenditures
CEPCI	Chemical Engineering Plant Cost Index
MeOH	Methanol
OPEX	Operative Expenditures
PtG	Power to Gas
PtMeOH	Power to Methanol
PtX	Power to X
RWGS	Reverse Water Gas Shift Reaction
SNG	Synthetic Natural Gas
STY	Space Time Yield
USD	US Dollars

Uppercase letters

C_{BM}	Bare Module Cost (\$)
$C_{BM, today}$	Current Bare Module Cost (\$)
C_i	Concentration of the component i (mol/m ³)
C_p	Equipment Purchase Cost (\$)
D	diffusion coefficient (m/s)
F	Stoichiometric Factor (H ₂ :CO ₂)
F_C	Cost Factor

F_e	Exchange Rate
F_M	Material Factor
F_P	Pressure factor
Re	Reynolds number
S_p	surface area of the catalyst particle (m ²)
U_T	global heat transfer coefficient (W/K/m ²)
X_i	Conversion of the component i
V_p	volume of the catalyst particle (m ³)
Y_i	Yield of the component i

Lowercase letters

a	Plant Lifetime (years)
d	reactor diameter (m)
i	Interest Rate (%)
k_i	local heat transfer coefficient (W/K/m ²)
n	order of reaction
r	reactor radius (m)

Greek letters

η	efficiency factor
ν_i	stoichiometric coefficient of the component i
ρ_i	density of the component i (kg/m ³)
φ	Thiele modulus
ΔH^R	reaction enthalpy (kJ/mol)

renewable electricity with a productivity of more than 5 metric tons of methanol per hour, showing that the production costs represent 2.5–15 times the current market price for methanol. Several studies focused on the assessment of the integration of PtMeOH and large CO₂-emitting plants, such as biomass-to-energy (Kourkoupas et al., 2016) and enhanced gas recovery plants (Luu et al., 2016). Two studies from the research group of Massardo, assessed the feasibility of PtMeOH from various renewable resources (Rivarolo et al., 2016) and from captured CO₂ (Bellotti et al., 2017). The interest in this topic is confirmed by two methanol production plants from CO₂ that have been recently installed in Iceland (by Carbon Recycling International, producing up to 10 t/d of methanol; Bowker, 2019) and in Germany (in the carbon2chem project, producing 30 t/d of methanol; Wich et al., 2020).

1.2. Existing research gaps

All the above-mentioned studies focus on large-scale and continuous production plants. However, the main renewable energy resources (e.g., wind, solar and to some extent run of river hydropower) are stochastic by nature, which means that their energetic output is subject to large temporal and geographic oscillations. These energy sources may be widely distributed in a territory and provide limited energy supply over restricted periods. Therefore, it is forecastable that many PtMeOH plants to be installed in the future will need to adapt to a limited H₂ supply. The use of point-source CO₂ is also a limiting factor for the scale of a methanol plant, as the carbon supply is dependent on the size of the CO₂-emitter plant. For all these reasons, the available studies are not sufficient to assess possible future decentralized PtMeOH processes that convert the locally available excess renewable energy into an easy-to-store energy carrier (i.e., methanol).

The scope of this study was the determination of the most suitable CO₂-to-methanol process configuration to utilize localized and intermittent H₂ sources. Hence, the main point distinguishing the study from the existing body of literature is the design of a small-scale process operating at low pressure. The need for low pressure stems from the significant difference in the boundary conditions between a PtMeOH and a classical methanol synthesis plant. Important process integration between methane reforming and methanol synthesis is not available.

This process integration is fostered by the presence of a large amount of waste heat from the reforming, which allows the production of steam to be expanded in a turbine, thus providing the required energy to the compressor (Bozzano and Manenti, 2016). Hence, in the PtMeOH process, this compression can only be performed by using external electricity, causing a decrease of the process performance. For this reason, plants operating PtMeOH through standard methanol synthesis technologies can be profitable only if supported by a low electricity price. For the same reason, the knowledge developed in PtMeOH coupled with biomass or coal gasification is not significant in the PtMeOH from CO₂, since the high temperature available in the gasifier significantly improves the possibilities of process integration (see, e.g., Zhang et al. (2020) for this process integration).

1.3. Scope and novelty of this study

The assessment of localized PtMeOH plants hence requires a completely different approach, identifying the best solutions to produce methanol at low pressure. In this paper, the process pressure was limited to 30 bar, which is the typical H₂ discharge pressure of an electrolyzer (de Vasconcelos and Lavoie, 2019). This raises important process challenges, as at this pressure the reaction is characterized by stringent thermodynamic limitations, limiting the CO₂ conversion (Jiang et al., 2020). For this reason, this study assesses the possible process configurations to overcome this limitation (i.e., recycling of the unreacted gas or further processing in a cascade configuration), with special focus on the profitability of these process options. This investigation has the benefit of underlining the possible bottlenecks that should be eliminated in further technological development. The special focus on small-scale applications using CO₂ as carbon source differentiates this study from the techno-economic analyses available in literature. This study elucidates for the first time the economic potential of a hybrid PtMeOH/PtG system (i.e., coupling methanol synthesis and biogas upgrading) thus realizing an important improvement in the economic performance of the integrated system. This approach is significantly different from the existing biogas-to-methanol processes, which are based on biogas steam reforming followed by a standard methanol synthesis from syngas starting from e.g., landfill gas (Gao et al., 2020), refuse-derived fuel

(Borgogna et al., 2019) or agricultural waste (Santos et al., 2018). A comparison of the conditions considered in this work with studies existing in the literature is provided in Table 1. It can be observed that the methanol production scheme considered here differs significantly from the studies available in the literature in terms of plant size and operating pressure of the methanol reactor.

According to the assumptions related to small-scale PtMeOH, the cost of the methanol produced in a simple cascade reactor configuration was first assessed, where intermediate condensation steps separate several reactors. Based on the first results, two different configurations to reuse the remaining H_2 were analyzed. The former involves recycling of the unreacted H_2 , while the latter is based on the utilization of the remaining H_2 in a Sabatier reactor for the co-production of CH_4 , which is less subject to thermodynamic limitations (Moioli et al., 2020). This latter configuration is of particular importance in the case of a biogas plant, where the main facilities for the post-treatment of biomethane are already present. From this analysis, it was possible to determine under which conditions the various processes become profitable and suggest technical solutions for the successful integration of PtMeOH in the context of the utilization of biogenic CO_2 or in coupling with anaerobic digestion plants.

2. Methodology

The objective of this study is to verify the economic feasibility of methanol production from localized small-scale renewable energy and CO_2 sources. This specific focus brings several limitations, which must be considered while defining the process scheme for analysis. The main limitations linked to the small-scale assumption are:

- The plant is operated in correspondence with localized biogenic CO_2 emission. Due to this, the availability of renewable electricity is limited, thus not allowing the installation of several energy-consuming compressors. Hence, the maximum pressure of the process is limited to 30 bar (i.e., the typical downstream pressure of an electrolyzer).

Table 1

Comparison of the conditions investigated in this study with the studies available in the literature.

Reference	Carbon source	H_2 source	Synthesis pressure (bar)	MeOH productivity (t/d)
(Pérez-fortes et al., 2016)	CO_2 (from point-source capture)	Pipeline	78	1320
Atsonios et al. (2016)	CO_2 (industrially captured)	Electrolysis	65	320
Rivera-Tinoco et al. (2016)	CO_2	Electrolysis	78	200
Kourkoupas et al. (2016)	CO_2 (from lignite plant)	Electrolysis	70	190
Rivarolo et al. (2016)	CO_2 (purchased)	Electrolysis	80	46
Bellotti et al. (2017)	CO_2 (captured)	Electrolysis	80	10–130
Wich et al. (2020)	Blast furnace gas	Electrolysis	80	30
Borgogna et al. (2019)	Refuse-derived fuel	Reforming	52	100
Gao et al. (2020)	Landfill gas	Reforming	50	360
Santos et al. (2018)	Agricultural waste/biogas	Reforming	50	5
This work	CO_2 (captured)/biogas	Electrolysis	30	4

- No external heat is available for the plant; hence, the possibility of process integration is limited.
- The costs for separation of MeOH from water are not considered due to a central work-up.
- Facilities to handle natural gas are present; hence, biomethane can be co-produced and sold.

The economic feasibility of the process is assessed in terms of annualized income from the operation of the PtMeOH plant with a lifetime of 15 years. It was assumed that the renewable products can be placed on the market at a preferential rate, corresponding to about four times the current market price of fossil-based products. This is confirmed by the current conditions of the reference market for biomethane (i.e., Switzerland; *Energie360*, 2021). The selling prices considered are reported in Table 2.

The economic performance of various options to valorize the output gas from the methanol synthesis section is calculated. First, the results of the simulation of operating a CO_2 -to-methanol reactor are presented. These results are necessary to understand the context of the study and to underline the main process challenges. Second, the economic performance of a simple power-to-methanol process is determined. Third, the recycle process is analyzed. Fourth, the effect of adding a CO_2 methanation reactor to valorize the unreacted gas after methanol synthesis is assessed. The structure of the study is summarized in Table 3.

2.1. Process simulation

The processes considered were modelled by solving in MATLAB (via the function *ode15s*) the canonical mass and heat balance for the desired components (CO_2 , CO , H_2 , H_2O , CH_4 and CH_3OH) in the differential form (1D pseudo-homogenous reactor model):

$$\frac{d(uc_i)}{dz} = \nu_i \eta \rho_b r \quad (1)$$

$$(u \rho_b c_{tot}) \frac{dT}{dz} = \nu_i \eta \rho_b r (-\Delta H_R) + \frac{4}{d_{tube}} U_T (T - T_e) \quad (2)$$

where ρ_b refers to the density of the catalyst bulk. The catalyst efficiency factor is calculated via the Thiele modulus:

$$\varphi = V_p / S_p \sqrt{\frac{(n+1)}{2} \left(\frac{k_c c_{i,s}^{n-1}}{D} \right)} \quad (3)$$

$$\eta = \frac{3}{\varphi^2} (\varphi \cdot \coth(\varphi) - 1) \quad (4)$$

The heat transfer coefficient is calculated as follows:

$$\frac{1}{U_A} = \frac{1}{k_i} + \frac{k_c}{\ln\left(\frac{r}{r_e}\right)} + \frac{1}{k_e} \quad (5)$$

k is calculated considering a stagnant and a dynamic contribution (Tsotsas, 2018):

$$k = k_0 + 0.024 \cdot \frac{(l \cdot Re)}{d_p} \quad (6)$$

For the explanation of symbols, please refer to the list of symbols in the Appendix. With the model above, it is possible to determine the axial

Table 2

Selling prices for the products.

Component	Value (USD/kWh)
CH_4	0.12
MeOH	0.20

Table 3

Summary of the processes modelled in this study (F is the H₂/CO₂ stoichiometric ratio; the stages refer to each reaction step, composed of reaction and separation of the products by condensation).

Case	Name	Pressure (bar)	F (–)	Number of stages (–)	Subcases
1	Cascade PtMeOH	20, 30	3, 5, 7	1 to 10	Without H ₂ valorization With H ₂ valorization None
2	Recycling PtMeOH	30	3, 5, 7	1 to 10	
3	Hybrid PtMeOH/PtG	30	3, 5, 7	1 to 10	Process from CO ₂ Process from biogas

concentration and temperature profiles in the cooled multi-tubular fixed-bed reactor. The tube diameter is 2 cm and the kinetic model used for the methanol synthesis is the Langmuir–Hinshelwood–Hougen–Watson model from [Vanden Bussche and Froment \(1996\)](#), simulating a commercial Cu/ZnO/Al₂O₃ catalyst. The kinetic model is in the form:

$$r_{MeOH} = \frac{k_{MeOH} \cdot P_{CO_2} P_{H_2} \cdot \left(1 - \frac{1}{K_{eq}} (P_{H_2O} P_{MeOH})\right)}{\left(1 + \frac{K_{H_2O}}{K_{H_2}} \frac{P_{H_2O}}{P_{H_2}} + \sqrt{K_{H_2} P_{H_2}} + K_{H_2O} P_{H_2O}\right)^3} \quad (7)$$

This kinetic model has been validated in several industrially relevant conditions ([Slotboom et al., 2020](#)) and the reactors modelled here lie within the validated parameter range. For the fixed-bed Sabatier reactor, the catalyst considered is Ni/Al₂O₃ and the model from Koschany et al. is used ([Koschany et al., 2016](#)). This model is in the form:

$$r_{Sab} = \frac{k_{Sab} \cdot P_{CO_2}^{0.5} P_{H_2}^{0.5} \cdot \left(1 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eq} P_{H_2}^2 P_{CH_4}}\right)}{\left(1 + K_{OH} \frac{P_{H_2O}}{P_{H_2}^{0.5}} + K_{H_2} P_{H_2} + K_{mix} P_{CO_2}\right)^2} \quad (8)$$

This model is also widely used in scientific practice and yields good results for simulations with the set of parameters considered here ([Fischer et al., 2019](#)). Both kinetic models used include kinetic and thermodynamic terms, hence allowing a complete description of the reactors over the entire parametric range considered. The reactors are modelled as externally cooled, with constant temperature of the cooling medium. The cooling temperature is adjusted to maximize the CO₂ conversion and the cooling medium is a thermal oil. The models are used to calculate the reactor volume needed and hence to calculate the reactor cost. The condensers are modelled as equilibrium stages reaching the target condensation temperature of 40 °C. The scale of the plant corresponds to a H₂ inlet of 360 Nm³/h. For the determination of the process performance the following indicators are used:

CO₂ conversion:

$$X_{CO_2} = \frac{CO_{2in} - CO_{2out}}{CO_{2in}} \quad (9)$$

Methanol yield (CO₂-based):

$$Y_{MeOH, CO_2} = \frac{MeOH_{out}}{CO_{2in}} \quad (10.1)$$

Methanol yield (H₂-based):

$$Y_{MeOH, H_2} = \frac{3 MeOH_{out}}{H_{2in}} \quad (10.2)$$

CH₄ yield:

$$Y_{CH_4} = \frac{CH_{4out}}{CO_{2in}} \quad (11)$$

The H₂/CO₂ ratio (F) is defined as:

$$F = \frac{H_{2in}}{CO_{2in}} \quad (12)$$

2.2. Cost estimation

The total costs for the process are accounted in terms of CAPEX (capital expenditure) and OPEX (operative expenditure). As this paper aimed at estimating the economic potential of methanol production in connection with small-scale CO₂ sources (such as biogas plants), only the essential process units were considered in the calculations. The process units considered for the calculation of CAPEX are:

- Reactors (size determined according to the rate-based model)
- Condensers
- Electrolyzer
- Compressor (for the recycling case only)

For the calculation of the OPEX, the following elements are considered:

- Electrical energy
- Biogas cost
- Maintenance and operation costs

Considering the scope of the work, no additional expenditures were considered (such as the cost of cooling water and waste disposal).

The process income is determined according to the selling price of the products methanol and methane. Due to the difficulties in small-scale handling, other possible incomes, such as the valorization of oxygen and waste heat, were not considered.

2.2.1. CAPEX

The CAPEX was calculated according to [Ulrich and Vasudevan \(2004\)](#). The total costs of the single pieces of equipment (bare module cost, C_{BM}) were calculated as a function of the type (C_p), material (F_M), volume and pressure (F_P), according to the formula:

$$C_{BM} = f(C_p, F_M, F_P) \quad (13)$$

The reactor volume was calculated based on the simulations. The bare module cost was determined using the volume, according to [Ulrich and Vasudevan \(2004\)](#). The bare modules costs for the base case (feed of 360 Nm³/h H₂ and stoichiometric H₂/CO₂ ratio) are reported in [Table 4](#). The reactor material was stainless steel in all cases.

The bare module costs were used as a basis for the calculation of the total installation costs, and the various cost elements required for installation and their incidence on the total costs are reported in [Table 5](#). The total equipment cost was then calculated as (F_C is the total cost factor):

$$C_{tot} = C_{BM} \cdot (1 + F_C) \quad (14)$$

The calculated costs were actualized to the current prices through the Chemical Engineering Plant Cost Index (CEPCI):

$$CEPCI = \frac{CEPCI (current)}{CEPCI (2004)} = 1.548 \quad (15)$$

Table 4

The bare module costs of the first reactor (values for a feed of 360 Nm³/h H₂ and H₂/CO₂ = 3:1).

	Pressure (bar)	Reactor cost (USD)	Condenser cost (USD)
C_{BM}	30	61,509	30,653
	20	51,441	29,662
	10	37,497	28,471

Table 5
Cost factors for the various components [32].

Element	Cost factors (in C_{BM})
Connections	0.4
Instrumentation	0.1
Electrical connections	0.2
Construction	0.13
Planning & permissions	0.3
Total (F_c)	1.13

The current CEPCI index was the value in January 2019.

According to the previously defined factors, it was possible to calculate the current total bare module cost:

$$C_{BM, today}(USD) = C_{BM} \cdot F_c \cdot CEPCI \cdot F_e \quad (16)$$

The bare module costs must be divided over the entire lifetime of the plant. To this end, the annualized investment cost ($C_{i,y}$) was calculated according to the values of Table 6 and the formula:

$$C_{i,y} = C_{BM, today} \cdot \frac{(1+i)^a \times i}{(1+i)^a - 1} \quad (17)$$

The investment costs for the electrolyzer (alkaline electrolyzer, AEL) were calculated as 1160 USD/kW_{el} (Witte et al., 2018a). The purchase of the electrolyzer was funded with a loan over the lifetime of the plant at an interest rate of 4%. When a compressor was present (recycling process), the CAPEX was calculated according to the nominal power required, following the method for centrifugal compressors elucidated in Ulrich and Vasudevan (2004). The power requirement of the compressor was calculated assuming an isentropic compression.

2.2.2. OPEX

The OPEX for the reactor-condenser system was estimated as 5% of the bare module costs (Gassner, 2010). The parameters for the estimation of OPEX for the electrolyzer are reported in Table 7. The electrolyzer provides a maximum of 360 Nm³/h of H₂, with an HHV-based efficiency of 77%. The CO₂ inlet flow was calculated according to the electrolyzer output. In this paper, the cost for CO₂ is neglected, as the process is supposed to be coupled to a plant producing CO₂ as a waste. When biogas is used as feedstock, the cost of biogas is accounted for at 0.06 USD/kWh (Witte et al., 2018a). This value should be interpreted as an opportunity cost, i.e., the price allocated to biogas in comparison to its possible alternative use in electricity production.

3. Results and discussion

As a first task, the technical performance of the CO₂-to-methanol reactor under various conditions was determined in terms of methanol yield. The model used allowed determining the kinetic and thermodynamic limitations with care, resulting in a detailed presentation of the reactor performance in the entire set of parameters considered. The reactor simulation results are shown in Fig. 1. The optimal working point was found at a temperature that considered kinetic and thermodynamic limitations: at low temperature, the catalyst is not sufficiently active to facilitate the reaction, while at high temperature conversion is limited by thermodynamics. Therefore, one can observe that the position of the maximum is shifted to higher temperature with increasing process pressure. At 30 bar (maximum pressure set for this study), the highest methanol yield at stoichiometric feed is ca. 15% at 225 °C. This

Table 6
Parameters for the division of the capital costs.

Element	Value
Interest rate i (%)	4
Lifetime a (y)	15

Table 7
Parameters of the electrolyzer.

Element	Value
Max. H ₂ production (Nm ³ /h)	360
Operation time (h/y)	4000
Electricity cost (USD/kWh)	0.08
Power (kW _{el})	1655
Efficiency (HHV-based)	0.77

is in line with that reported in the literature (Slotboom et al., 2020). Note that the CO₂ conversion allowed by thermodynamics is significantly lower than the corresponding value in the standard process from syngas (Zhong et al., 2020). The CO₂-based methanol yield can be improved by increasing the amount of H₂ present in the reaction mixture. In this case (shown in Fig. 1b) the kinetics are minimally affected, but the thermodynamic limitations are significantly shifted. Hence, at 30 bar, the maximum point is seen at 225 °C in all cases shown, but the MeOH yield is 23% at $F = 5$ and 26% at $F = 7$. The excess H₂ is thus positive for product formation, but it creates the problem of the effective utilization of the remaining H₂ after separation of the liquid products. This operation with a large excess of H₂ is used in industry to maximize the product yield by operating a large recycling stream (Bozzano and Manenti, 2016). However, this H₂ valorization strategy may be challenging on a small scale due to the large recompression blower required. Based on the process simulation results presented above, the profitability of various process configurations was determined, as described in the following sections.

3.1. Cascade process

The first process considered is the cascade process. In this configuration, as shown in Fig. 2, H₂ is produced in the electrolyzer and fed to the first reactor together with CO₂. No compression is needed for H₂, as the reactor operates at the same pressure as the outlet of the electrolyzer. The reactor outlet temperature is set as at the optimal temperature for the specified conditions (i.e., according to pressure and CO₂/H₂ ratio). The products are cooled to the condenser temperature where the liquid products, MeOH and H₂O, are separated from the gas stream. The resulting gas stream (composed of CO₂, CO and H₂) is fed to the subsequent reactive stage, where the reaction takes place again. The process is repeated for n stages. Note that this process is representative also of reactors with in-situ product removal, e.g., membrane reactors (Gallucci, 2018). The technical performance of the system at various CO₂/H₂ ratios and number of reactive stages is shown in Fig. 3. One can see that for the case with largest excess of H₂ (H₂/CO₂ = 1:7), the curve approaches full conversion of CO₂ to methanol after 10 reactive stages, while for the stoichiometric mixture the methanol yield reaches a maximum of 80%. The economic assessment depends on the H₂ valorization strategy. Therefore, the separate cases of process with and without specific H₂ valorization are reported separately in the following.

3.1.1. Cascade process without H₂ valorization

In the first assessment, the economic performance of the system was calculated without assigning a value to the unreacted hydrogen, as it is contaminated with CO₂. The results of this techno-economic analysis are shown in Fig. 4. The cascade process configuration does not result in profitability in any of the considered conditions at an electricity price of 0.08 USD/kWh. This is in line with that observed in the literature for small-scale CO₂-to-methanol processes (Baena-Moreno et al., 2020). As the operation uses an expensive reactant (i.e., H₂), the process configuration with excess H₂ has the highest costs compared to revenues. Initially, the increase in the number of reactor steps causes a decrease in the process losses. The curve increases until reaching a maximum, which is located, under the conditions of Fig. 4a, above 80% yield to methanol. The origin of this maximum is the existence of a maximum in the

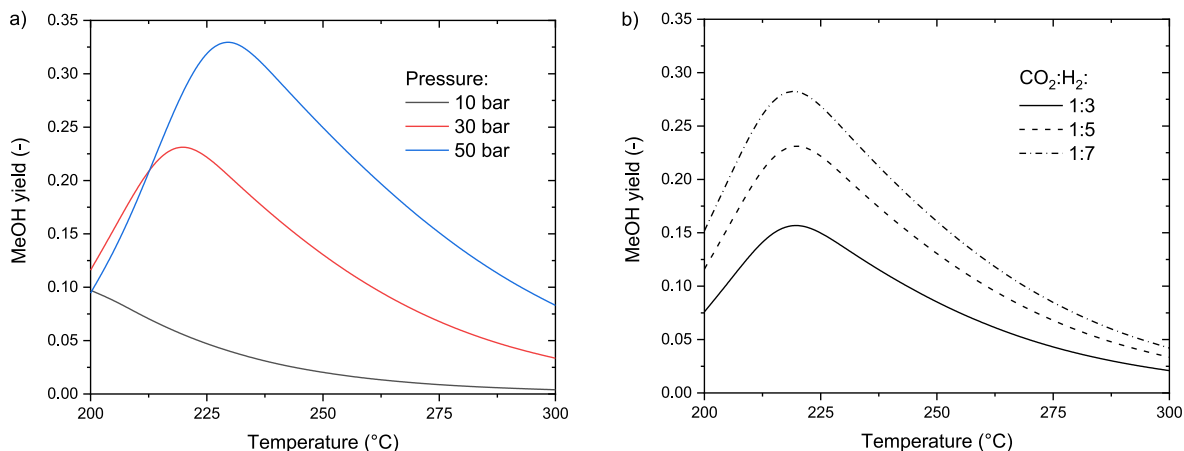


Fig. 1. Results of the process simulation: methanol yield as a function of a) reactor outlet temperature and pressure ($\text{CO}_2/\text{H}_2 = 1:5$) and b) temperature and CO_2/H_2 ratio ($P = 30$ bar).

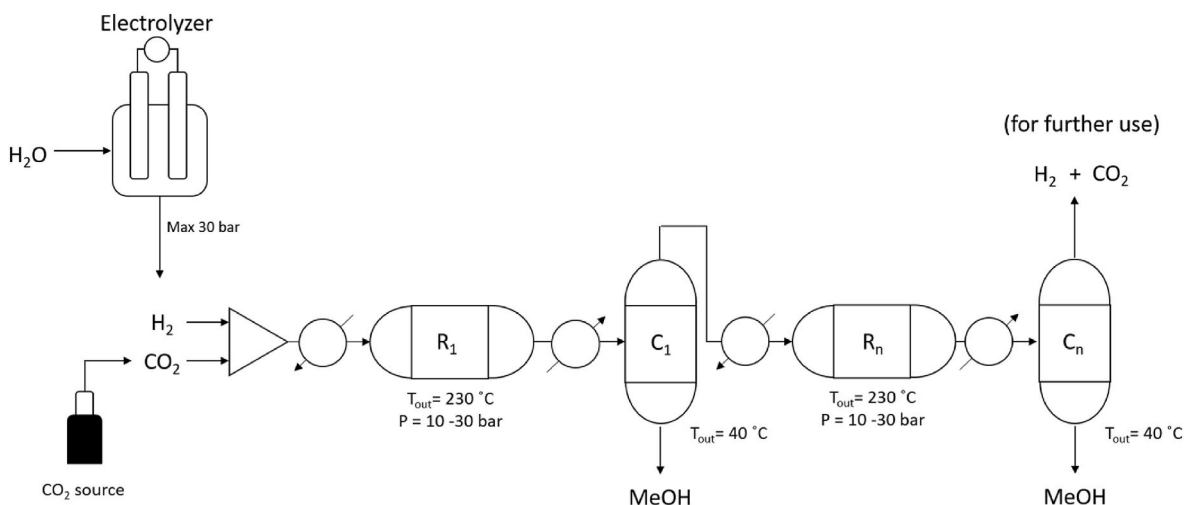


Fig. 2. Scheme of the cascade process: methanol synthesis is performed in several consecutive steps with intermediate condensation.

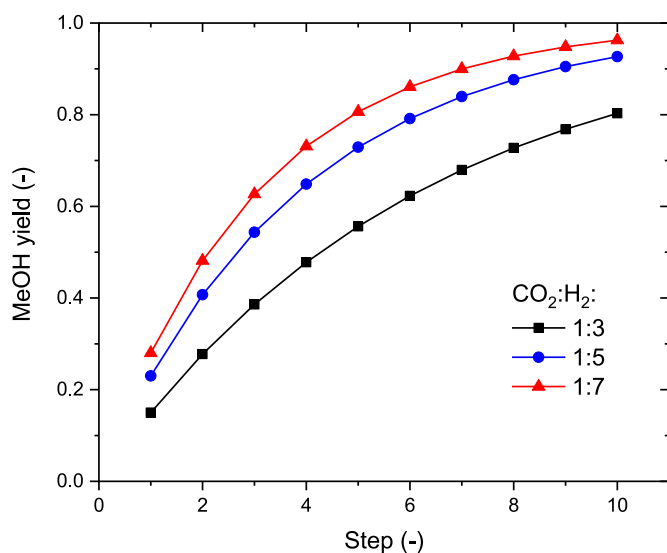


Fig. 3. The evolution in the total yield to methanol over the various reaction stages with different stoichiometric ratios ($P = 30$ bar, $T = 225$ °C).

space-time yield (STY) for this process type (Moioli et al., 2019). In the region above 80% yield, the increase in the number of stages causes an increase in the costs not compensated for by the higher amount of product formed. In fact, the investment cost increases linearly with the number of units while the increase in the total amount of product formed is less than linear. This maximum is clearly visible for the configurations with $F = 5$ and $F = 7$, where 80% methanol yield is reached after 7 and 5 steps, respectively. Furthermore, one can observe that at low conversion values (below 50%) the decrease in losses with the number of stages is higher for the configuration with lower yield per pass (i.e., $F = 3$). This is due to the lower amount of H_2 that is flared per unit of product in the $F = 3$ case compared to the configurations working with excess H_2 . To reach the break-even point at the best configuration of Fig. 4a ($F = 3$ and $Y_{\text{MeOH}} = 0.8$), the electricity price should be below 0.045 USD/kWh. The change in pressure (Fig. 4b) has a remarkable effect on the process profit, favoring the process at higher pressure. This is in line with that reported in the literature (Pérez-fortes et al., 2016). These elements suggest that the yield per pass is the key element in the determination of the process profit.

Further insights into the profitability improvement for the process are given by an analysis of the cost breakdown. Fig. 5 shows the distribution of the process costs for the process operated at 30 bar and with $F = 3$. To underline the trends, the extreme cases of 1 and 10 stages are displayed. The dominance of OPEX in the process is evident. In the case

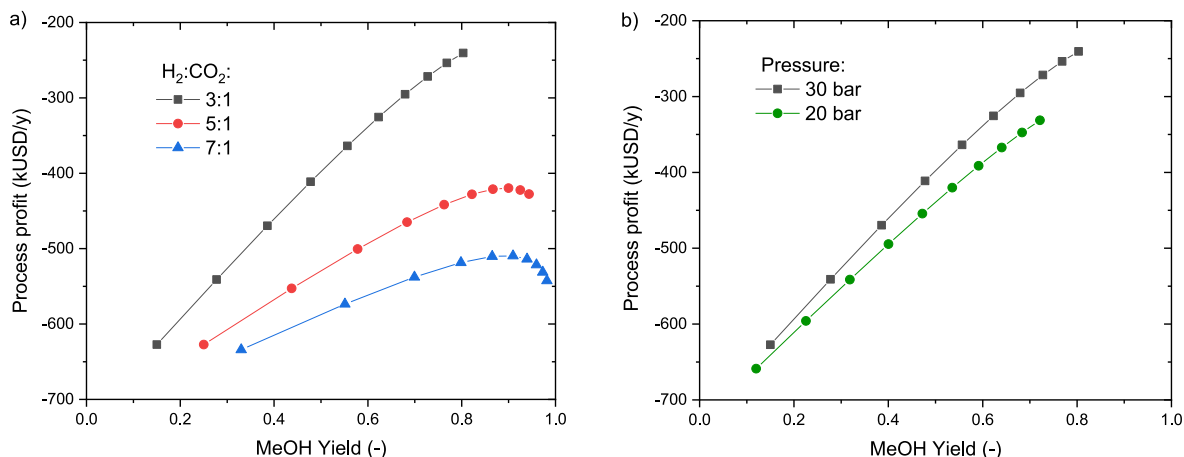


Fig. 4. Process profit (revenues minus costs) in the cascade methanol production calculated varying a) CO_2/H_2 ratio (at 30 bar and 225 °C) and b) pressure (at $H_2/CO_2 = 3:1$ and T = 225 °C).

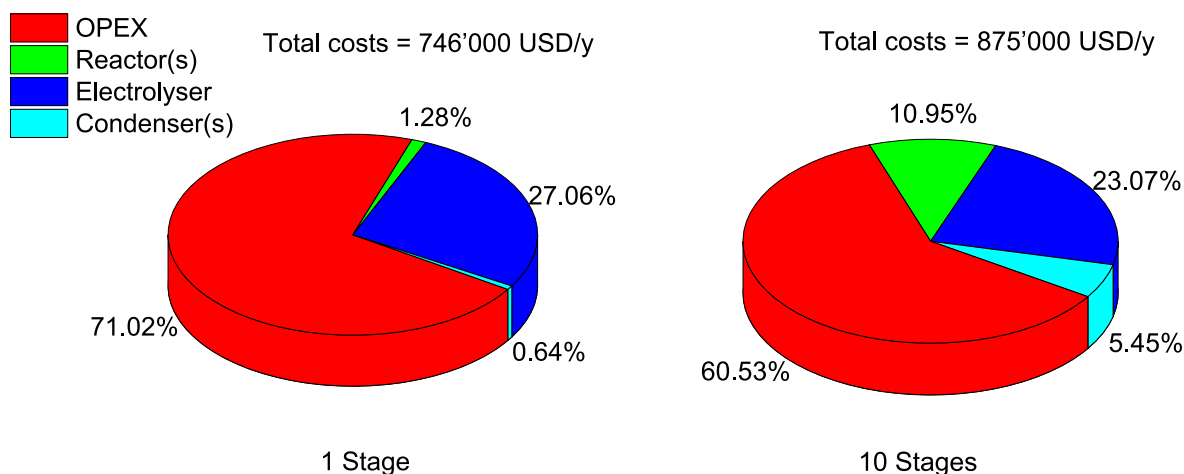


Fig. 5. Distribution of the costs for 1 and 10 stages ($CO_2/H_2 = 1:7$, P = 30 bar and T = 225 °C).

of a single stage, the OPEX account for 71% of the costs. The expenses for the electrolyzer dominate the CAPEX. For 10 stages, the share of CAPEX increases, but the OPEX still makes up 61% of the total expenditure. This picture is a key element in the understanding of the main limitations connected with the PtMeOH process on a small scale. The cost of methanol in this case is strongly influenced by the cost of the raw material, i.e., H_2 (Atsonios et al., 2016). This means that the methanol produced in this way shows economic figures typical of fine chemical production rather than commodity manufacturing. Therefore, the normal strategies for the technological improvement of methanol synthesis (e.g., suitable reactor design to reduce the CAPEX) in this case are not effective. On the contrary, the search for an optimized working point should follow determination of the optimal STY and of appropriate utilization of the remaining reactants. The whole process can become profitable only when H_2 can be fully converted into valuable product after the methanol section. For this reason, further process configurations to perform this operation were investigated.

3.1.2. Cascade process with H_2 valorization

Even though the valorization of the waste H_2 stream is challenging, it is important to assess the effects on the economic performance of allocating a selling price to the tail gas. This operation can be regarded as the search for candidate coproducts to be synthesized from the tail gas of methanol production. Two possible scenarios of selling price for the waste H_2 were investigated, considering the specific costs of production

of green H_2 . With the economic assumptions of this study, it is possible to determine the required price for the H_2 produced to cover the expenses of the PtMeOH system. The values used are reported in Table 7. In the first case, the price of was set to cover the cost of electricity (OPEX) for the production (OPEX-only case). The resulting price was 0.37 USD/ Nm^3 . In the second case, the CAPEX related to the purchase of the electrolyzer was also included in the price, thus resulting in a break-even value equal to 0.51 USD/ Nm^3 (OPEX + CAPEX case). The high product value required for the profitable operation of this type of PtMeOH plant confirms the need for significant incentives to keep these plants on the market, as discussed in the literature (Pérez-forbes et al., 2016). The calculated revenues for the cascade methanol process in the two cases are shown in Fig. 6. It is worth noting that in both cases the process costs are higher than the possible income from the products. As in the previous case, the lowest losses are observed for F = 3. This is due to the highest H_2 -based MeOH yield obtained in this process configuration, thus producing higher income from the products (as methanol is a more valuable product than H_2 according to the assumptions made).

In the OPEX-only case, for F = 3 one can see the presence of a maximum, which is absent for the other F-values. This is because of the STY effect, as explained previously. The absence of a maximum with F = 5 and F = 7 is instead due to the large amount of waste H_2 remaining in any configuration and ideally valorized at high price. Therefore, the maximum in the revenue function would be found at a methanol yield value below the minimum shown in Fig. 6a. On the other extreme of the

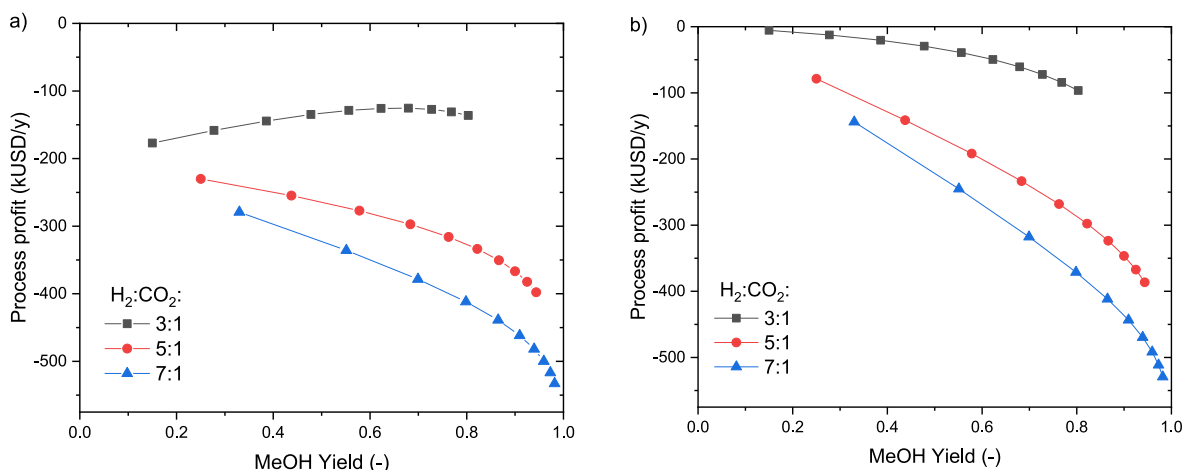


Fig. 6. a) Process profit (revenues minus costs) of the cascade system with an H₂ value of 0.37 USD/Nm³ (cost of electricity for H₂ production, OPEX case); and b) Process profit (revenues minus costs) of the cascade system with an H₂ value of 0.52 USD/Nm³ (break-even price of H₂ production via AEL, OPEX + CAPEX case). P = 30 bar, T = 225 °C.

figure, in analogy with Fig. 4a, one can see the fall in revenues when approaching the full yield to methanol, which is due to the low additional CO₂ conversion that is achieved in the final reactors, despite their large volume. In the CAPEX + OPEX case, the supposed H₂ value is high enough to allow the maximum to disappear even from the curve for F = 3. Here, the production of additional methanol is less profitable than selling the waste H₂; therefore, the increase in methanol yield corresponds to a decrease in the profitability of the process. Hence, in all the configurations the production of methanol is discouraged in comparison to the direct use of H₂.

From the observations in these sections, one can draw some initial conclusions to be considered in the development of a PtMeOH plant:

- The optimal configuration of the PtMeOH plant strongly depends on the valorization strategy adopted for the unconverted gases.
- When the waste gas has a low value (which is generally true, due to the presence of CO₂), the optimal configuration corresponds to the maximum STY of the methanol production. However, the process can be profitable only with a low electricity price (<0.045 USD/kWh).
- The pure PtMeOH is therefore economically feasible only in pure energy storage mode, i.e., the storage of cheap energy, if available.

- Another possibility to make the PtMeOH process economically feasible is the coupling of methanol production with another syngas-based process that can valorize the waste gas stream.

According to these considerations, in the next sections the most relevant ways to valorize the waste CO₂/H₂ stream from the methanol process will be analyzed.

3.2. Recycling process

The state-of-the-art solution for the utilization of unreacted H₂ involves the recycling of the gas to the reactor by recompression (Bozzano and Manenti, 2016). A schematic representation of the process is shown in Fig. 7. The process scheme is similar to the cascade process, with the difference of the recompression and recycling of the unreacted gas. In this case, additional CAPEX and OPEX are related to the purchase and operation of the recompression blower. A purge stream is necessary to avoid accumulation of H₂ in the configurations operating with over-stoichiometric H₂ concentrations. The economic performance of this process was calculated to understand how this specific configuration fits into the PtMeOH process at a small scale. In the technical evaluation of the process, the methanol yield was set to 98% and the required recycle ratio to achieve this goal calculated. The 98% yield value was

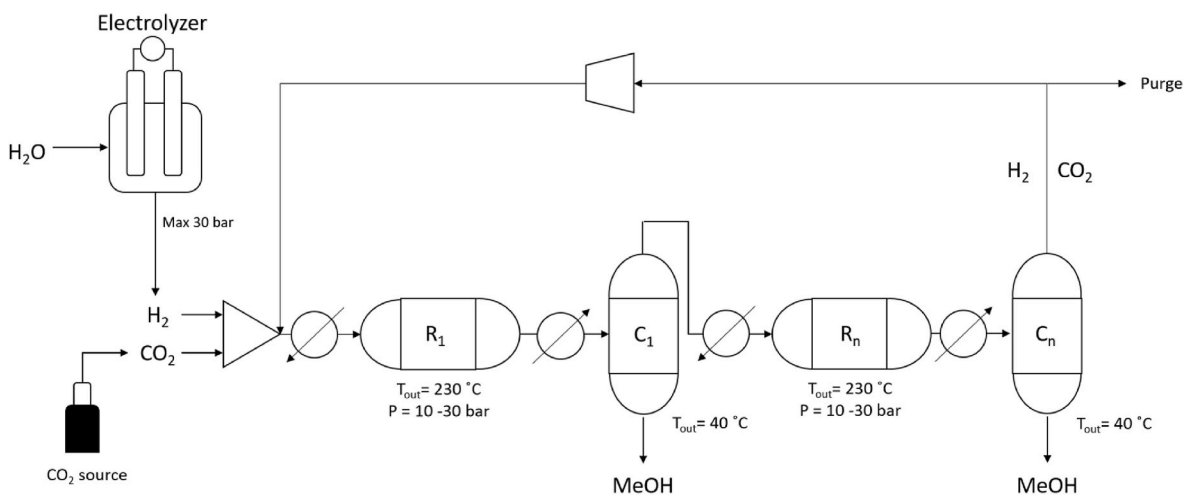


Fig. 7. Scheme of the recycling process: methanol synthesis is performed in several consecutive steps with intermediate condensation, and the remaining reactants are recycled.

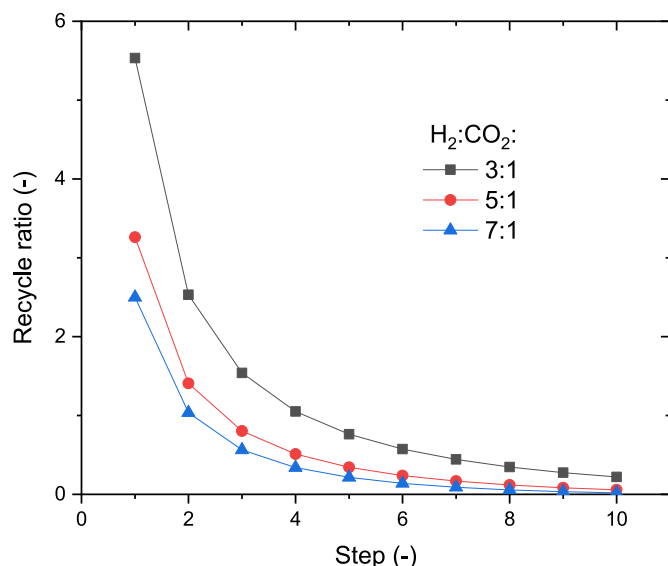


Fig. 8. Required recycle ratio to reach 98% yield to methanol with varying number of stages and stoichiometric ratio ($P = 30$ bar, $T = 225$ °C).

chosen to minimize the amount of waste gas while limiting the required reactor dimensions (which would be excessively large for a higher target yield). The results of the calculations are reported in Fig. 8. The required recycling ratio decreases rapidly with the number of stages due to the increase in conversion per pass. This results in a trade-off between the reactor cost and compression cost because a low number of reactors requires a large compressor and vice-versa. Additionally, a larger number of reactors causes a larger pressure drop per pass, increasing the compression work. The total recompression work required is limited, and the difference in energy requirements due to different recycling streams has a marginal impact on the economic performance of the system.

The calculated process profit for the various recycle configurations is shown in Fig. 9. A sensitivity analysis for the best point ($F = 7$, one reactive step) is reported in the Appendix (Figure A1). In the current conditions, the recycling process is also not profitable for any number of reactive stages at an electricity price of 0.08 USD/kWh. By analogy with the simple cascade process, the performance of the system worsens with

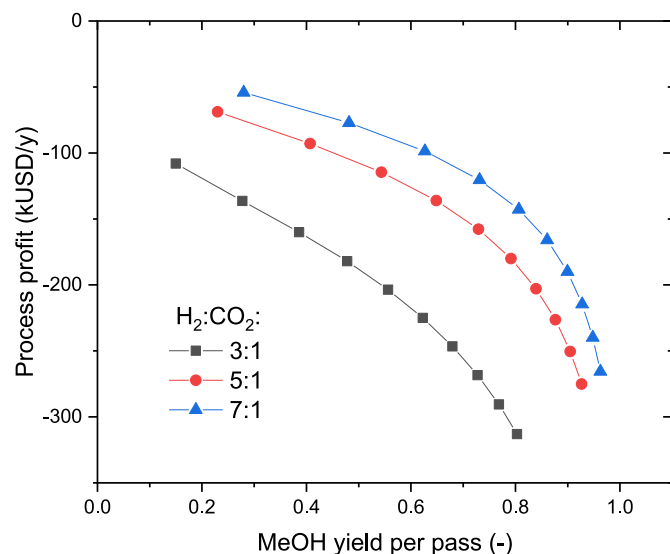


Fig. 9. Process profit (revenues minus costs) for the recycle process (total methanol yield = 98%; $P = 30$ bar).

the increase in the number of stages due to the increase in CAPEX. Interestingly, the effect of the stoichiometric ratio is reversed in this case: the excess of hydrogen significantly improves the economic performance of the system. This is the effect of the higher conversion per step that can be achieved with a higher F -number. As already observed, hydrogen is the most important cost of the process, so that, in this case, the profit from re-utilization of the additional hydrogen is greater than the supplementary costs of compression. For this reason, for instance, the curve at $F = 7$ shows a better performance than the equivalent curve in the cascade process with a high value given to the waste stream. This confirms what is observed for the large-scale PtMeOH process, where yield can be increased by high pressure and high recycle ratio (Koytsoumpa et al., 2020). From these results, it is evident that a small improvement in the reactor performance (using a better catalyst working at slightly lower temperature or by a reactor concept shifting to some extent the thermodynamic equilibrium) would make the recycling process profitable at $F = 7$ with a single reactor. Fig. 10 shows the cost breakdown for the case of $F = 3$, with 1 and 10 stages. Compared to the simple cascade process, the contribution of CAPEX to the total costs is more relevant. This is due to both the need for a larger reactor (due to the larger volume of gas to process) and to the need for the recycling compressor. Looking at the 10-reactive-stage configuration, one can observe that the total fraction of CAPEX is more than 50% of the total costs. This is due to the large expense of reactors and condensers not completely compensated for by a smaller compressor.

To elucidate completely the sensitivity of the results on the assumptions made, a sensitivity analysis of the most important parameters was performed. The results are displayed in the Appendix (Figure A1). The most relevant parameter is the electricity price (i.e., the cost of H_2). For this parameter, a variation of price in the range $\pm 20\%$ causes a change in the calculated process profit of $\pm 150\%$. Hence, the profitability of the system depends strongly on the H_2 cost. Another important influence on the results is the operating hours of the system. An increase in operation time of $\pm 20\%$ increases the profitability of the system from ca. -50,000 USD/y to a slightly positive value. This shows the need to operate the system for as long as possible in a regime of low electricity prices. This is difficult for the recycling process because the start-up and shut-down of the system requires a long time due to the large excess of H_2 required by the system. Hence, an increase in profitability of this system may be difficult to achieve, due to the difficulty of switching the system on and off according to oscillations in the electricity price.

To assess whether the process can be profitable under more favorable conditions, the calculations were repeated to find the minimum electricity price that allows the operation of the system at the break-even point. The break-even electricity price for the three configurations and one single reactive stage are displayed in Table 8; these are 0.064, 0.070 and 0.072 USD/kWh for $F = 3$, $F = 5$ and $F = 7$, respectively. The revenues can equal the costs at electricity prices that are not too low. However, the quantity of methanol produced per pass in the optimal case is low ($< 30\%$ yield per pass), thus requiring a large consumption of electricity due to large recycle ratios. This has an influence on the possible use of the system as an energy storage process as, in this case, the fraction of input energy incorporated in the products is lower (and the fraction of energy consumed in the compression is higher). These results show how the presence of the compressor can increase the economic performance of the process, but it incurs important supplementary CAPEX, which are difficult to compensate on a small scale. Additionally, the best-performing process requires large recycling streams and thus large pieces of equipment. This limits the applicability of this process to small scale due to possible space constraints. Therefore, the recycling scheme remains an important process solution at a large scale, where the repartition of costs is different and the compression steps can be integrated with other operations (Pérez-fortes et al., 2016). The direct use of electricity to operate the compressor causes a net decrease in the energy storage capability of the system (Moioli et al., 2019), which is, in general, disadvantageous for small-scale applications

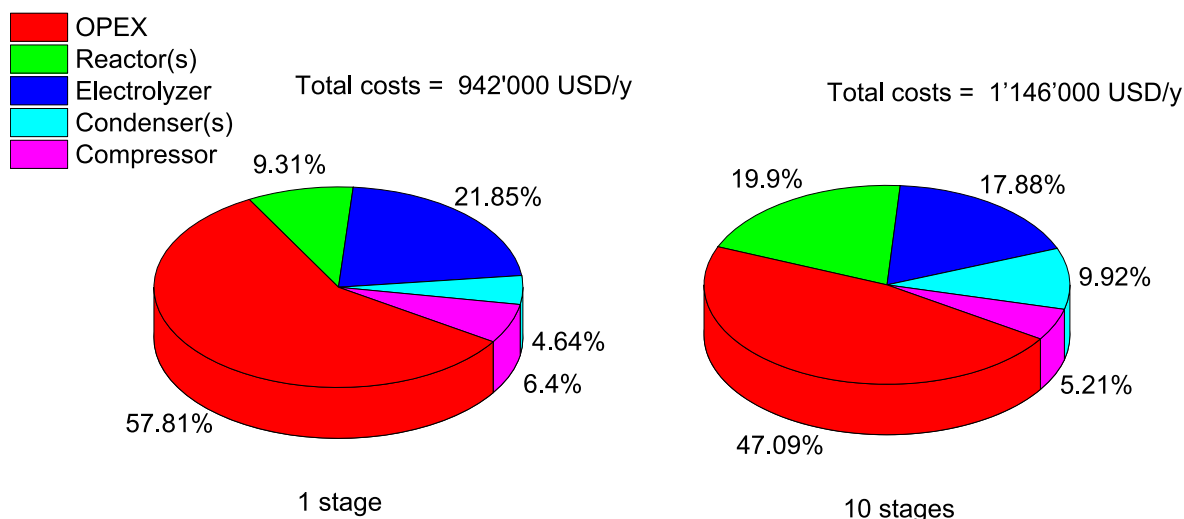


Fig. 10. Cost breakdown for the recycle process with 1 and 10 steps (F = 3).

Table 8

The selling prices considered in the valorization of waste H₂.

Case	H ₂ Price (USD/Nm ³)
Cover OPEX	0.37
Break-even (OPEX + CAPEX)	0.51

where the energy supply may be limited. However, the recycling process remains the best process choice from the configurations considered so far to obtain high yield to methanol at an affordable cost.

3.3. Cascade process coupled with methane production

Another process option for the valorization of CO₂ in the presence of H₂ combines the reaction to methanol in the cascade process with finalization of the CO₂/H₂ conversion in an additional reactor operating the CO₂ methanation reaction. The process scheme is shown in Fig. 11. In this case, the methanol synthesis reaction takes place over several reactors with intermediate condensation to separate the products; after the final reactor of the methanol section the composition of the unreacted gas is adjusted to the 4:1 H₂/CO₂ stoichiometric ratio of the

Sabatier reaction. This is made by splitting part of the feed stream before the methanol section, bypassing this part of the process. The bypass stream is taken from the H₂ feed for the F = 3 case (where the outlet stream from the methanol section shows a 3:1 H₂/CO₂ stoichiometric ratio) or from the CO₂ feed for the F = 5 and F = 7 cases (where the outlet stream from the methanol section shows a H₂/CO₂ ratio above 4:1). The remaining reactants are converted to methane in the finishing Sabatier reactor, where full conversion is achieved (Moioli et al., 2020). In the calculation, the feed of 360 Nm³/h of H₂ was kept constant and the other parameters (CO₂ feed and bypass stream) were adapted to fulfil the stoichiometric ratios of the two reactive sections (F for methanol and 4:1 for methanation). For a correct interpretation of the technical results, it is convenient to refer to the H₂-based methanol yield, which is shown in Fig. 12a. To complement the technical results, the actual total H₂/CO₂ ratio (ratio of H₂ and CO₂ feed in the system and not in the single section) is presented in Fig. 12b. The H₂-based methanol yield increases with the number of stages, approaching the theoretical limit for a large number of reactors. The theoretical limit is the maximum amount of H₂ that can be converted in the methanol section according to the F-factor. As an example, considering 1 mol of CO₂ and F = 5, the maximum amount of H₂ that can be converted to methanol is 3 mol, leaving 2 mol of H₂ to be converted in the methanation section.

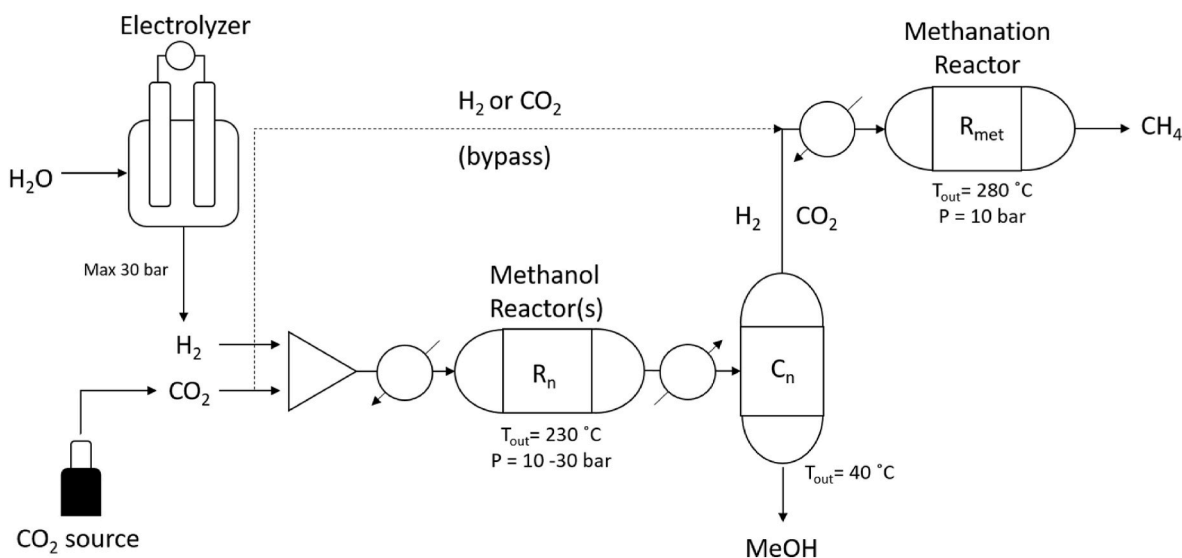


Fig. 11. Process scheme of the hybrid PtMeOH/PtG process.

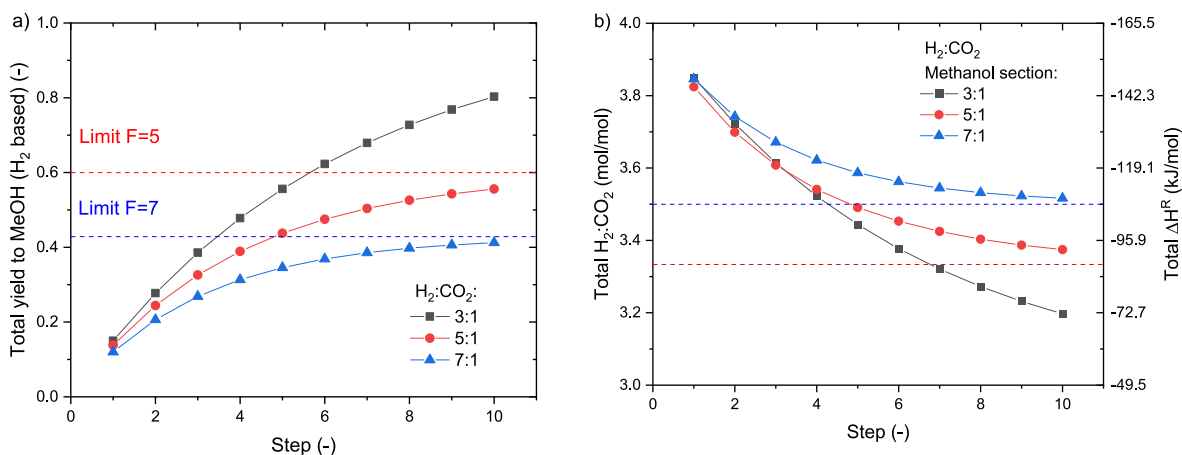


Fig. 12. a) H₂-based methanol yield in the hybrid PtMeOH/PtG process, and b) actual H₂/CO₂ ratio (P = 30 bar).

Therefore, the theoretical maximum in methanol yield for $F = 5$ is 0.6. This means that, at equal yield in the methanol section, the amount of methane for valorization of the unreacted H₂ is higher for higher F -values. Since it was assumed that methanol has a higher value than methane, it can be concluded that at higher F -value the profitability of the system will be lower. This phenomenon is also reflected in the actual H₂/CO₂ ratio, with an increase in this factor in parallel with the increase in the F -factor. This means that more H₂ is necessary to fully convert the CO₂ at in the feed stream, decreasing the thermal efficiency of the entire system as more heat is released in the Sabatier reaction than in the methanol synthesis.

These qualitative trends were verified by calculating the economic performance of the process in all the configurations explained above. These results are reported in Fig. 13a. A sensitivity analysis for the best point ($F = 3$, 5 reactive steps) is reported in the Appendix (Figure A2). The revenues from selling the products (methane and methanol) do not cover the process costs in any of the investigated configurations. The most promising process works at $F = 3$. As stated before, this is due to the lower amount of H₂ necessary per unit of CO₂. In this configuration, the profit function shows a clear maximum located at five reactive stages for the methanol section. This is in line with the maximum trend of the STY curve, as reported in a previous study (Moioli et al., 2019). For a greater number of stages, the process profit decreases rapidly due to the increase in CAPEX, similar to that explained in Section 3.2. The production of methane does not compensate for this decrease in the profitability as the amount of methane synthesized under these conditions is limited (due to

the high methanol yield). This is evident when looking at the cost breakdown, where the share of OPEX in the total cost is dominant (68.81%) for one reactive stage but reduced to 51.52% for 10 reactive stages, as visible in Fig. 14.

For higher F -values, the higher total H₂/CO₂ ratio (compare Figs. 13a and 12b) causes an increase in OPEX, which is not compensated by a decrease in the CAPEX or by an increase in revenues. This latter phenomenon is elucidated in Fig. 13b, where one can see that the process revenues, at equivalent MeOH yield, are significant higher for lower F -values. This is due to the lower amount of additional methane that must be produced under these conditions. Additionally, one can observe that for higher F -values the extent of the maximum decreases, flattening the profit curve. This is due to a different OPEX/CAPEX ratio, with greater need for H₂ to achieve the desired MeOH yield. Hence, one can locate the maximum at three reactive steps for $F = 5$ and at two steps for $F = 7$. In order to determine the influence of additional parameters on the results, a sensitivity analysis for the $F = 3$ case was performed. The results are displayed in the Appendix (Figure A2). The electricity price (hence the H₂ price) is the most influential parameter; in fact, a 20% decrease in its cost would cause an increase in profitability of more than 100%. The influences of the other parameters are less pronounced, with a variation in profitability of ca. 40% for a parameter variation of 20%.

On the basis of that observed above the electricity price required to reach the break-even point for these processes was calculated, and the results are reported in Table 9. The required electricity price ranges from 0.05 USD/kWh for $F = 3$ to 0.043 USD/kWh for $F = 7$. These values are

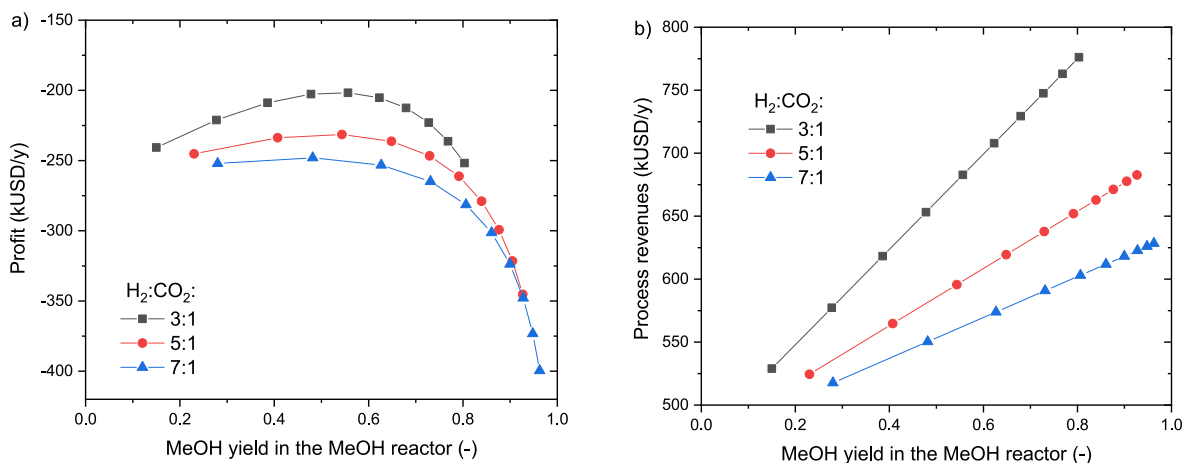


Fig. 13. a) Process profit (revenues minus costs) for the hybrid PtG/PtMeOH, and b) process revenues for the hybrid PtMeOH/PtG process with different F -factors (P = 30 bar).

Table 9

The break-even electricity price for the various recycle configuration considered.

H ₂ /CO ₂ ratio	Break-even electricity price (USD/kWh)
3	0.064
5	0.070
7	0.072

Table 10

Break-even electricity price for the hybrid PtMeOH/PtG process operating with CO₂ and biogas as feedstock.

Break-even electricity price (USD/kWh)		
H ₂ /CO ₂ (–)	PtMeOH + PtG from pure CO ₂	PtMeOH + PtG from biogas
3	0.050	0.073
5	0.045	0.065
7	0.043	0.062

significantly lower than those calculated for the recycling process; however, the absence of recycling and the limited dimensions of the equipment required may compensate for the theoretical higher profitability of the recycling process in small-scale applications. In fact, this would possibly increase the capability of the system to follow the electricity availability curve (Rivarolo et al., 2016); therefore, the choice between the two process types should follow a cautious examination of the boundary conditions, such as the availability of electricity, CO₂ source and available space. To further elaborate this concept, the possibility of coupling the hybrid PtMeOH/PtG process with biogas upgrading was assessed, as elucidated in Table 10.

3.4. Process from biogas

In the hybrid PtMeOH/PtG process coupled with biogas, the CO₂-containing feed stream is cleaned biogas. The composition of the biogas considered is 40% CO₂ and 60% CH₄. The process flowsheet is shown in Fig. 15. The biogas is mixed with the H₂ stream according to the desired value of F and fed into the methanol production section. By analogy with the simple PtMeOH/PtG process, according to the F-value part of the biogas or of the H₂ bypasses the methanol section. The unreacted gases after the methanol section (CO₂, CH₄ and H₂) are then fed into the methanation reactor where the CO₂ conversion is completed. This process configuration is particularly suitable for the upgrading of biogas, as methane is already present at the feed and can be processed as inert over the Cu/ZnO/Al₂O₃ used in the methanol reactor (Lange, 2001). The advantage of this configuration over the simple

methanation of biogas is the co-production of a liquid fuel, which can be stored over long time periods and easily transported to other locations without requiring a dedicated infrastructure. Therefore, it is possible to separate the biogas upgrading section (producing methane) and the energy storage section (synthesizing methanol as a liquid and storable product; Baena-Moreno et al., 2020).

Technically, the process works in the same way as the example given in Section 3.3. The main difference is the dilution of the products in methane, which does not significantly change the technical performance of the process. The presence of methane plays an important role in the economic calculations. The calculated difference between revenues and costs for the process with various F-factors is displayed in Fig. 16a. A sensitivity analysis for the best point (F = 3, 5 reactive steps) is reported in the Appendix (Figure A3). Even in this case, the PtMeOH process is not profitable at an electricity price of 0.08 USD/kWh. The trends are similar to those of the previous cases, but the process losses are lower. In fact, the increase in value of CH₄ from biogas (which is a by-product of the process) to biomethane contributes to the revenues of the process. Therefore, in the most promising case (F = 3 and five reactive stages), the losses are 50,000 USD/year, significantly lower than in the simple PtMeOH/PtG process, where the losses are 200,000 USD/year. The curve for F = 3 shows an evident maximum at five reactive stages, followed by an increase in the losses due to the increase in investment cost. This trend is only partially replicated for the curves at F = 5 and F = 7, as the maximum is not so evident and is located at lower number of steps. Additionally, the losses increase quickly after the maximum due to the influence of the methanation step on the global economic performance of the process (Witte et al., 2018b). In fact, in this case a high share of the fed H₂ (main source of costs) is converted into a less valuable product (methane), as shown in Fig. 16b. The asymptotic MeOH/CH₄ ratio is relatively low for high F-factors, hence limiting the revenues from energy stored in the products. Further insights can be obtained by analysis of the cost breakdown for F = 3 with 1 and with 10 reactive stages in the methanol section, as displayed in Fig. 17. The main cost is linked to biogas purchase. This causes both the increase in expenses compared to the pure PtMeOH/PtG process (due to the assumption of no-cost CO₂) and the direct increase in the amount of product, as biogas is purified together with energy storage. The share of other operating expenses (i. e., electricity) is also large, ranging from 39.82% in the case of one reactive stage to 30.62% for 10 stages. In the case of one reactive stage, the electrolyzer dominates the CAPEX, while the costs of reactors and electrolyzer have similar shares in the configuration with 10 stages.

As in the previous section, the economic performance of the system was recalculated to find the break-even electricity cost; the results are reported in Table 10. Thanks to the marginal profit obtained by the coupling of PtX and biogas upgrading, the process is profitable even at

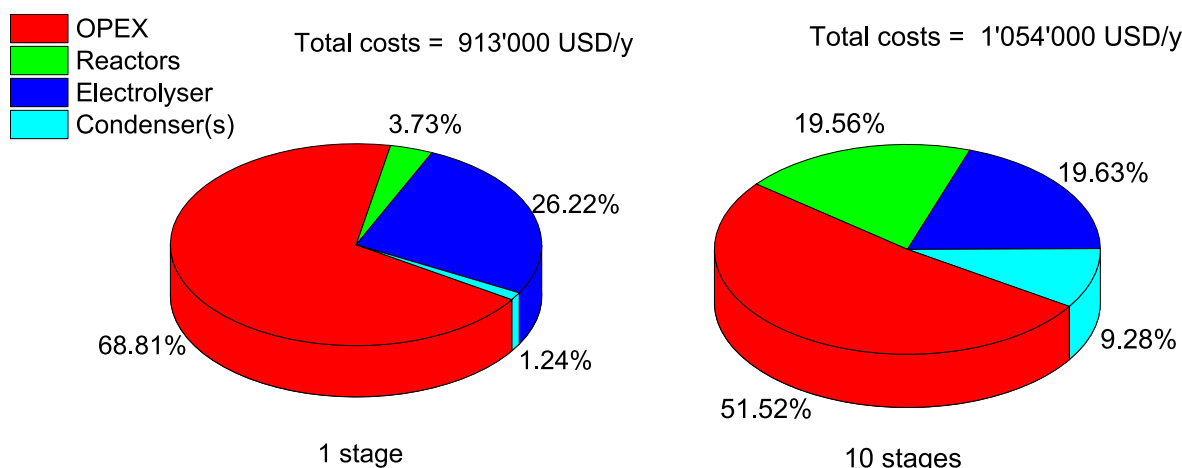


Fig. 14. Cost breakdown for the integrated PtMeOH/PtG process for 1 and 10 stages of methanol production.

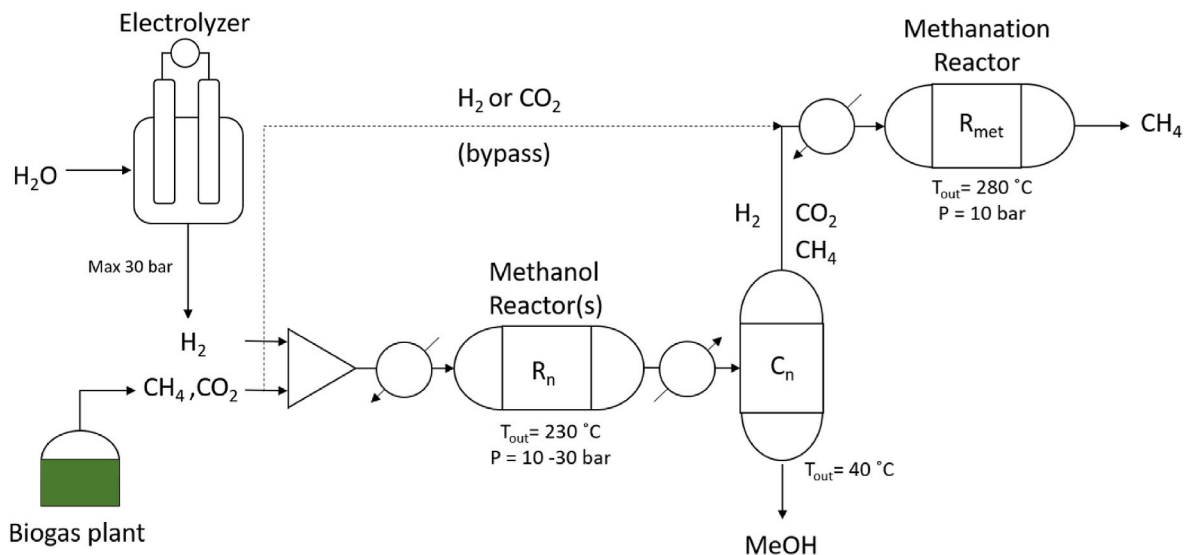


Fig. 15. Process configuration for the hybrid process: methanol synthesis and Sabatier reaction are performed to convert the CO_2 contained in biogas.

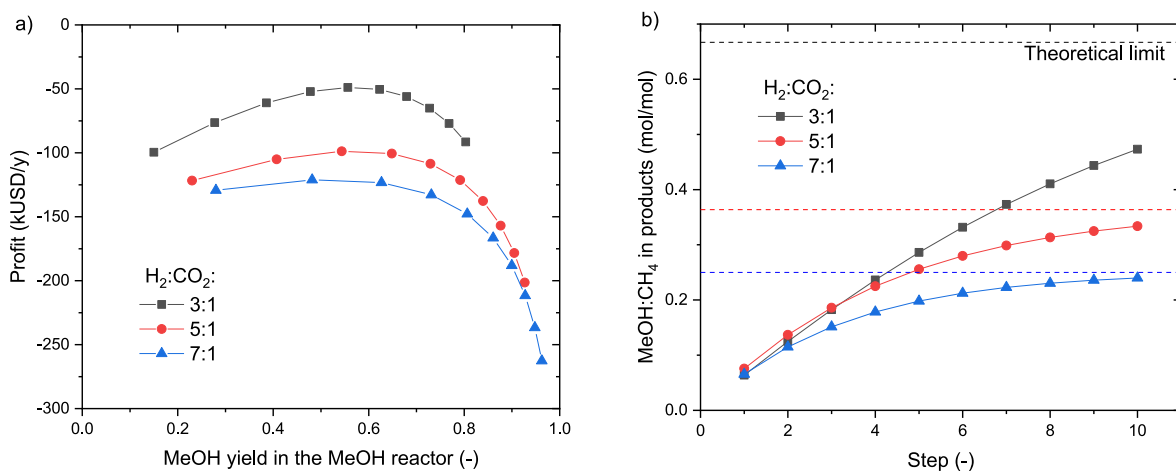


Fig. 16. a) Process profit (revenues minus costs) for the hybrid PtMeOH/PtG process coupled with biogas upgrading and b) CH_4/MeOH ratio in the products, including the CH_4 already present in the biogas feed ($P = 30$ bar).

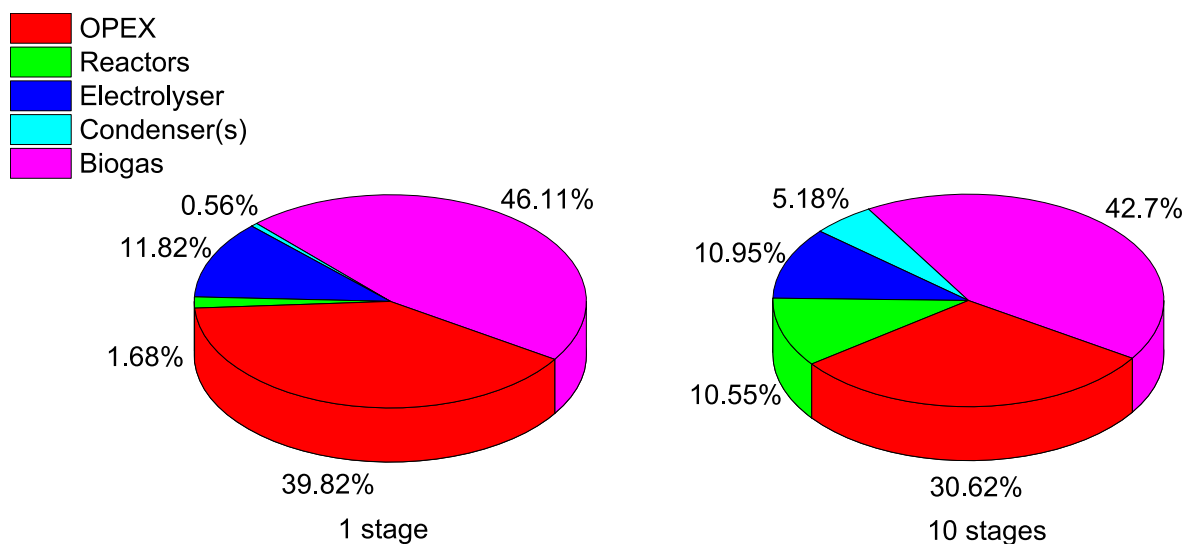


Fig. 17. Cost breakdown for the hybrid PtMeOH/PtG process coupled with biogas upgrading ($F = 3$) which is a by-product of the process.

relatively high electricity price. The break-even electricity price is 0.073 USD/kWh for $F = 3$, 0.065 for $F = 5$ and 0.062 for $F = 7$. These values are lower than those observed for methanol production from biogas in the steam reforming route (Gao et al., 2020). However, the amount of CO_2 stored in the products in the PtMeOH route is significantly higher, ensuring a better environmental sustainability of the process. The calculated break-even electricity price is in line with that of the recycling process. The total amount of methanol produced in the cascade process is lower than in the recycling process. Therefore, one can conclude that the PtMeOH can be operated profitably in both configurations (recycle and cascade) if the following conditions are realized:

- Low price of CO_2 (e.g., from localized and concentrated emitters)
- Low electricity price
- Operation of the methanol section under optimum conditions and reuse of the unreacted H_2 in profitable processes.

Additionally, it is concluded that recycling is preferable to produce methanol in high yield (e.g., for the use in the chemical industry) and that the cascade process is more suitable to produce methanol as liquid fuel in the context of energy storage at small scale through exploitation of localized CO_2 emissions. In fact, the recycling process requires a compressor and large pieces of equipment but produces large quantities of methanol, while the cascade process can work with smaller equipment but requires the co-production of other compounds to be profitable.

3.5. Comparison of processes

Fig. 18 compares the break-even electricity price for the three final process configurations analyzed (i.e., recycling, cascade and cascade from biogas). One can see that the required electricity price for profitable operation is about the same for the recycling process and cascade from biogas hydrogenation. With a required electricity price of more than 0.07 USD/kWh this process may be profitable under specific market conditions as this electricity price is close to the spot price in several periods of the year. This is very similar to that observed at large scale (Pérez-fortes et al., 2016), that the PtMeOH process can be profitable in the appropriate economic framework. The performance of the cascade process from CO_2 is instead significantly lower due to the significant amount of methane co-produced and to the low margin achieved by this product. Hence, the recycling process should be the reference process for methanol production from CO_2 , while methanol production from process streams composed of CO_2 and other valuable products could be better performed in a cascade process. However, while the cascade process allows for a certain degree of flexibility (i.e., the system can be integrated with other CO_2 purification systems to avoid operation in periods with high electricity price), the recycling process requires longer times for start-up, hence requiring a stable (low) electricity price. The determination of the best process for methanol production from biogas is challenging as the production via PtMeOH is economically less favorable than the route via steam reforming, but the former route shows a better environmental impact. Hence, the policy framework may be determining in the choice of the process for this operation.

4. Conclusions

In this study, the economic feasibility of small-scale methanol production from CO_2 in the context of energy storage was analyzed. This was determined by calculating the potential profit of several process configurations, underlining the differences existing. The most promising process configurations for the reaction are the recycling route with large H_2 excess and the cascade route coupled with appropriate CO_2 purification procedures, such as biogas upgrading. The economic assessment showed a slightly worse performance of the processes presented compared to that of state-of-the-art large-scale power-to-methanol

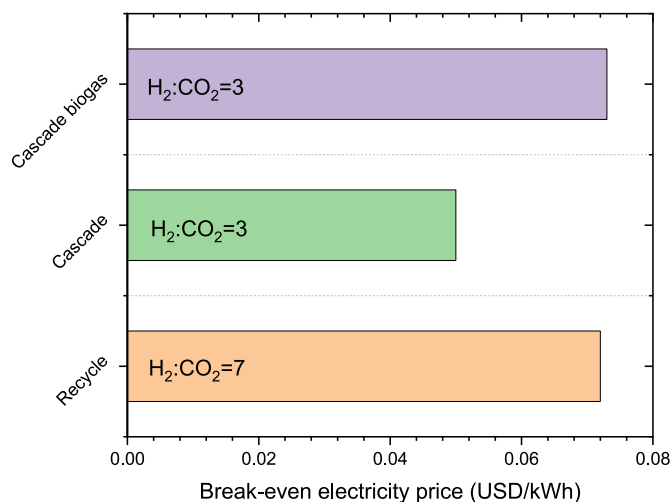


Fig. 18. Comparison of the break-even electricity price for the three final process configurations analyzed.

processes but compensated by a greater flexibility of operation. For both small-scale processes considered, the break-even electricity price in the assumed market conditions is about 0.07 USD/kWh. As this value lies close to the current electricity price for a large part of the year, the small-scale production of methanol from CO_2 may become an interesting option for the valorization of localized renewable energy production or for the removal of limited CO_2 emissions. In this context, the cascade process may be beneficial as it can better adapt to oscillations in the feedstock availability. Additionally, this latter process can be better coupled with other processes, avoiding the need for important purge streams. However, the feasibility of the reaction routes analyzed is still dependent on the presence of important incentives to produce renewable fuels that ensure the existence of a market for the methanol produced. These limitations may be overcome in the future by research into new reactor designs, which may significantly decrease the capital cost of these solutions, for example by in-situ product removal (e.g., by membrane separation). An important decrease in investment cost would make PtMeOH more attractive, significantly incentivizing the use of localized energy resources.

CRediT authorship contribution statement

Emanuele Moiola: Conceptualization, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Funding acquisition. **Anne Wötzel:** Conceptualization, Methodology, Formal analysis. **Tilman Schildhauer:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Funding acquisition, 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.

Acknowledgements

This work received funding from the project “Efficient Small-Scale methanol synthesis from biogas” supported by the Swiss Federal Office for Energy (project number SI/502147) and from the Synfuels initiative of the board of the ETH domain (ETH Rat). The authors acknowledge the support from the Energy Systems Integration (ESI) platform at the Paul Scherrer Institute. A.W. acknowledges the supervision from Prof. Dr.-Ing. habil. Wolfgang Lippmann during the preparation of her M.Sc.

thesis based on this work.

Appendix

A sensitivity analysis was performed for the best performing configurations in the processes: recycle, hybrid PtMeOH/PtG and hybrid PtMeOH/PtG with biogas upgrading. The parameters investigated are CAPEX (reactors, condensers and compressor), electrolyser purchase cost, cost of electricity, operating hours per year, methanol yield per pass and biogas cost. The parameters were varied in the range $\pm 20\%$. The process parameters of the three cases are reported in [table A1](#).

Table A1
Parameters of the cases selected for sensitivity analysis

Case	F (–)	Nsteps (–)
Recycle process	7	1
PtMeOH/PtG	3	5
PtMeOH/PtG with biogas upgrading	3	5

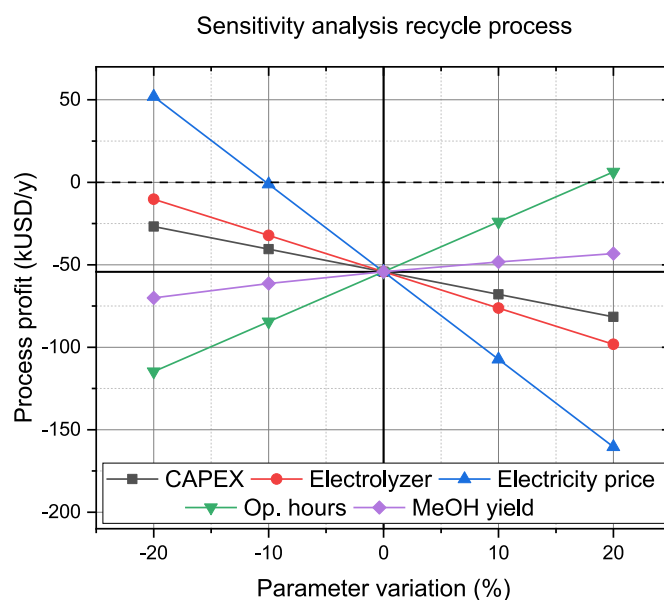


Fig. A1. Sensitivity analysis for the recycle process.

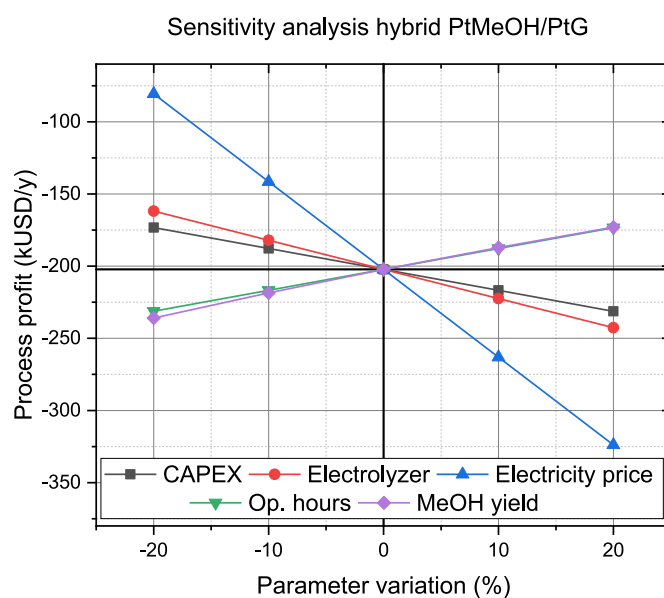


Fig. A2. Sensitivity analysis for the hybrid PtMeOH/PtG process.

Sensitivity analysis PtMeOH/PtG with biogas upgrading

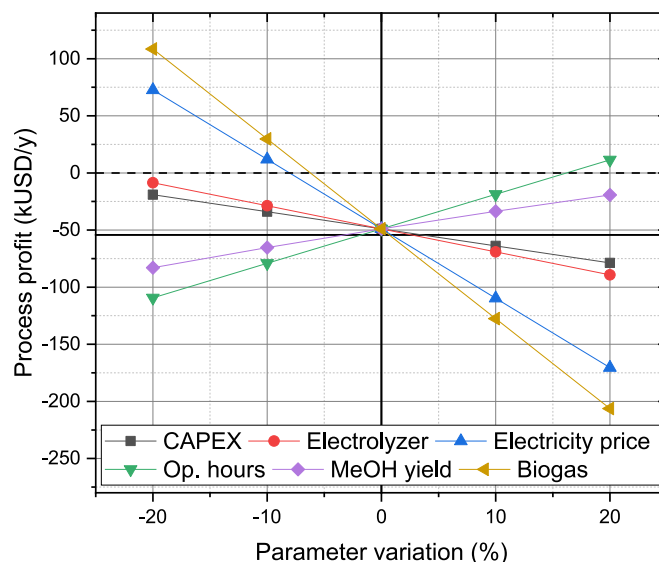


Fig. A3. Sensitivity analysis for the hybrid PtMeOH/PtG process, coupled with biogas upgrading.

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