

## **Title Page**

**Title:** Eco-techno-economic analysis of methanol production from biogas and power-to-X

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## **Abstract**

Methanol is a key ingredient for the chemical industry. In order to foster the transition into carbon-neutral future, it would be of great interest to reduce the fossil carbon footprint of the methanol synthesis by investigating alternative routes. A potential way to produce methanol in a sustainable manner is to utilize biogas, which is a carbon-neutral feedstock. However, it is challenging to provide enough biogas to large-scale plants. For this reason, we investigate in this paper the possibility of producing methanol in small-scale decentralised plants. We analysed the techno-economic-environmental performance of the downscaling of the standard methanol production via steam reforming and we compared it with the novel synthesis via direct CO<sub>2</sub> hydrogenation with green H<sub>2</sub>. We observed that, with cheap electricity and high methanol value, these processes are both profitable, with a slight advantage for the steam-reforming route. Additionally, the direct CO<sub>2</sub> hydrogenation route can be improved by developing tailor-made less costly equipment, thus showing a potential for application in an energy storage context (i.e., with extremely cheap electricity). We also observed that the use of biomethane as feedstock for centralized methanol production shows a similar performance as the localized methanol synthesis, due to the high cost of the raw material. Therefore, we can conclude that, with every technology analysed, the shift towards a biogas-based methanol manufacture results in a more expensive product and that small-scale localized production may play a role in the bio-based methanol supply.

**Keywords:** Power-to-Methanol, Methanol synthesis, Biogas, Eco-techno-economic analysis, renewable energy, small-scale energy storage

## **1. Introduction**

The current tendency towards the defossilisation of the chemical industry and the energy sector is calling for the development of new processes, utilizing unconventional, yet

renewable resources. One of these is biogas. Biogas is a key element for the circular economy, as it enables the energetic recycle of biogenic waste residues and its valorisation towards various products <sup>1,2</sup>. Biogas is a mixture of mainly CH<sub>4</sub> and CO<sub>2</sub>, which can serve as a source of renewable natural gas and carbon. Unfortunately, the development of chemical processes based on biogas is challenging due to the production in small-scale plants, often in remote locations <sup>3</sup>. For all these reasons, biogas is usually valorised through electricity production in combined heat and power (CHP) plants. However, due to the tendency to decrease the incentives for electricity production and to the difficulties in heat valorisation, the interest towards other forms of valorisation of biogas is high <sup>4</sup>. In the context of energy storage, biogas can play a significant role, since the CO<sub>2</sub> contained in this gas can be used as a feedstock for chemical synthesis in combination with renewable H<sub>2</sub> <sup>5</sup>. Among the various possible products in the power-to-X (PtX) processes, methanol may play an important role. This is due to several advantageous properties of methanol, including the storage in liquid form at room temperature and the possible use as a fuel in combustion engines and fuel cells <sup>6</sup>.

Methanol synthesis is performed industrially via reforming of natural gas (eq.1) with steam in large scale, followed by the reaction of CO and H<sub>2</sub> (eq.2):



$$\Delta H_R^0(298\text{ K}) = +206 \frac{\text{kJ}}{\text{mol}}$$



$$\Delta H_R^0(298\text{ K}) = -91 \frac{\text{kJ}}{\text{mol}}$$

In parallel to these reactions, over the commercially used Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, the reverse water gas shift reaction (RWGS) occurs, which allows converting the CO<sub>2</sub> eventually present in the stream. The stoichiometry of the RWGS reaction is (equation 3):



$$\Delta H_R^0(298 \text{ K}) = 41.5 \frac{\text{kJ}}{\text{mol}}$$

This standard methanol synthesis process is performed in large-scale plants, delivering several thousand tons per day of product <sup>6</sup>. Over the last few years, the methanol production from CO<sub>2</sub> became the focus of many researchers. The reaction to consider is a linear combination of eq. 2 and 3:



$$\Delta H_R^0(298 \text{ K}) = -49.5 \frac{\text{kJ}}{\text{mol}}$$

This reaction occurs over the standard methanol synthesis catalyst as well as over tailor-made materials <sup>7</sup>. Despite the relative simplicity of the reaction, the implementation of the new CO<sub>2</sub>-based process is hindered by several techno-economic limitations. In particular, the methanol synthesis from CO<sub>2</sub> suffers of significant thermodynamic limitations, which limit the possible conversion per pass <sup>8</sup>. Therefore, special reactors working with high pressure and/or large recycle ratios are needed <sup>9</sup>. This limits the applicability of the method to locations where the electricity price is constantly low <sup>10</sup>. Furthermore, the availability of CO<sub>2</sub> is often limited to small-scale, thus requiring a downscaling of the existing processes. This creates then problems in the direct application of the standard high-pressure methanol synthesis, due to the absence of the heat integration that in large scale allows obtaining the compression of gas at low cost (through expansion of the hot gas resulting from steam reforming) <sup>6</sup>.

The use of biogas in the methanol synthesis was recently at the base of several studies where the majority considered steam reforming of the methane in biogas and subsequent methanol synthesis while only few considered use of the CO<sub>2</sub> separated from biogas and its conversion with renewable hydrogen. Thermodynamic analyses of the biogas to methanol process were prepared by Vita et al. <sup>8</sup> and by Rosha et al. <sup>11</sup>, confirming that thermodynamic limitations are the main issue in the development of the technology. Gray et al. <sup>12</sup> calculated

the energy balance of power-to-fuel processes integrated with biogas plants. Tozlu <sup>13</sup> investigated the economic performance of synthetic fuel production from biogas, calculating a methanol cost of ca. 630 €/t. Chein et al. <sup>14</sup> analysed the methanol production from biogas reforming, identifying the combined use of dry and steam reforming as the most promising option. The methanol production from methane dry reforming was analysed by Rosha et al. <sup>11</sup>, who indicated the most convenient conditions for the process. Similarly, Entesari et al. <sup>15</sup> indicated the most convenient conditions to safely operate steam/dry reforming units, in order to avoid catalyst deactivation by coking. Santos et al. <sup>16</sup> studied the methanol synthesis from landfill gas, palm oil effluent, corncobs and sorghum fermentation, via biogas steam reforming. Borgogna et al. <sup>17</sup>, reported a process producing methanol via syngas originated from solid waste gasification. Biernacki et al. <sup>18</sup> performed a LCA analysis of the impact of methanol production from electricity and CO<sub>2</sub> from waste water treatment. An LCA study for power-to-fuel strategies combined with biogas plants was performed by Eggemann et al. <sup>19</sup>. Nguyen and Zondevaran <sup>20</sup> performed an economic and environmental analysis of the use of CO<sub>2</sub> capture in the methanol production. In this sense, also Meunier et al. <sup>21</sup> considered an amine-based CO<sub>2</sub> capture unit as a base for the methanol synthesis with H<sub>2</sub> from water electrolysis. Lee et al. <sup>22,23</sup> performed instead several studies about the valorisation of landfill gas in the synthesis of methanol. One special case of biogas utilisation towards the combined production of electricity, heat and chemicals (including methanol) was reported by Furtado-Amaral et al. <sup>24</sup>. Baena-Moreno et al. <sup>25</sup> identified the potential of co-production of bio-methane and bio-methanol from biogas, identifying that a subsidy of 40 €/MW is necessary to profitably operate small-scale biogas plants. Gabrielli et al <sup>26</sup> performed a comparison of the performance of methanol synthesis processes from point CO<sub>2</sub> capture, direct air capture (DAC) and using biomass as feedstock, showing that the biomass route with CCS is the most promising in terms of process efficiency and environmental footprint. The direct production of methanol from methane can

be envisaged as an option for the small-scale methanol production. However, the reaction yield for this technology is currently too low for an efficient exploitation in practical applications <sup>27</sup>.

Despite the large amount of literature on the topic, a complete comparison of the biogas to methanol processes in terms of process efficiency, carbon footprint and economic performance is currently missing. This paper aims at closing this gap by comparing in a coherent way the small-scale processes for biogas conversion to methanol. To do so, several process alternatives are defined involving either biogas reforming, or direct hydrogenation of the CO<sub>2</sub> present in biogas. The processes are optimized with respect to several parameters and the main key performance indicators efficiency, costs and CO<sub>2</sub> mitigation were calculated. We then compared these processes with the state-of-the-art large-scale process from natural gas and with an equivalent process operated with biomethane, i.e., upgraded biogas that was injected to the gas grid as biomethane and transported via the gas grid to a central large-scale methanol synthesis plant.

## **2. Computational methods**

### **2.1. Simulated processes**

The methanol production processes to analyse were selected according to the technologies available at a reasonable TRL level. For this reason, this paper analyses two different groups of processes according to the source of H<sub>2</sub> (internal via steam reforming or external by water electrolysis with renewable electricity), and hence to the presence of a CO/CO<sub>2</sub> mixture or only CO<sub>2</sub> at the inlet of the methanol reactor. For the same reason, the selected unit for renewable H<sub>2</sub> production is an alkaline electrolyser. In the first category of simulated methanol production processes, the methane present in the biogas is reformed to produce H<sub>2</sub> with successive methanol synthesis. In the second category, the methane contained in the biogas does not participate in the reactions due to thermodynamic limitations at the reaction temperature (as shown by Vita et al. <sup>8</sup>) and methanol is synthesized from the CO<sub>2</sub> contained in

the biogas and green H<sub>2</sub>. We calculated additionally the performance of a standard PtMeOH process (i.e., with captured CO<sub>2</sub>) and of the large-scale methanol synthesis from biomethane and from natural gas. The main parameters of the analysed process configurations are reported in table 1. The detailed process schemes for all the configurations analysed are shown in the supplementary information. The reactors are sized to provide the largest CO<sub>2</sub> conversion possible. The models are based on mass and energy balances over infinitesimal slices of the reactor (pseudo-homogeneous 1D model). The details on the models used are reported in supplementary information, including the system of differential equations solved to yield the reactor simulations (equations S5-S15). The resulting systems of differential equations were implemented in Matlab and solved with the *ode23s* routine. The optimal set of parameters for the process units were determined using the *fmincon* function. The optimal process alternatives are found by direct comparison of the various options studied.

Table 1 Details of all the process configurations analysed in this study. MeOH steps refers to the number of units operating reaction, cooling and separation of the products

Macro-case	Short name	Heat source for SR	H <sub>2</sub> addition	CO <sub>2</sub> removal	H <sub>2</sub> :CO <sub>2</sub> ratio	MeOH steps	Valorization unreacted gases
Biogas reforming	1a	Biogas combustion	Yes	No	As stoichiometry	3	Recycle
	1b	Biogas combustion	No	Yes	As stoichiometry	3	Recycle
	2a	Biogas POX	Yes	No	As stoichiometry	3	Recycle
	2b	Biogas POX	No	Yes	As stoichiometry	3	Recycle
PtMeOH with biogas	3a	None	Yes	No	3:1	3	Methanation
	3b	None	Yes	No	7:1	3	Methanation
	4a	None	Yes	No	3:1	10	Methanation
	4b	None	Yes	No	7:1	10	Methanation
	5	None	Yes	No	3:1	3	Recycle
Reference PtMeOH	6	None	Yes	No	3:1	3	Recycle

Large scale from biomethane	LS	Biomethane partial oxidation	No	Yes (by upgrading)	As stoichiometry	N/A	Recycle
Large scale from fossil natural gas	Ref	Natural gas partial oxidation	No	No (eventual CO <sub>2</sub> addition)	As stoichiometry	N/A	Recycle

### 2.1.1. Biogas reforming

The process flow diagram of the methanol production process via biogas reforming is illustrated in figure 1a. In this case, the biogas is heated up to high temperature (above 800 °C), where the production of H<sub>2</sub> and CO from CH<sub>4</sub> is favoured. The oxidizer used for the reforming is steam. The heat required for the endothermic reaction is obtained by combustion of part of the biogas. This is performed either by direct combustion of this fraction in the external part of the reformer (i.e. the combustion gases are released, case 1) or by direct partial oxidation in the process stream (i.e. the combustion gases remain in the process stream, case 2). The inlet temperature of the reformer is the adiabatic flame temperature. In case the adiabatic flame temperature is too high (especially in the oxy-combustion case), part of the combustion gases is recirculated to keep the temperature in an acceptable range (below 1100 °C to avoid damage to the equipment). In both cases, the reformed gas is not compliant with the required stoichiometry for methanol synthesis:

$$\frac{3\text{CO}_2+2\text{CO}}{\text{H}_2} = 1 \quad (5)$$

Therefore, an adaptation of the composition is required. This can be done either by addition of H<sub>2</sub>, produced in an electrolyser (case a) or by the removal of the CO<sub>2</sub> in excess (by membrane separation prior to reforming, case b). The membrane separation unit is the most suitable solution under the technical and economical point of view for this process scale <sup>28</sup>. The electrolyser is an alkaline type, modelled with a shortcut model, considering a sharp split separation and a second principle efficiency of 0.7 kW<sub>HHV,H2</sub>/kW<sub>el</sub> <sup>29</sup>. This is a typical value for both alkaline and PEM electrolyzers. The resulting stream is compressed to the methanol



synthesis pressure and the reaction is operated in a series of reactors with intermediate condensation of the products. The number of stages is selected such that a high CO conversion per pass (>95%) is achieved. The remaining gas, mainly composed of CO<sub>2</sub> and H<sub>2</sub>, is recompressed and recycled to the reactor. The detailed descriptions of the biogas reforming process schemes are reported in section 2.1 of the supplementary information.

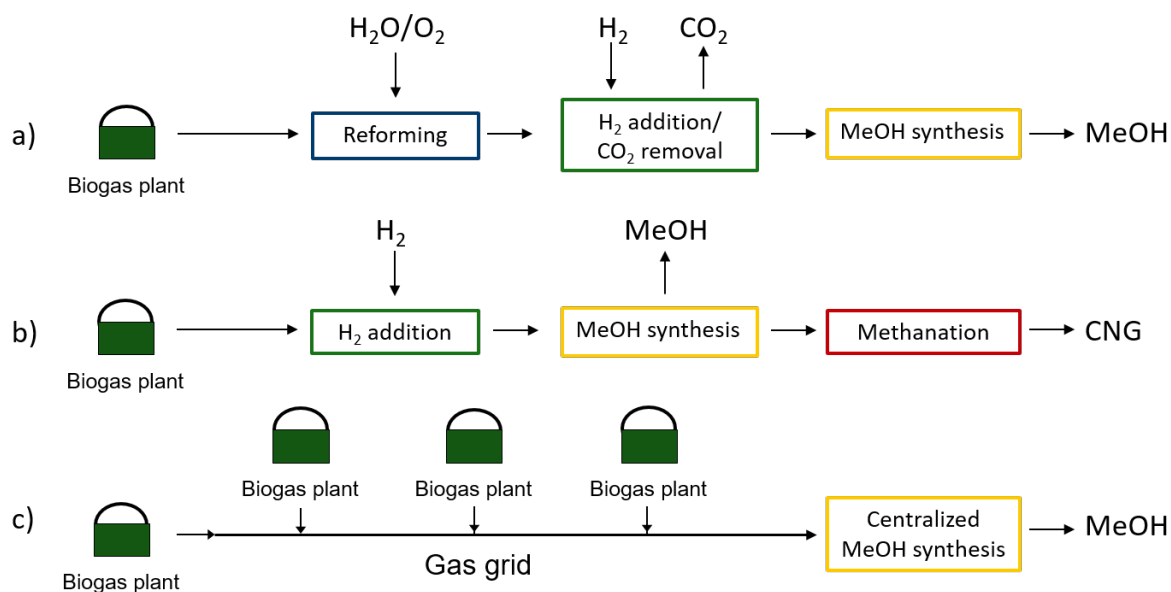


Figure 1 schematic representation of the analysed process schemes: a) biogas is reformed to syngas and methanol is synthesised after adjustment of CO<sub>2</sub>/CO/H<sub>2</sub> ratio. b) The CO<sub>2</sub> in the biogas is used for the methanol synthesis with addition of H<sub>2</sub> (and eventual methanation of unreacted CO<sub>2</sub> and H<sub>2</sub>). c) Large scale centralised production of methanol from the reforming of biomethane collected from several biogas upgrading plants.

### 2.1.2. PtMeOH with biogenic CO<sub>2</sub>

In the PtMeOH process with biogenic CO<sub>2</sub>, biogas is upgraded by reaction of CO<sub>2</sub> with H<sub>2</sub> produced by an electrolyser. This is schematically displayed in figure 1b. Biogas is compressed, mixed with H<sub>2</sub>, and compressed to the methanol synthesis pressure. The reactive section is composed of several reactors in series with intermediate condensation of the products. The methanol synthesis from CO<sub>2</sub> is challenging due to stringent thermodynamic limitations. Hence, we analysed two different configurations: three (case 3) and 10 (case 4) reactive stages in the methanol synthesis section. The 10 stages are a limit case to represent a plant focused to methanol production. Even though this large number of stages may be difficult

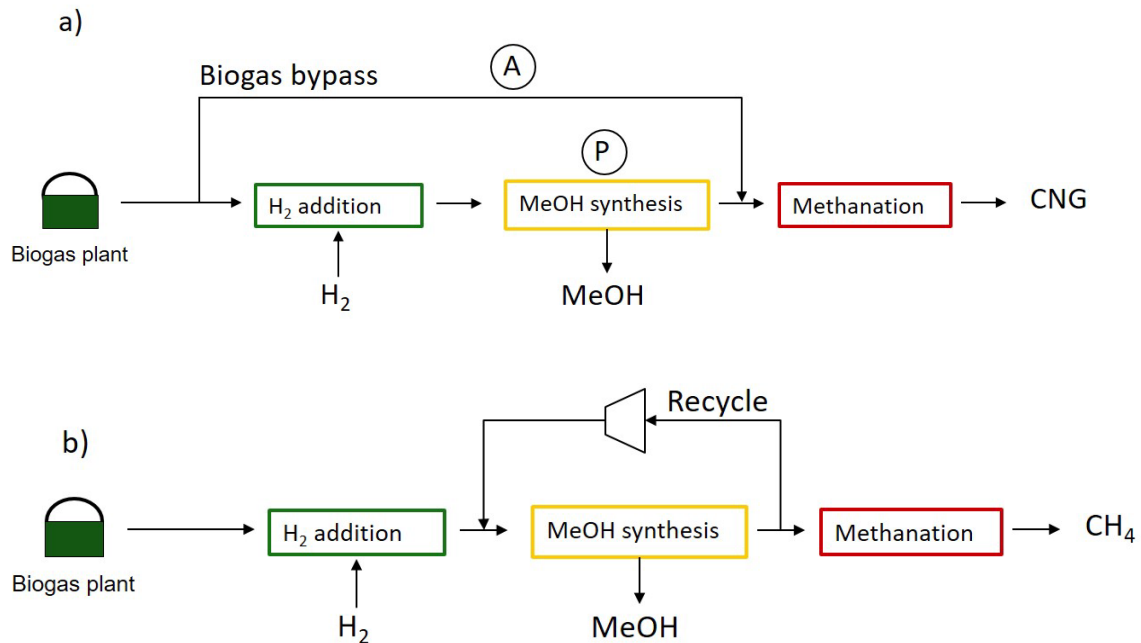
to realise, specific strategies for the small-scale manufacturing of this solution can be envisaged in case methanol production is particularly profitable. The gas remaining after the methanol reactors is then fed to a CO<sub>2</sub> methanation reactor, where the H<sub>2</sub> left can be converted into methane up to required grid quality<sup>30</sup>. The resulting synthetic natural gas stream (composed of the newly synthesized SNG and the CH<sub>4</sub> originated from biogas) is then compressed to 200 bar and stored as CNG. Additionally, it is possible to shift the thermodynamic equilibrium by operating the methanol synthesis with excess H<sub>2</sub>. This is obtained bypassing the methanol section with part of the biogas, which is then mixed with H<sub>2</sub> only prior to the methanation reactor. This operation is schematically represented in figure 2a. The effect of the stoichiometric ratio is analysed by performing the eco-techno-economic calculations at H<sub>2</sub>:CO<sub>2</sub>=3 (case a) and H<sub>2</sub>:CO<sub>2</sub>=7 (case b). For a detailed description of these process schemes, please refer to section 2.2 of the supplementary information.

### 2.1.3. Benchmark processes

Some further processes were analysed and used as benchmark cases. The first benchmark case is the PtMeOH process with biogenic CO<sub>2</sub>, performed with a valorisation of the unreacted gas by means of internal recompression and recycle (case 5). Therefore, the unreacted CO<sub>2</sub> and H<sub>2</sub> are further converted to methanol, increasing the quantity of methanol produced. However, in this configuration a recycle compressor is needed, requiring a significant energy input. This process is illustrated in figure 2b.

We analysed a reference PtMeOH process (case 6, figure 2c) operated with pure CO<sub>2</sub>. This is similar to case 5: CO<sub>2</sub> is compressed to the electrolyser discharge pressure, mixed with H<sub>2</sub> and compressed to the process pressure. Afterwards, the reaction is performed over three reactive stages with intermediate condensation of the products (the number of stages will be discussed in section 3.2.2) and the unreacted gases are recycled via a recompression blower.

As a last comparison, we simulated the methanol production in a standard large-scale plant using natural gas as feedstock. In this process, similarly to case 1, methane is reformed with steam and the heat required is provided by combustion of a fraction of the natural gas. Afterwards, CO, CO<sub>2</sub> and H<sub>2</sub> are converted to methanol in the pressurized methanol reactor and the unreacted gas is recycled via a recompression blower. The main advantage of large scale lies in a better process integration, which allows significant energy savings compared to the small-scale configuration. The process modelling follows the methodology described by Collodi et al.<sup>31</sup>. In the case where the process is operated with green methane, we suppose that several biogas plants deliver biomethane (i.e. after biogas upgrading) to the gas grid. In this way it is possible to have sufficient green methane to operate the large-scale plant, as shown in figure 1c (case LS). The technical operation of the plant is then identical as in the case of production from natural gas (case REF), but the cost of the feedstock and the environmental impact are significantly different, as exposed in the following sections.



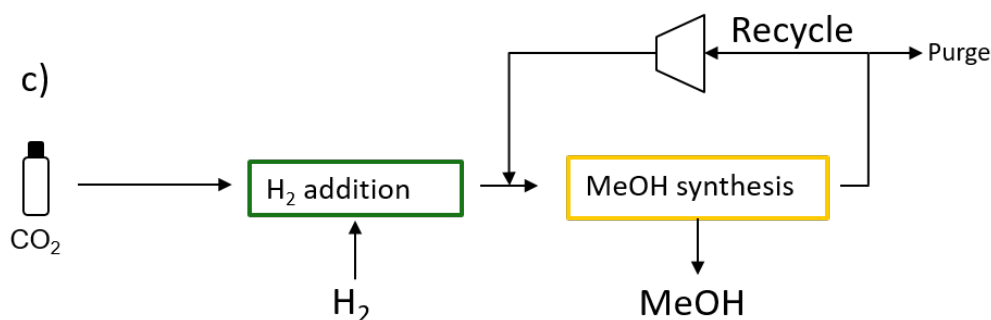


Figure 2 Schematic representation of: a) the process scheme used for optimization of the PtMeOH process with biogenic  $\text{CO}_2$ . A refers to the amount of biogas bypassed from the methanol synthesis section (i.e. determining the  $\text{H}_2:\text{CO}_2$  ratio) and P to the pressure in the methanol synthesis reactors (i.e. determining the methanol yield; b) the PtMeOH process with recycle from biogas; c) the PtMeOH process from  $\text{CO}_2$  (with recycle).

## 2.2. Process models

We assumed that the biogas available is cleaned from the impurities and composed of 60%  $\text{CH}_4$  and 40%  $\text{CO}_2$ . The process modelling involves three reactors: steam reforming, methanol reactor and  $\text{CO}_2$  methanation reactor. All the reactors are modelled with rate-based reactor models. For the steam reforming reactor, the catalyst considered is Ni-based and the kinetic model by Xu and Froment<sup>32</sup> is used. The reactor is modelled with a pseudo-homogeneous 1D model, including the presence of intra-phase diffusional limitation with the Thiele modulus method. The steam reformer is operated at low pressure (below 5 bar). The methanol synthesis reactor is operated with a  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst and the model is developed on the base of the kinetic model from Vanden Bussche and Froment<sup>33</sup>. The model is chosen because it satisfactorily describes the reaction in the conditions studied, as highlighted by the recent studies by Slotboom et al.<sup>34</sup> and by Bisotti et al.<sup>35</sup>. This reactor is modelled with a pseudo-homogeneous 1D model, as no significant intra- or interphase mass and heat transfer limitations are expected in this reactor. The  $\text{CO}_2$  methanation occurs over the  $\text{Ni/Al}_2\text{O}_3$  catalyst developed and modelled by Koschany et al.<sup>36</sup>. This reactor is modelled with a pseudo-homogeneous 1D model, including the presence of intra-phase diffusional limitation with the Thiele modulus method. The detailed description of the reactor models is reported in the supplementary information (section 1). The reactor models are used to define  $\text{CO}$ ,  $\text{CO}_2$  and

H<sub>2</sub> conversion, CH<sub>4</sub> and MeOH yield and the dimension of the equipment. The condensers are modelled as equilibrium stages at 40 °C, using the ideal gas law. The coolant for the condensation steps is water. The final product is raw methanol, which is purified in a centralized makeup plant, external to the considered plant. The compressors are considered as multistage isentropic devices, with an efficiency of 72%.

The main performance indicators are defined as follows.

CO conversion:

$$X_{\text{CO}} = \frac{\text{CO}_{\text{in}} - \text{CO}_{\text{out}}}{\text{CO}_{\text{in}}} \quad (6)$$

CO<sub>2</sub> conversion:

$$X_{\text{CO}_2} = \frac{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}}{\text{CO}_{2\text{in}}} \quad (7)$$

H<sub>2</sub> conversion:

$$X_{\text{H}_2} = \frac{\text{H}_{2\text{in}} - \text{H}_{2\text{out}}}{\text{H}_{2\text{in}}} \quad (8)$$

Methanol yield:

$$Y_{\text{MeOH,CO}_2} = \frac{\text{MeOH}_{\text{out}}}{\text{CO}_{2\text{in}}} \quad (9)$$

CH<sub>4</sub> yield:

$$Y_{\text{CH}_4} = \frac{\text{CH}_{4\text{out}}}{\text{CO}_{2\text{in}}} \quad (10)$$

The H<sub>2</sub>:CO<sub>2</sub> ratio is defined as:

$$F = \frac{\text{H}_{2\text{in}}}{\text{CO}_{2\text{in}}} \quad (11)$$

The process efficiency is defined as:

$$\eta_e = \frac{\sum_{\text{prod}=1}^n \text{HHV}_{\text{prod}}}{\text{HHV}_{\text{biogas}} + \text{HHV}_{\text{H}_2} + W_{\text{compr}}} \quad (12)$$

The carbon balance of the plant determines the environmental performance of the processes. A detailed scheme of the boundary conditions selected is reported in the supplementary information (figure S58). The CH<sub>4</sub> and CO<sub>2</sub> originated from biogas are

considered carbon neutral, as the carbon contained was captured from the atmosphere during plant growth. The CO<sub>2</sub> emission in the biogas production are neglected, to make the results of this study independent from the origin of the biogas. The carbon from the feedstock is either recovered in the products or it is emitted in the form of CO<sub>2</sub> following combustion (e.g. in the burners of the reformer). Additionally, we consider the CO<sub>2</sub> emissions related to the production of electricity for the electrolyser and the compressors. This results in additional CO<sub>2</sub> emissions according to the source of electricity. In this study, we distinguished between two cases: electricity produced with the standard EU energy mix (446 gCO<sub>2</sub>/kWh<sub>e</sub><sup>37</sup>) and use of energy from photovoltaics (45 gCO<sub>2</sub>/kWh<sub>e</sub><sup>38</sup>). The carbon balance thus gives the resulting environmental efficiency indicator:

$$\eta_{\text{CO}_2} = \frac{\text{CH}_4^{\text{in}} + \text{CO}_2^{\text{in}} - \text{CO}_{2,\text{el}}^{\text{out}} - \text{CO}_{2,\text{proc}}^{\text{out}}}{\text{CH}_4^{\text{in}} + \text{CO}_2^{\text{in}}} \quad (13)$$

This indicator shows how much of the initial carbon is stored in the products (methane and methanol). A negative value of the indicator means that the CO<sub>2</sub> emitted in the process is higher than the amount of carbon present in the products.

## 2.3. Cost estimation

### 2.3.1. CAPEX

The methodology from<sup>39</sup> is used for the calculation of the capital expenditures. These are calculated via a bare module cost, which is function of the type of equipment, material, volume and pressure, according to the formula:

$$C_{BM} = f(C_p, F_M, F_P) \quad (14)$$

The material considered is stainless steel in all the cases. The bare module costs are the basis for the calculation of the total installation costs. These depend from the various factors reported in table 2. The total equipment cost is calculated as:

$$C_{tot} = C_{BM} \cdot (1 + F_c) \quad (15)$$

The calculated costs are actualized to the current prices through the Chemical Engineering Plant Cost Index (CEPCI). The CEPCI is calculated as:

$$CEPCI = \frac{CEPCI (current)}{CEPCI (2004)} = 1.548 \quad (16)$$

The current CEPCI index is the value for January 2019. The factors defined above are used to calculate the current total bare module cost as:

$$C_{BM, today}(\text{€}) = C_{BM} \cdot (1 + F_C) \cdot CEPCI \cdot F_e \quad (17)$$

The investment costs for the electrolyser are calculated as 1200 €/kW<sub>el</sub><sup>29</sup>. The cost of the small-scale reformer is calculated as 10'600 €/Nm<sup>3</sup><sub>NG</sub><sup>40</sup>. The CAPEX of compressors is calculated according to the nominal power required, following the method for centrifugal compressors elucidated in<sup>39</sup>.

### 2.3.2. OPEX

The main parameters for the calculation of the operative expenditures are reported in table 2. The annual operation and maintenance expenditures for the equipment are estimated as 5 % of the bare module costs<sup>41</sup>. For the electrolyser, this is reduced to 1.5%, due to the absence of rotating devices<sup>29</sup>. The HHV-based efficiency of the electrolyzer is assumed as 70%. The operation hours per year are 8000 for the reforming case (feedstock available all the year) and 6000 for the PtMeOH case (renewable H<sub>2</sub> available only during part of the year). For cases 1-5, the biogas inlet is 200 Nm<sup>3</sup>/h. For case 6, an equivalent amount of CO<sub>2</sub> (80 Nm<sup>3</sup>/h) was considered. The cost of biogas is accounted for with 0.06 €/kWh<sup>29</sup>. The cost of water considered is 1 €/m<sup>3</sup>.

*Table 2 the cost factors for the various components and the parameters for the economic assessment*

Element	Cost factors (on $C_{BM}$ )
Connections	0.4
Instrumentation	0.1
Electrical connections	0.2
Construction	0.13
Planning & permissions	0.3

<b>Total (<math>F_c</math>)</b>	<b>1.13</b>
Element	Value
Plant lifetime (y)	15
Water cost (€/m <sup>3</sup> )	1
Electricity cost (€/kWh)	0.05
CH <sub>4</sub> value (€/kWh-HHV based)	0.12
MeOH value (€/kWh-HHV based)	0.20
Biogas cost (€/kWh-HHV based)	0.06

### 2.3.3. Income

We assumed that the bio-based products are awarded a higher value than the current market price for fossil-based products, according to the current regulatory framework in Switzerland. This results in a price ca. 4 times higher than the fossil fuels, that is 0.20 €/kWh for methanol and 0.12 €/kWh for methane<sup>29,42</sup>. No income is accounted for the electrolyser waste heat, as this is delivered at low temperature, limiting the options for process integration.

### 2.3.4. Economic indicators

In order to assess the economic performance of the processes, the discounted cash flow was calculated considering a discount rate of 6% and a plant lifetime of 15 years (lifetime of the electrolyser as estimated by the manufacturer). Net present value (NPV), internal rate of return (IRR) and payback time (PB) were calculated as follows:

$$NPV (\text{€}) = \frac{\sum_1^t R_t}{(1+i)^t} \quad (18)$$

$$\frac{\sum_1^t R_t}{\left(1+\frac{IRR}{100}\right)^t} = 0 \quad (19)$$

$$\frac{\sum_1^t R_{PB}}{(1+i)^{PB}} = 0 \quad (20)$$

$R_t$  indicates the cash flow at the year  $t$  (€).

## 3. Results and discussion

### 3.1. Biogas reforming

In biogas reforming, we distinguish between a configuration in which the combusted gases from the reformer are released in the atmosphere (case 1) and one case in which the



oxidation takes place in the reformer (case 2). This choice has an important impact on the amount of  $H_2$  to add or  $CO_2$  to remove to obtain the correct stoichiometric ratio for the methanol synthesis. The quantity of gas to add or remove in the various cases is reported in table 3. We can observe that the amounts are larger in case 2. This is due to the larger reformer productivity. These quantities are at the basis of the different technical and economic performance of the four process configurations, as reported in figure 3a. Figure 3a shows the amount of methanol produced and the total investment required. The configurations with  $H_2$  addition produce a significantly larger quantity of methanol, thanks to the full conversion of the biogenic carbon contained in the reformed product. In particular, the process configuration 2a shows the largest methanol productivity of this study, equal to 6 t/d. However, this latter configuration also requires the highest investment (ca. 5M €) due to the large electrolyser needed. The configurations with  $CO_2$  removal show a lower productivity, because an important share of biogenic carbon is emitted as  $CO_2$  (productivity ca. 3.25 t/d). Figure 3b shows the IRR for these processes. The IRR varies between 25 % for the case 1a and 17 % for case 2b. This is in line with the values calculated in similar conditions by Gao et al.<sup>22</sup>. The processes with externally heated reformer are economically more promising, because the costs for  $CO_2$  removal are reduced. In particular, case 1a is slightly more profitable than case 1b due to the larger methanol productivity. Furthermore, the need to adjust the  $CO_x:H_2$  ratio before or after the reformer calls for the installation of a membrane, which increases the CAPEX of process 1b, without increasing the productivity. However, these results are influenced by the (relatively) low price of electricity, which makes the operation of the electrolyser affordable. If the cost of electricity increases (see SI for the detailed sensitivity analysis), case 1b would become favored over case 1a. This is also evident in the calculation of process efficiency, reported in figure 4. Process 1b has a slightly higher efficiency, thanks to the use of  $H_2$  only originated from biogas. The efficiency of process 1a is instead negatively affected by the efficiency of the electrolyser.

The cost of H<sub>2</sub> production via electrolysis is also at the base of the lower economic performance of case 2. The high CAPEX and OPEX of the electrolyzer cause a drop of the income from process 1a to 2a. In fact, the cost of H<sub>2</sub> required to fully convert the biogenic CO<sub>2</sub> to methanol is not fully compensated by the larger productivity. Therefore, the cost of avoiding direct CO<sub>2</sub> emissions is high. The analysis of the carbon balance shows that, however, the elimination of CO<sub>2</sub> emissions at the methanol synthesis plant is not sufficient to improve the environmental balance, as shown in figure 4a (right section). In fact, the carbon footprint of process 2a is not better than process 1a. In the case of feed of the electrolyser with the electricity from the standard EU grid, the carbon balance of process 2a is even negative (the process is a net CO<sub>2</sub> emitter), while the balance of process 1a is slightly positive (slight CO<sub>2</sub> emission avoided, thanks to the biogenic carbon source). When the electrolyser is fed with electricity from PV, the carbon balance is similar for the two configurations, with a slightly better performance for process 1a than process 2a (55% vs. 50% CO<sub>2</sub> emission saved). Case 2b is the worst performing process, due to the low methanol productivity and the large cost of the CO<sub>2</sub> separation, which must entirely be performed with expensive devices (e.g. membranes). This is confirmed by figure 4b, reporting the cost breakdown per ton of product. Process 2b shows the highest specific CAPEX among the processes with biogas reforming, importantly affecting the economic performance. It is interesting to observe that the cost of the feedstock has the most relevant share in all the processes and it is inversely proportional to the amount of methanol produced. In fact, the addition of H<sub>2</sub> from electrolysis allows the production of additional methanol, reducing the specific cost of biogas per ton of product. However, the large cost of H<sub>2</sub> produced via electrolysis does not significantly improve the economic performance of the system in the conditions analysed. Therefore, the coupling of energy storage and biogas reforming does not improve the economic performance of the latter, but it can make energy

storage affordable. This is in line with what observed in literature regarding the need of negative CO<sub>2</sub> prices for the profitable methanol production from CO<sub>2</sub><sup>42</sup>.

Table 3 Required additional H<sub>2</sub> or CO<sub>2</sub> removal in the various configurations

	H <sub>2</sub> addition [Nm <sup>3</sup> /Nm <sup>3</sup> <sub>biogas</sub> ]	CO <sub>2</sub> removal [Nm <sup>3</sup> /Nm <sup>3</sup> <sub>biogas</sub> ]
1a	0.434	-
1b	-	0.145
2a	1.414	-
2b	-	0.47

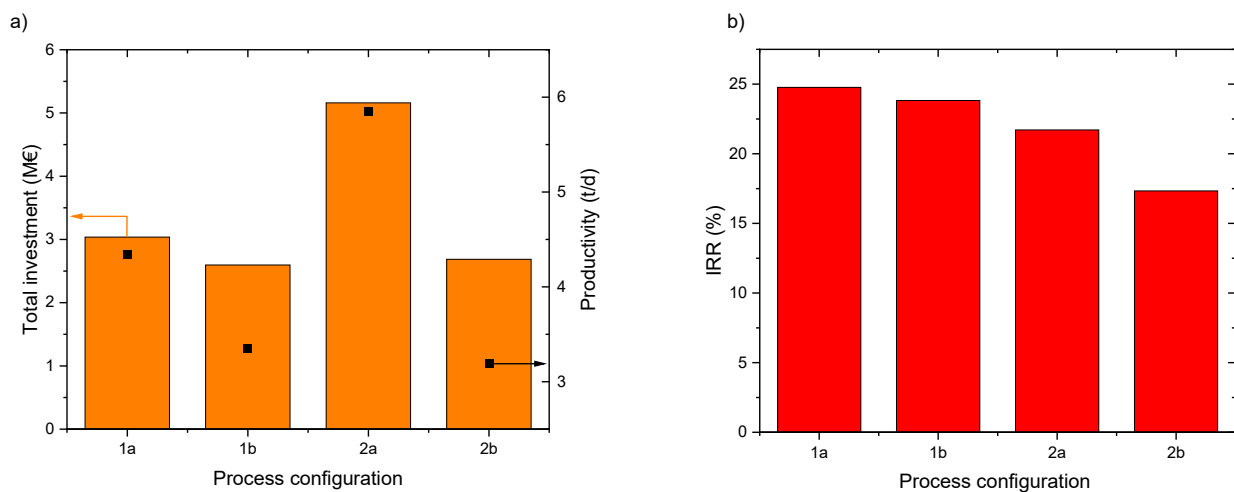


Figure 3 a) Comparison of the required investment per ton of methanol product and b) calculated internal rate of return for the four configurations of methanol production from biogas reforming. Cases as in table 1 ( $P=70$  bar for all the cases).

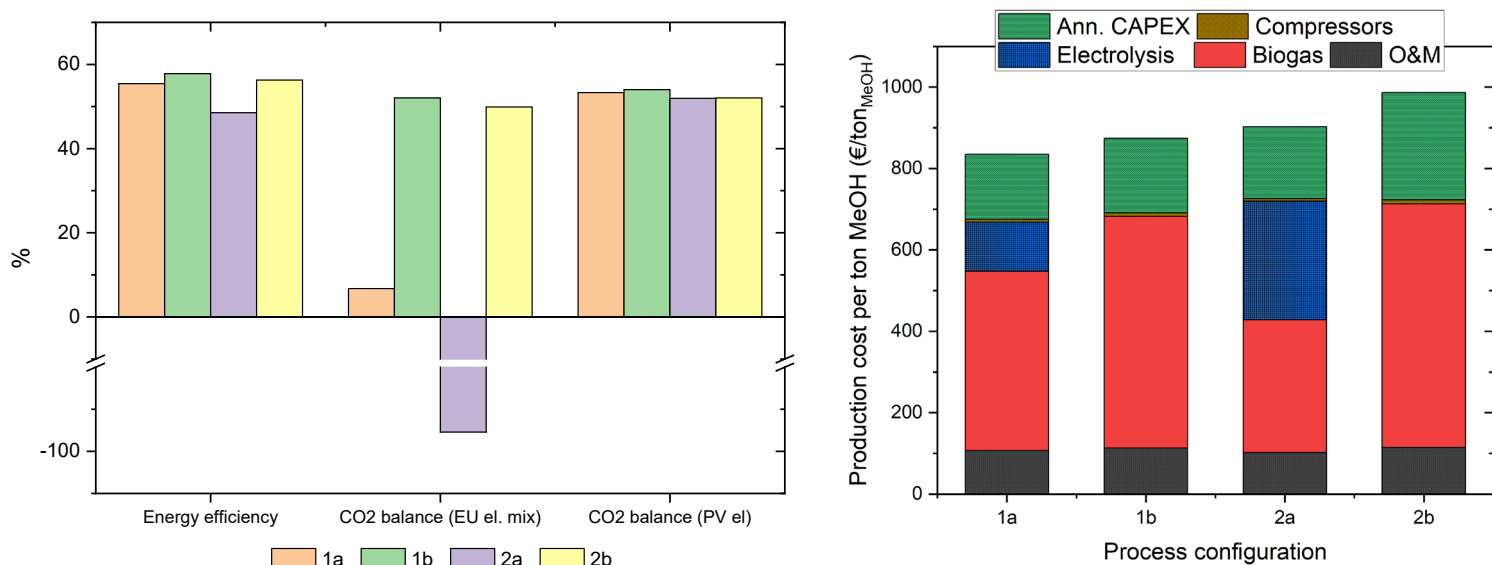


Figure 4 a) Environmental indicators for the four configurations of biogas reforming; b) Distribution of production costs per ton of methanol in the four configurations of biogas reforming

### 3.2. PtMeOH from biogenic CO<sub>2</sub>

#### 3.2.1. Hybrid process for with methanation

##### *Process optimization*

In the PtMeOH process, the parameters influencing the reaction yield and efficiency are numerous. Therefore, prior to the economic analysis, it is necessary to operate a technical analysis of the possible process configurations, to identify the optimal conditions. Considering the process scheme of figure 2a, it is possible to reduce the degrees of freedom to two parameters. In fact, once the stoichiometric H<sub>2</sub>:CO<sub>2</sub> ratio and the pressure are fixed, the yield (parameter P) in each reaction stage can be determined univocally (assuming the outlet temperature of the methanol reactor equal to the optimal value, which is in the range 230-250 °C). The inlet stream contains CH<sub>4</sub>, according to the biogas specifications previously defined (i.e. 40 mol./mol. % of CH<sub>4</sub>). CH<sub>4</sub> is considered inert for the methanol synthesis. The flow rate of the bypass stream (parameter A) must be compliant with the requirement of H<sub>2</sub>:CO<sub>2</sub>=4 ratio prior to the CO<sub>2</sub> methanation reactor. Hence, by imposing these two parameters (denoted with (A) and (P) in figure 2), it is possible to calculate the process efficiency (eq. 10) and the molar

fraction of methanol in the products. These indicators depend on the number of reactive stages in the methanol synthesis section. The results for three and 10 stages are reported in figure 5. The temperature is kept constant to the point of maximum methanol yield by adapting the cooling rate. For three stages, we can observe that the efficiency function shows a clear maximum at 40 bar and  $H_2:CO_2=4$ . This is due to the contrasting effects of the increase of methanol yield and compression cost with pressure. It is worth recalling here that we assume that  $H_2$  is delivered at 30 bar from the electrolyzer and therefore the results are dependent from this assumption. The maximum of efficiency with stoichiometric ratio can instead be explained by the initial positive effect of increasing this parameter on the methanol yield. The decrease in efficiency after the maximum is due to the large amount of methane co-produced in the process (being methane a less efficient energy storage molecule than methanol <sup>43</sup>). This effect is evident in figure 5b, where the methanol fraction in the products is displayed. In this case, methane is the dominating product in most of the conditions studied, with high share of methanol at high pressure (>60 bar) and low stoichiometric ratio. This is due to the low methanol yield after three reactive stages, which calls for an important methane production to consume the remaining  $CO_2$ . The results are significantly different for the case of 10 reactive stages: here the maximum in energy efficiency is located between 30 and 40 bar and at a stoichiometric ratio equal to 3 (figure 5c). The origin of this difference is the higher methanol yield, which reduces the advantage of operating at high pressure or in excess of  $H_2$ . Consequently, a lower amount of methane is produced to valorise the remaining  $H_2$ , so that the methanol fraction in the products is higher (figure 5d). Hence, it is evident that, if the methanol synthesis section produces a significant amount of methanol, the operation in excess of  $H_2$  is not convenient in terms of storage efficiency and total methanol production.

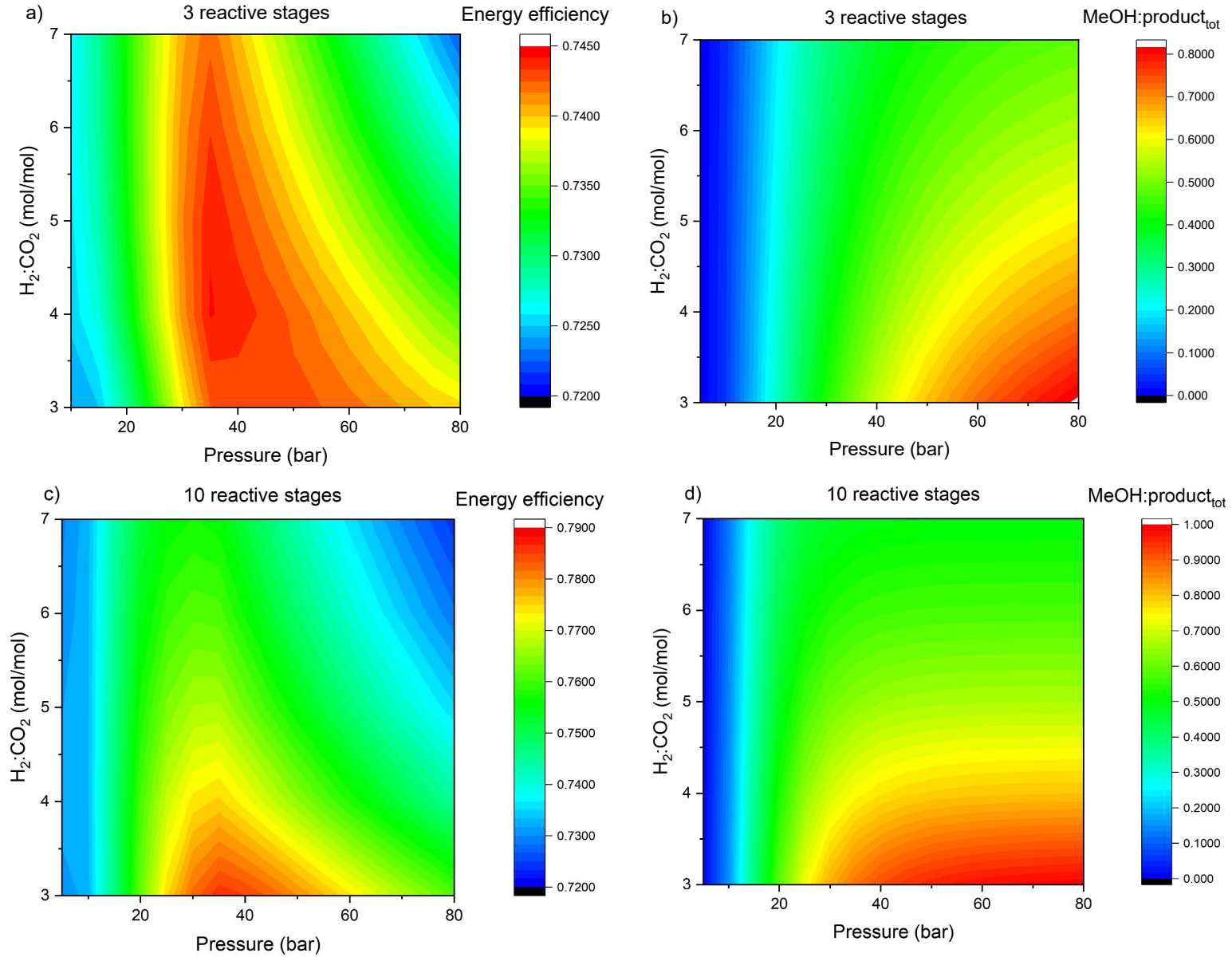


Figure 5 the calculated a) overall energy efficiency (eq.10) and b) methanol fraction in the products at different pressures and  $H_2:CO_2$  ratio for three reactive stages in the methanol synthesis section. Figures c) and d) reports the same information for 10 reactive stages.

### Eco-techno-economic analysis

For the sake of simplicity, we limited the eco-techno-economic analysis to the cases  $H_2:CO_2=3$  (case 3a and 4a for 3 and 10 reactive steps, respectively) and  $H_2:CO_2=7$  (case 3b and 4b for 3 and 10 reactive steps, respectively). The calculated IRR at different pressures for these process configurations is reported in figure 6. For three reactive steps (figure 6a), the IRR increases with pressure and it is comprised in the range between 14 and 20 %. The stoichiometric ratio has no influence on the results at low pressure, while the excess of  $H_2$

positively influences the IRR at 70 bar. This is due to the significant larger share of methanol in the products at higher pressure (see also fig. 5b) and the better utilization of the three methanol synthesis stages with excess  $H_2$  (larger yield per pass). For 10 reactive stages (figure 5b), the results are significantly different. The cases with  $H_2:CO_2=3$  performs significantly better than the cases with  $H_2:CO_2=7$ . This is due to the better space-time yield in the former cases, while the performance of the latter cases is negatively affected by the low yield achieved in the last reactive stages. Interestingly, the maximum in the IRR is found for  $H_2:CO_2=3$  and 30 bar. Hence, an increase of pressure is in this case not favourable for the profitability of the system. This is again due to the higher space time yield of the former case, with a more favourable MeOH:CH<sub>4</sub> ratio. In fact, in the latter case, the product stream is almost only composed of MeOH (see figure 5d).

According to the results of figure 6, we proceeded with the eco-techno-economic analysis of the most promising process configurations in terms of IRR. These are found at 70 bar for the 3 steps arrangements (case 3a and 3b), at 30 bar for 10 steps and  $H_2:CO_2=3$  (case 4a) and at 70 bar for 10 steps and  $H_2:CO_2=3$  (case 4b). The total investment required is displayed in figure 7a. We can observe that the variation in the total investment is narrow, because the difference in equipment needed is limited (only a few vessels of difference, while the electrolyser remains of similar size). However, this investment is distributed on a different variety of products as shown by the scatter points of figure 7a. In the  $H_2:CO_2=3$  case, the productivity of methanol is significant (2 and 2.5 ton per day for 3 and 10 steps, respectively), while in the  $H_2:CO_2=7$  case the product distribution is dominated by methane (slightly more than 1 ton/d methanol produced in both cases 3b and 4b). This is reflected in distribution of the costs in the various process configurations (total costs per ton of product – methane and methanol), as shown in figure 7b. For all the configurations, biogas is the most relevant cost, followed by electrolysis. For the processes with  $H_2:CO_2=7$  the annualized CAPEX are more

relevant, but still covering a limited share of the total costs. It is worth noticing that the total cost per ton of product is minimum in the configuration 4a, where the maximum methanol is produced.

For what concerns the energy efficiency, the configurations with 10 reactive stages show a better performance, as shown in figure 8. This is due to the intrinsically higher energy storage efficiency of methanol than CNG. For the same reason, the configurations with  $H_2:CO_2=3$  are favoured over the processes with excess  $H_2$ . In absolute terms, the best performing process is 4a, with an efficiency of ca. 80 %, significantly higher than the cases with biogas reforming. The second panel of figure 8 shows that all the processes considered in this section are net  $CO_2$  emitter if the electricity is originated from the standard EU mix. This is due to the energy storage nature of these processes. However, when the electricity is originated from photovoltaics, the results are significantly improved, as displayed in the third panel of figure 8. The amount of the initial carbon that is stored in the products is ca. 80 %, thanks to the absence of direct  $CO_2$  emissions in the process and to the low carbon footprint of the  $H_2$  production. In this sense, the direct hydrogenation of  $CO_2$  from biogas results in a better environmental performance than the production of  $H_2$  from biogas for the methanol synthesis, due to the significantly better carbon efficiency of the latter process. A detailed comparison of the two systems is performed in the last section of this work.



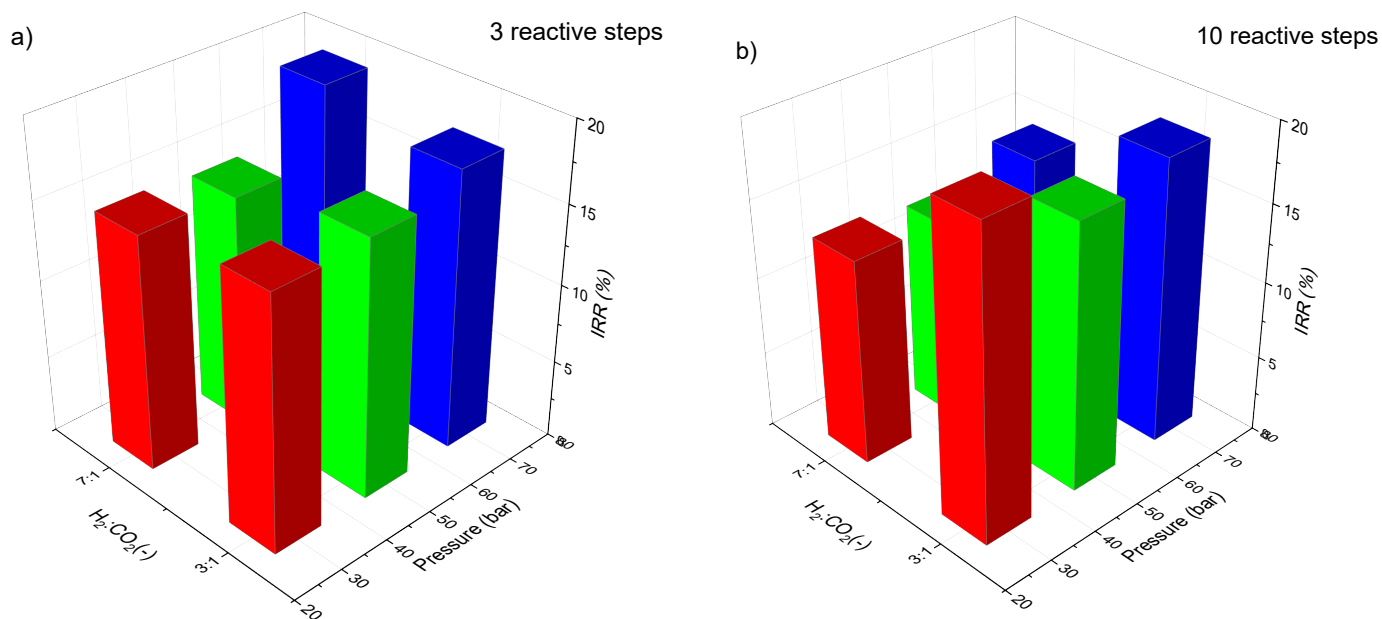


Figure 6 The calculated IRR for the hybrid PtMeOH/PtG process from biogas with a) 3 reactive steps, b) 10 reactive steps.

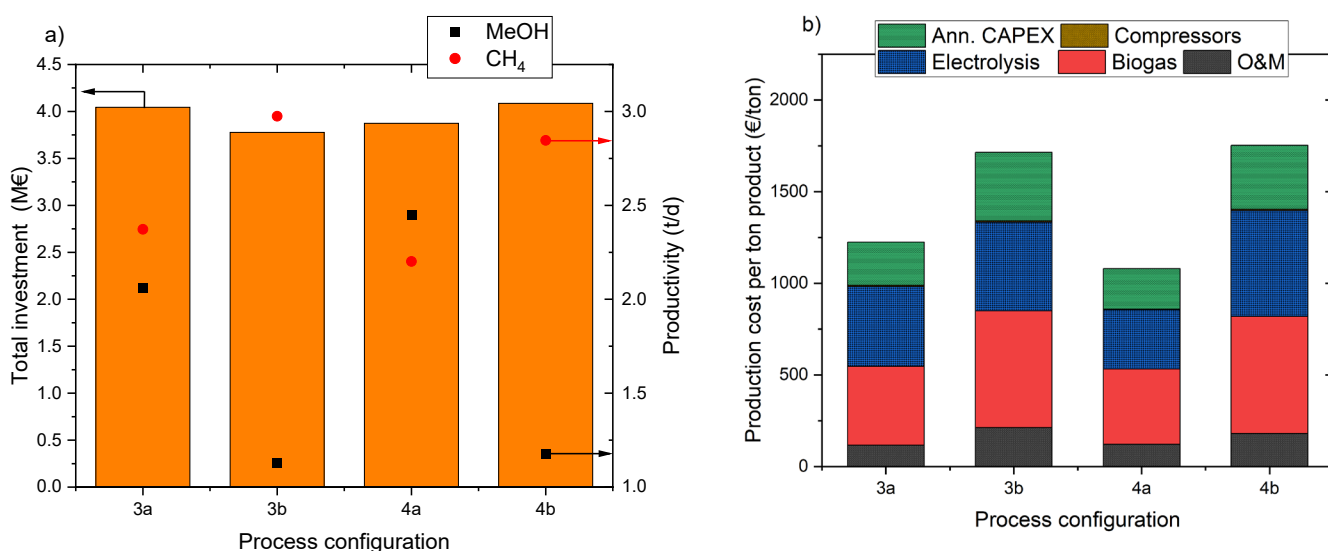


Figure 7 a) The total investment required and productivity to methane and methanol for the various PtMeOH configurations considered. b) The production costs per ton of methanol produced. Cases as in table 1 (30 bar for the case 4a, 70 bar for the remaining).

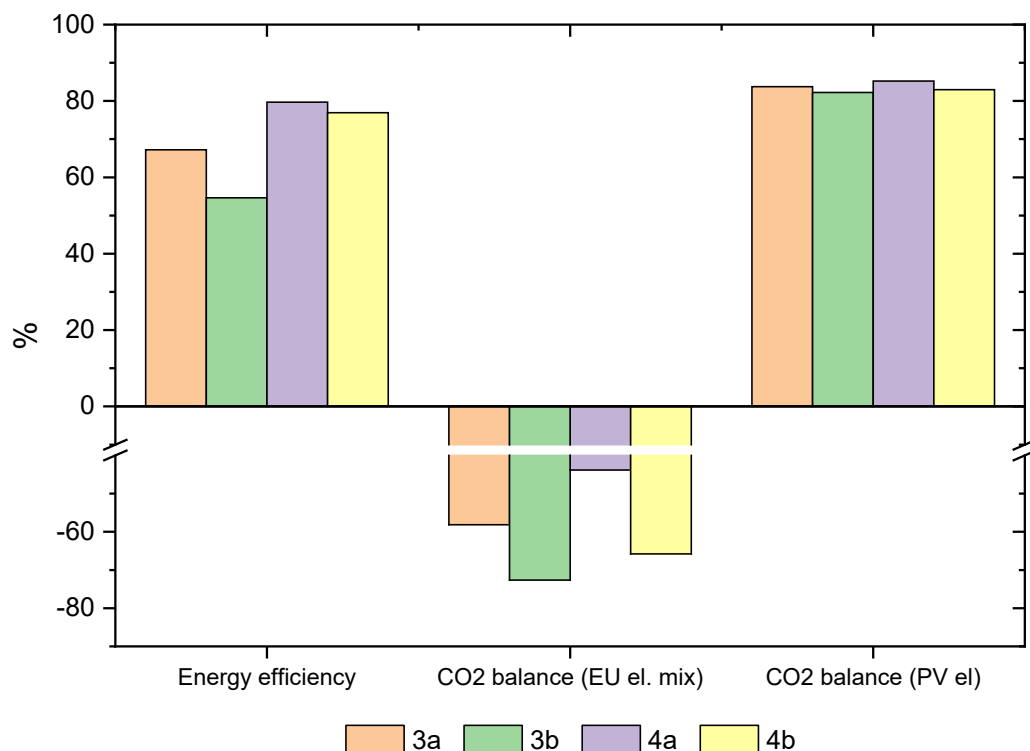


Figure 8 Environmental indicators for the four configurations of PtMeOH from biogas

### 3.2.2. PtMeOH with recycle

In the case of the PtMeOH process with recycle, we calculated the optimal number of reactive stages to be performed prior to the recycle loop in the standard power to methanol process. The results are displayed in figure 9. The figure should be interpreted as follows: after every process step, it is possible to further utilize the reactants either in a recompression and recycle or in a further reaction step. We calculated the cost of these two alternatives, reported as black squares or red circles, respectively. We observed that the cost of the recycle stream is almost constant, due to the contrasting effect of the decreasing flow rate with the increasing number of steps (due to the higher conversion) and the increasing pressure drop to recover. The cost of the reactors increases with the number of stages because of the larger number of vessels (reactors, condensers and heat exchangers) required. We can observe that the crossing point is placed between three and four stages. Therefore, we can conclude that the optimal system is composed of 3-4 reactive stages with successive recycle of the unreacted gas. The shift of the

optimal point with pressure is linked to the higher conversion, which decreases the STY for the successive steps.

We calculated the IRR of cases 5 and 6 considering the optimal number of stages. The results, compared with cases 3a and 4a, are reported in figure 10. We can observe that the IRR of these two benchmark cases is significant lower, with a value of ca. 16 % for the recycle process with biogas and ca 8 % for the standard PtMeOH process from CO<sub>2</sub>. The origin of this lower performance is the high cost of recycle for case 5 and the absence of the marginal profit from biogas upgrading for case 6. It is therefore evident that the profitability of PtMeOH is strongly dependent on the coupling with other processes.

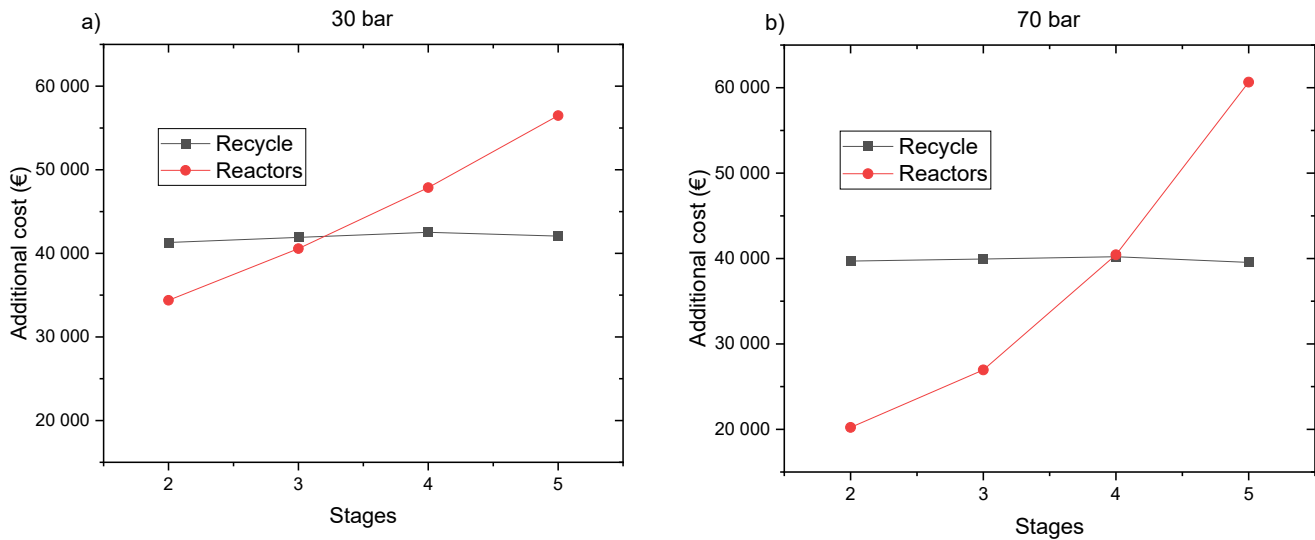


Figure 9 the additional cost required to install a recycle compressor or an additional reactor as a function of the number of reactive stages in the methanol synthesis section.

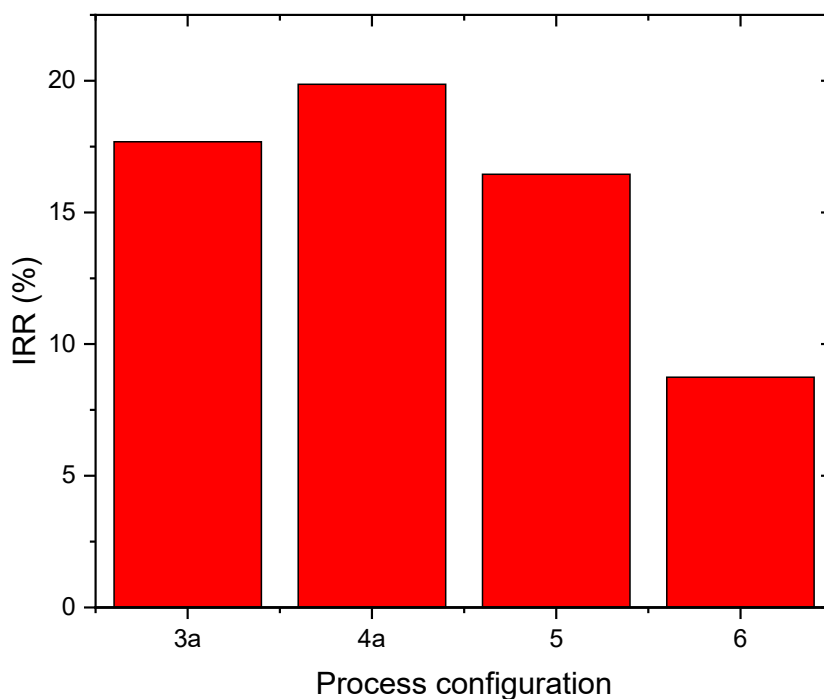


Figure 10 Comparison of IRR for various configuration of the PtMeOH process. (Pressure=30 bar for case 4a, 70 bar for the other processes).

### 3.3. Comparison of process options

In the view of the valorisation of biogas through the synthesis of methanol, it is convenient to consider the possibility of producing methanol in the standard large-scale methanol plants, using the carbon-neutral methane produced by biogas upgrading as feedstock. The main advantage of the centralized methanol production lies in the improved process integration, allowing significant savings in terms of energy (in particular in the methane steam reforming section) <sup>6</sup>. This results in a lower need of fuel, improving the profitability of the system. However, the significant cost of biomethane (ca. 4 times higher than fossil methane) causes a significant decrease in the profitability compared to the standard methanol synthesis process. The calculated indicators for this process and the comparison with the most relevant processes discussed so far are displayed in figure 11a. The IRR of the large-scale process is slightly higher than the case 1b and it is the highest of this study. However, it is important to

note that this study neglects the cost of the distribution infrastructure for biomethane. Hence, the large scale has an advantage only when the gas supply infrastructure for biomethane is already available or can be installed with limited effort (e.g. retrofitting of existing plants). Additionally, special attention should be posed on the availability of sufficient biomethane or certificates. In the general comparison of the IRR calculated for the various processes, we can observe that the processes with methane reforming have largely a better performance over the direct CO<sub>2</sub> hydrogenation. In particular, the CO<sub>2</sub> hydrogenation not coupled with biogas utilization (pure PtMeOH) has the poorest performance. This clearly states that the CO<sub>2</sub> utilization has an important cost, so that the methanol production from this route is penalized with the current technological and regulatory framework. However, there is a potential for technological improvement in the case of the cascade processes (case 4), for example by reducing the expenses for the various stages. This may result in a decrease of the investment cost and a consequent increase of the profitability of the system. In order to fully understand the differences between the process studies, it is convenient to refer to the process efficiency (figure 11a, central panel). Here we can observe that the direct biogas hydrogenation is favoured over the other processes. This is due to the larger production of methane and methanol, thanks to the conservation of the original methane from biogas. The direct PtMeOH process from CO<sub>2</sub> shows instead a similar efficiency as the processes with methane reforming, due to the influence of the efficiency of the electrolyzer (and the large amount of H<sub>2</sub> required). Hence, we can conclude that the methanol synthesis from CO<sub>2</sub> hydrogenation may be convenient in a context where electricity becomes drastically cheap, such as in the cases where energy storage is necessary (i.e. in periods of significant electricity overproduction). For this reasons, the further development of this technology is strongly connected to the regulatory framework, which may favour the development of an energy storage infrastructure via synthetic fuels. In any case, the processes with direct CO<sub>2</sub> hydrogenation offer a better option

to avoid CO<sub>2</sub> emissions, as shown in the third panel of figure 11a. The small-scale biogas reforming is particularly penalized on this aspect, because of the significant amount of CO<sub>2</sub> produced in the reforming furnace. This could be improved by installation of a post-combustion CCS unit, which, however, would further decrease the process efficiency. Therefore, we can conclude that the biogas reforming is currently the economically best process for methanol production from biogas, but the lower efficiency and higher CO<sub>2</sub> footprint of this process may penalize its development in future, in case of a different legislation in terms of CO<sub>2</sub> emission and electricity pricing.

To fully understand these last aspects, we compared the cost breakdown for these processes, as shown in figure 11b. We included the current costs of a large-scale methanol production plant from natural gas (case REF in the figure). We can observe that the cost of the fuel is already now the most important part of the plant balance. Therefore, the change towards a carbon neutral fuel (i.e. the use of biomethane) already increases significantly the production cost of methanol, from ca. 300 €/t to ca. 1000 €/t. Hence, even considering the state-of-the-art technology, a biogas-based methanol production causes an increase in the methanol break-even price. The small-scale methanol synthesis routes proposed in this work show an economic performance in the same range of the centralized production, showing that there is a techno-economic potential for this type of processes. This is in part due to the possibility of operating this latter directly from biogas, a cheaper raw material than biomethane. However, this potential can be unlocked only if the transition is supported from decision makers, mainly offering incentives for the production of green methanol. To complement these results a table with the sensitivity analysis on the payback time of the various configurations is reported in supplementary information.

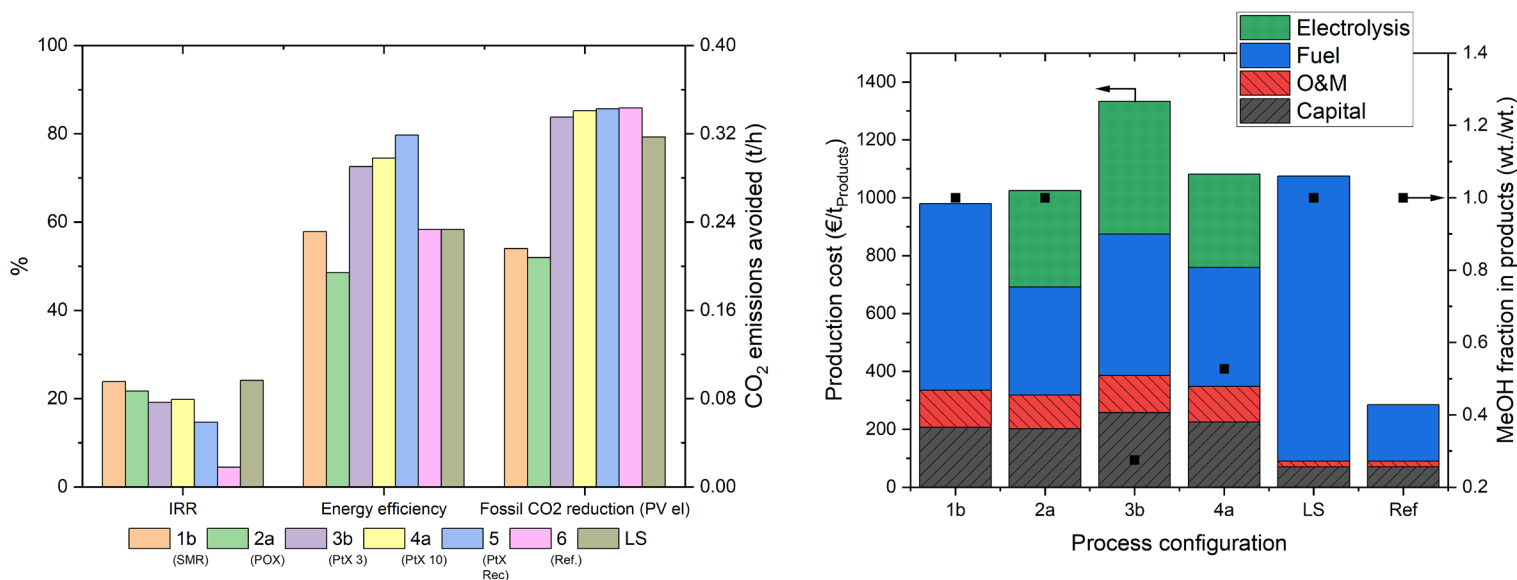


Figure 11 a) Comparison of the internal rate of return (IRR), energy efficiency and CO<sub>2</sub> balance for the most relevant process configurations considered in this study (data for large scale plant elaborated from <sup>31,44,45</sup>). The calculated avoided CO<sub>2</sub> are obtained from comparison with the use of biogas in CHP. b) Production cost of methanol from biogas for the most relevant process configurations considered in this study (product includes both methane and methanol).

## 4. Conclusions

In this study, we provided a comprehensive eco-techno-economic analysis of the possible routes for the production of methanol from biogas. We analysed the possible process options for methanol synthesis via small-scale steam reforming, direct CO<sub>2</sub> hydrogenation and centralised production from biomethane, calculating the key performance indicators and highlighting the optimal conditions for each process. With the favourable economic assumptions made (methanol price=0.2 €/kWh and electricity price=0.05 €/kWh), all the processes can be operated profitably. Due to the different cost of hydrogen, the small-scale synthesis via steam reforming is economically favoured over the direct CO<sub>2</sub> hydrogenation. However, this latter process shows better energy efficiency and carbon balance, which may result in a better economic performance in case of changes in the economic and regulatory framework (i.e. lower price of electricity or introduction of a carbon tax). We also observed that the economic performance of a large-scale centralized methanol synthesis plant is not significantly better than the localized options if the production is based on biomethane. This shows that the discrimination among the possible green methanol synthesis routes will be determined by the policies in terms of incentives for the use of

cleaner feedstock or for the coupling of methanol synthesis and energy storage. In the former case, incentives towards the valorisation of renewable resources, such as biogas/biomethane, would decide the match in favour of the steam-reforming configuration. In the latter case, a more favourable framework for the use of excess electricity for hydrogen production, would significantly improve the economic performance of the methanol production via power-to-X. In any case, we demonstrated that all the proposed processes are technically sound and feasible and that the discrimination among the options depends on the specific conditions of the plant location. The determination of the most suitable process configuration therefore depends from the concrete legal and incentive framework in the location of the plant. Furthermore, we observed that the cascade process might be further improved in terms of capital cost requirements, resulting in an additional potential for economic optimization.

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### **CRedit authorship contribution statement**

**Emanuele Moioli:** Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Funding acquisition. **Tilman Schildhauer:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Funding acquisition.

### **Declaration of Competing Interest**

The authors declare no conflict of interest.



## Supporting Information

Detailed process models and result for all the process configurations analysed in the manuscript.

This information is available free of charge via the Internet at <http://pubs.acs.org/>

## Nomenclature

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

$C_{BM}$  = Bare Module Cost (\$)

$C_{BM, today}$  = Current Bare Module Cost (\$)

$C_p$  = Equipment Purchase Cost (\$)

$F$  = Stoichiometric Factor ( $H_2:CO_2$ )

$F_C$  = Cost Factor

$F_e$  = Exchange Rate

$F_M$  = Material Factor

$F_P$  = Pressure factor

$W_p$  = Compression work (kJ/mol)

$X_i$  = Conversion of the component  $i$

$Y_i$  = Yield of the component  $i$

$a$  = Plant Lifetime (years)

$i$  = Interest Rate (%)

$\Delta H^R$  = reaction enthalpy (kJ/mol)

## References

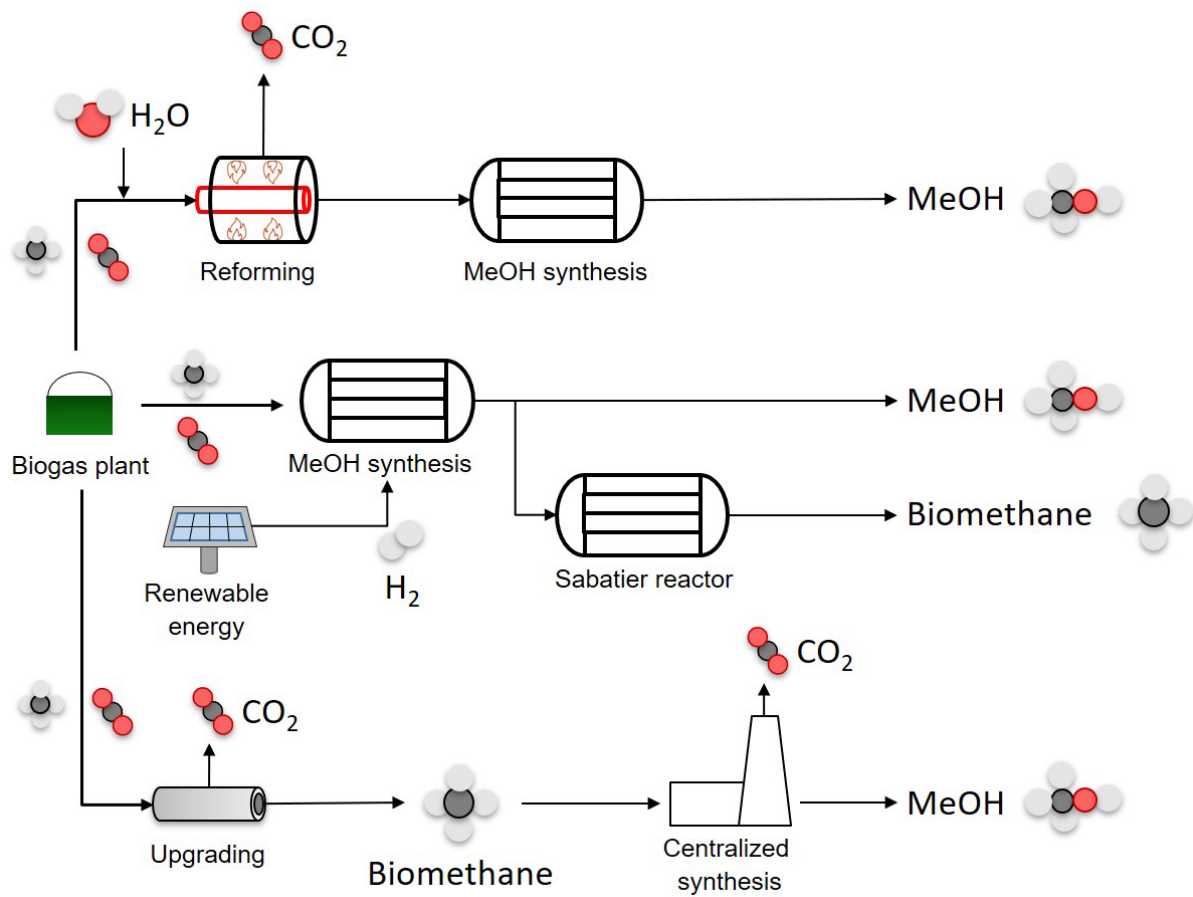
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Which process to produce methanol from biogas?