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Bio-methane and bio-methanol co-production from biogas: A profitability analysis to explore new sustainable chemical processes

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Abstract

Herein a potential synergy between biogas upgrading and CO₂ conversion to bio-methanol is investigated. This novel idea arises as an alternative path to the traditional biogas – to – bio-methane route which involves CO₂ separation. In this work a techno-economic analysis of the process was performed to study the profitability for potential investors. A total of 15 scenarios were analysed. Different biogas plant sizes were examined as baseline scenarios: 100, 250, 500, and 1000 m³/h. Furthermore the potential effect of governmental incentives through bio-methane subsidies (feed-in tariffs

and investment percentage) was studied. Finally a sensitivity analysis was developed to study the effect of keyparameters. The results of the baseline scenarios demonstrated that not profitable results can be obtained without subsidies. Bio-methane subsidies as feed-in tariffs proved to be effective for the 500 and 1000 m³/h plant sizes. For a feed-in tariff subsidy of 40 €/MW, 500 m³/h biogas production plants are remarkably profitable (net present value equal to 3106 k€). Concerning 1000 m³/h biogas production plants, 20 €/MW of subsidies as feed-in tariffs gives similar net present value result. Our results point out that only big biogas production can produce bio-methanol at profitable margins under 90-100% of investment subsidied. The sensitivity analysis showed that electricity, natural gas and bio-methanol price can affect considerably to the overall profitability, converting predicted positive cases in negative scenarios.

Highlights

- Novel strategy for synergizing bio-methane and bio-methanol production
- Profitability evaluation of the novel green process
- Analysis of subsidies effect on the process
- Small biogas plants are unprofitable without remarkable subsidies
- Large plants are deemed profitable when affordable subsidies are implemented

Keywords

Bio-methane production; Bio-Methanol; Biogas upgrading; CO₂ utilisation; Green-Chemicals; Waste valorization;

1. Introduction

The growing trend of renewable energy consumption has remarkably increased during the last decades (Destek and Sinha, 2020; Zafar et al., 2019). This acceleration responds mainly to two factors: depletion of fossil fuels; and greater concentration of greenhouse gases (GHG) in the atmosphere. This scenario has motivated the scientific community to intensify the study of sustainable development policies (Bilgili et al., 2017; García-Gusano et al., 2017). The movement of current government towards more environmental-friendly energy consumption policies relies on two key factors: maturity of technology and economy. Renewable energy technologies have proved their readiness for replacing traditional fossil fuels (Mas'ud et al., 2015; Mondal et al., 2016). Indeed, the technology maturity explains the above mentioned growing trend on renewable sources. Nevertheless, sustainable energy production costs are still barely competitive in comparison with traditional energy sources (Amran et al., 2020; Gong et al., 2019).

Among the renewable energy platforms, biogas production from biomass stands out due to its double-fold benefit: (i) avoiding the treatment of large amount of organic wastes; and (ii) production of a gas product with an acceptable calorific value. Biogas is essentially composed by CH₄ (60%) and CO₂ (40%) (Baena-Moreno et al., 2019a), although it may also contain impurities such as H₂S, CO, H₂O, N₂, H₂, NH₃ and siloxanes (le Saché et al., 2019). Biogas can be used in a combined heat and power (CHP) unit for electricity production. This process releases the CO₂ contained in the biogas to the atmosphere, making this option a not 100% green electricity production path. Another interesting alternative is to upgrade biogas via CO₂ scrubbing, obtaining a high purity bio-methane that can partially replace natural gas minimising the consumption of natural resources (Baena-Moreno et al., 2019b, 2019c; Bose et al., 2019). However, the upgrading costs still hampers its implementation at commercial scale. Only in those countries where governmental incentives are offered, bio-methane production plants are more abundant. There are two kind of governmental incentives typically applied: bio-

methane subsidies through feed-in tariffs or via investment percentage. The first one put an extra-price for each megawatt injected to the natural gas grid, whereas the second one provides to the investor a percentage of the total investment cost. Nevertheless, there is much debate about the biogas incentives to favour the technology take off. Indeed, only a few studies can be found dealing with these kind of analyses (Cucchiella et al., 2019; Cucchiella and D'Adamo, 2016; D'Adamo et al., 2019; Ferella et al., 2019).

CO₂ utilisation from biogas mixture is a promising alternative that may help to circumvent biogas upgrading costs (Baena-Moreno et al., 2019d; Baena-Moreno et al., 2019e; Bennett et al., 2014; Fernández-Dacosta et al., 2018). Multiple CO₂ capture and utilisation technologies can be found in the literature (Baena-moreno et al., 2018; Le Saché et al., 2018; Price et al., 2019; Vega et al., 2020; N. Zhang et al., 2020), wherein for example the production of carbonates, syngas, hydrates or methanol take a leading role (Fabián-Anguiano et al., 2019; Lee et al., 2020; Samimi et al., 2018; Stroud et al., 2018; Z. Zhang et al., 2020). Up till now, the implementation of CO₂ utilisation from flue gases at industrial scale is not feasible since the worldwide amount of CO₂-derived products would be much higher than the market needs. Nevertheless, in the case of biogas upgrading, the amount of CO₂ available as raw material (and therefore the CO₂-derived products) could be fittable in the market needs. Moreover, the overall economic performance of the biogas upgrading process could be balanced by selling the CO₂-derived product.

Regrettably, there is a lack of techno-economic evaluations of biogas upgrading and CO₂ utilisation costs in the literature. The work herein presented aims to encourage researchers in this area to fill this knowledge gap and contribute to the successful development of biogas technologies. Our proposal deals with the profitability analysis of biogas upgrading to produce bio-methane and the simultaneous production of bio-methanol from the extracted CO₂. Under these premises and to the best of authors' knowledge, no works have been performed to date in this direction. Bio-methanol

production from CO₂ was selected since methanol is an important commodity and its production process via CO₂ hydrogenation has been previously addressed (Pérez-Fortes et al., 2016a; Van-Dal and Bouallou, 2013). The overall process scheme is represented in Figure 1. In the process three different stages can be identified: biogas upgrading, electrolysis and bio-methanol production. Biogas upgrading allows the production of bio-methane which can be injected into the natural gas grid for replacing natural gas. On the other hand, a high purity CO₂ stream is obtained from the upgrading stage. Obtaining bio-methanol from CO₂ requires a hydrogen source. In our approach, hydrogen is generated via electrolysis using renewable energy resources. Finally, the last stage aims to combine both the CO₂ obtained in the biogas upgrading stage and the hydrogen produced via water electrolysis to obtain bio-methanol as value added ending product.

Nowadays, the global methanol production reaches 140 Mt (Statista, 2020), of which 90% is produced from natural gas (Dalena et al., 2018). Natural gas reforming to methanol includes three main steps which are synthesis gas production, syngas conversion into crude methanol and methanol purification through a complex distillation system (Dalena et al., 2018). Even though the conversion – flow rates of this path are high, methanol from natural gas reforming entails a significantly high carbon footprint (Li et al., 2018). Thus, renewable alternatives for methanol production needs to be explored (Rivarolo et al., 2016). In this sense, despite our proposal deals with lower plant capacities, producing methanol from biomass is still appealing since it might remarkably reduce the environmental impact compared to the traditional fossil fuel route.

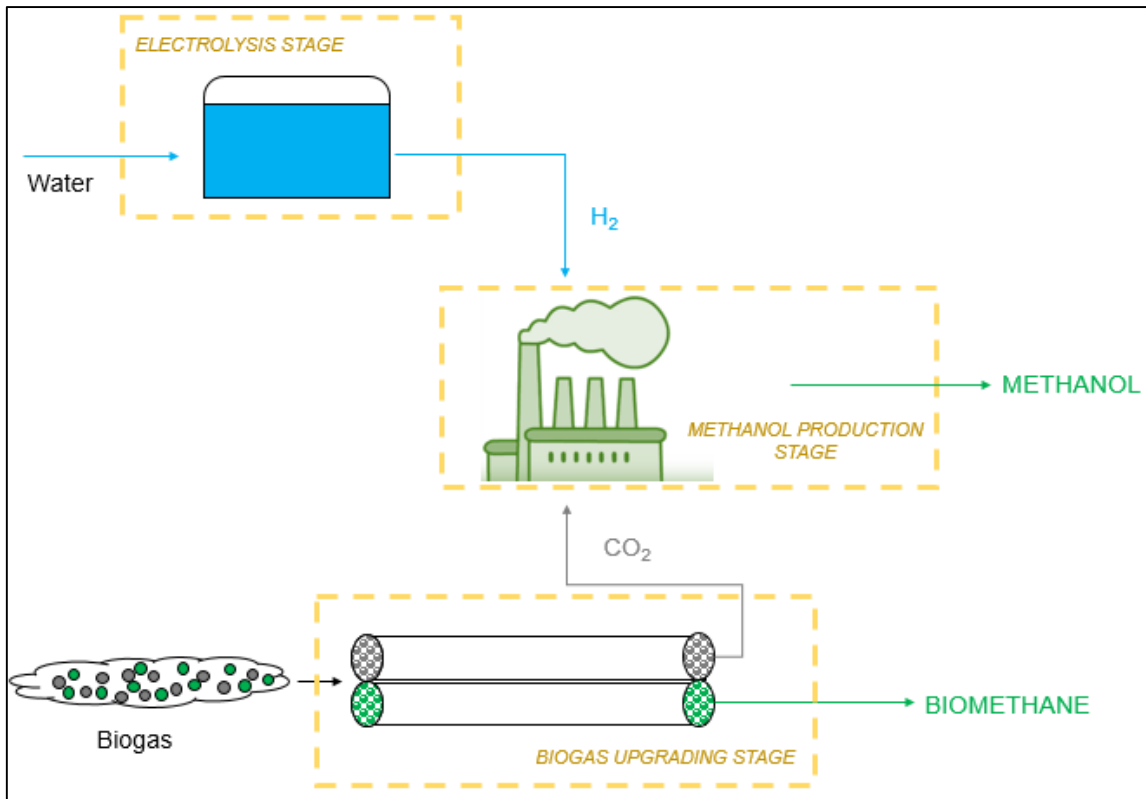


Figure 1. Biogas upgrading and bio-methanol production from CO_2 process scheme.

The main goal of our work is the economic evaluation of the process described in Figure 1 in terms of profitability. Our study was aimed to cover different casuistics, as for example different plant sizes or natural gas – electricity prices. Thus, our work provides useful data for researchers exploring this topic. Profitability study was performed through the well-established Discounted Cash Flow (DCF) method. DFC method was applied including a exhaust analysis of the typical indicators: Net Present Value (NPV), Discounted Payback Time (DPBT), Internal Rate of Return (IRR) and Profitability Index (PI). Four biogas production plant sizes have been examined. The sizes selected were in agreement with the classification presented in a previous work (Cucchiella and D'Adamo, 2016): small plants (100 m^3/h , 250 m^3/h), medium plants (500 m^3/h), and big plants (1000 m^3/h). The hypothetical bio-methane & bio-methanol production plant was assumed to be built in Spain for sake of data selection (i.e. natural gas price, electricity price and labour cost). The influence of governmental incentives through bio-methane

subsidies on profitability results are also analysed. Both existing types of subsidies (feed-in tariffs and investment percentage) were evaluated. This point aims to serve as a useful guide for policy-makers because it allows: 1) Estimating the subsidies values needed to reach profitability in bio-methane production plants; and 2) Focusing on bio-methane production plant sizes which are more prone to be profitable. Furthermore, an exhaust sensitivity analysis to examine the influence of the main parameters on profitability results was performed in agreement with the scenarios explained in section 2.3.

2. Methodology

2.1 Process description and modelling

The process described in Figure 1 was divided into three differentiated stages which are biogas upgrading, electrolysis and bio-methanol production. It was assumed that the biogas production plant was already operating and therefore there was no need of capital investment. Moreover, it was assumed an ideal biogas composition of 60% CH₄ – 40% CO₂ composition. Biogas upgrading stage produces bio-methane, and the separated CO₂ is fed to the bio-methanol production stage. Membrane technology is one of the most promising technologies for biogas upgrading since it allows to reduce the investment cost and obtain a high purity bio-methane stream (Cucchiella et al., 2019). Therefore, membrane technology was selected for the purpose of our work. As there are a wide variety of data available in the literature for the sizes proposed (Cucchiella et al., 2019; Cucchiella and D'Adamo, 2016), they were directly implemented in the economic model. The electrolysis plant selected for the production of hydrogen was an alkaline electrolyser (AE) since it is the one recommended by suppliers because of its commercial availability (Bolat and Thiel, 2014). In agreement with previous works, a small scale electrolyser of 0.6 MW is enough to feed up the needs of the bio-methanol production plant (Pérez-Fortes et al., 2016b). Regarding the bio-methanol production stage, no

economic data were found for the sizes herein considered. Therefore, this stage was first modelled techno-economically in agreement with data previously published for CO₂ hydrogenation to bio-methanol (Pérez-Fortes et al., 2016a; Van-Dal and Bouallou, 2013). Further information of the data and the process layout used are detailed in: “Appendix I. Modelling and economic data of bio-methanol production stage”.

2.2 Economic model assessment

Eqs. (1)-(4) describe the profitability indicators selected for the development of DFC method. DFC method is based on the difference between the cash inflows (I_t) and the cash outflows (O_t). The discount rate parameter (r_d) has the function of reflecting the time effect. More parameters included in these equations are: the project lifetime (n); the present time (t); and the investment cost (C_{inv}). I_t calculation is described in Eq. (5) and it consists on: bio-methane sale ($R_{bio-methane}$); governmental incentives obtained through bio-methane subsidies ($R_{subsidies}$) (only in the scenarios needed); and bio-methanol sale ($R_{bio-methanol}$). $R_{bio-methane}$ is obtained through the bio-methane produced ($Q_{bio-methane}$) and the natural gas price (p_{NG}) (Eq. (6)). In those scenarios where bio-methane subsidies are considered, they are calculated considering the specific price of subsidy ($p_{subsidies}$) (Eq. (7)). A similar equation is employed for obtaining the revenues of bio-methanol selling (Eq. (8)), which depends on bio-methanol produced ($Q_{bio-methanol}$) and bio-methanol price ($p_{bio-methanol}$).

$$NPV = \sum_{t=0}^n \frac{I_t - O_t}{(1+r_d)^t} \quad (1)$$

$$\sum_{t=0}^{DPBT} \frac{I_t - O_t}{(1+r_d)^t} = 0 \quad (2)$$

$$\sum_{t=0}^n \frac{I_t - O_t}{(1+IRR)^t} = 0 \quad (3)$$

$$PI = \frac{\sum_{t=0}^n \frac{I_t - O_t}{(1+r)^t}}{C_{inv}} \quad (4)$$

$$I_t = R_{\text{bio-methane}} + R_{\text{subsidies}} + R_{\text{bio-methanol}} \quad (5)$$

$$R_{\text{bio-methane}} = Q_{\text{bio-methane}} * p_{\text{NG}} \quad (6)$$

$$R_{\text{subsidies}} = Q_{\text{bio-methane}} * p_{\text{subsidies}} \quad (7)$$

$$R_{\text{bio-methanol}} = Q_{\text{bio-methanol}} * p_{\text{methanol}} \quad (8)$$

For the calculation of O_t , Eq. (9) was employed. It is formed by the costs of the three different stages defined, as described by each subscript. All the parameters included in Eq. (9) were obtained with Eq. (10)-(31). The correspondences of each subscript are the following: “BU” corresponds to the biogas upgrading stage; “EL” corresponds to the electrolysis stage; and “MP” corresponds to the bio-methanol production stage. The common costs of each stage are: the investment (C_{inv}), which is supposed to be covered by a third party loan (C_{loan}); the interest of loan (C_{il}); maintenance and overhead (M&O) (C_{mo}); depreciation (C_{df}), insurance (C_{ins}), installation (C_{inst}) and electricity (C_e). The investment costs of the bio-methanol production stage were estimated in agreement with the modelling results. The economic data and parameters used for the bio-methanol production stage investment can be checked in Appendix I. The labour cost (C_{lab}) is a general plant cost and the number of operators is assumed per size of plant. It was assumed that the distance from the natural gas grid to the plant is minimal so the cost of bio-methane transportation was not included.

$$O_t = (C_{loanBU} + C_{ilBU} + C_{moBU} + C_{dfBU} + C_{insBU} + C_{eBU}) + (C_{loanEL} + C_{ilEL} + C_{moEL} + C_{dfEL} + C_{insEL} + C_{eEL}) + (C_{loanMP} + C_{ilMP} + C_{moMP} + C_{dfMP} + C_{insMP} + C_{eMP}) + C_{lab} \quad (9)$$

$$C_{\text{loanBU}} = \frac{C_{\text{invBU}}}{n_1} \quad (10)$$

$$C_{\text{ilBU}} = [C_{\text{invBU}} - C_{\text{loanBU}} * (t + 1)] * r_{\text{int}} \quad (11)$$

$$C_{\text{moBU}} = C_{\text{invBU}} * p_{\text{mo}} \quad (12)$$

$$C_{\text{dfBU}} = C_{\text{loanBU}} * p_{\text{df}} \quad (13)$$

$$C_{\text{insBU}} = C_{\text{invBU}} * p_{\text{ins}} \quad (14)$$

$$C_{\text{instBU}} = C_{\text{invBU}} * p_{\text{inst}} \quad (15)$$

$$C_{\text{eBU}} = Q_{\text{biogas}} * C_{\text{ueBU}} * p_{\text{e}} \quad (16)$$

$$C_{\text{loanEL}} = \frac{C_{\text{invEL}}}{n_1} \quad (17)$$

$$C_{\text{ilEL}} = [C_{\text{invEL}} - C_{\text{loanEL}} * (t + 1)] * r_{\text{int}} \quad (18)$$

$$C_{\text{moEL}} = C_{\text{invEL}} * p_{\text{mo}} \quad (19)$$

$$C_{\text{dfEL}} = C_{\text{loanEL}} * p_{\text{df}} \quad (20)$$

$$C_{\text{insEL}} = C_{\text{invEL}} * p_{\text{ins}} \quad (21)$$

$$C_{\text{instEL}} = C_{\text{invEL}} * p_{\text{inst}} \quad (22)$$

$$C_{\text{eEL}} = Q_{\text{hydrogen}} * C_{\text{ueEL}} * p_{\text{e}} \quad (23)$$

$$C_{\text{loanMP}} = \frac{C_{\text{invMP}}}{n_1} \quad (24)$$

$$C_{\text{ilMP}} = [C_{\text{invMP}} - C_{\text{loanMP}} * (t + 1)] * r_{\text{int}} \quad (25)$$

$$C_{\text{moMP}} = C_{\text{invMP}} * p_{\text{mo}} \quad (26)$$

$$C_{\text{dfMP}} = C_{\text{loanMP}} * p_{\text{df}} \quad (27)$$

$$C_{\text{insMP}} = C_{\text{invMP}} * p_{\text{ins}} \quad (28)$$

$$C_{\text{instMP}} = C_{\text{invMP}} * p_{\text{inst}} \quad (29)$$

$$C_{\text{eMP}} = Q_{\text{bio-methanol}} * C_{\text{ueMP}} * p_e \quad (30)$$

$$C_{\text{lab}} = C_{\text{labu}} * n_{\text{op}} \quad (31)$$

The parameters from Eq. (10)-(31) which have not been described previously are the following by order of appearance: years of loan payback (n_l); percentage of M&O (p_{mo}); percentage of depreciation (p_{df}); percentage of insurance (p_{ins}); percentage of installation (p_{inst}); unitary electricity cost of biogas upgrading, electrolysis or bio-methanol production (C_{ueBU} ; C_{ueEL} ; C_{ueMP}); electricity price (p_e); unitary labour cost (C_{labu}); and operators number (n_{op}). All the inputs needed to solve the feasibility study are reported in Table 1.

Table 1. Inputs used in the economic feasibility study.

Data	Value	Reference
p_{NG} (€/MWh)	18.48	(European Commission, 2019)
p_{methanol} (€/t)	350	(Pérez-Fortes et al., 2016b; Wiesberg et al., 2016)
C_{invBU} (€/m³/h)	100 m ³ /h – 6000 250 m ³ /h – 4500 500 m ³ /h – 2250 1000 m ³ /h – 1500	(Cucchiella and D'Adamo, 2016)
C_{invEL} (€/kW)	1980	(Pérez-Fortes et al., 2016b)
C_{invMP} (k€)	100 m ³ /h – 1639 250 m ³ /h – 1712 500 m ³ /h – 1799 1000 m ³ /h – 1932	See Appendix I
n_l (y)	15	(Cucchiella et al., 2019)
n	20	Assumed
r_d (%)	5	(Ferella et al., 2019)
r_{int} (%)	3	(Cucchiella et al., 2019)
p_{mo} (%)	10	(Cucchiella et al., 2018; Pérez-Fortes et al., 2016a)
p_{df} (%)	20	(Cucchiella et al., 2015; Ferella et al., 2019)
p_{ins} (%)	1	(Cucchiella and D'Adamo, 2016)
p_{inst} (%)	20	(Pérez-Fortes et al., 2016a, 2016b)
C_{ueBU} (kWh/m³ biogas)	0.29	(Cucchiella and D'Adamo, 2016)
C_{ueEL} (kWh/KW Hz)	1.62	(Pérez-Fortes et al., 2016b)
C_{ueMP} (MWh/t bio-methanol)	0.37	(Pérez-Fortes et al., 2016a; Van-Dal and Bouallou, 2013)
p_e (€/kWh)	0.13	(PORDATA, 2019)

C_{labu} (€/y/worker)	15750	(BOE, 2018)
n_{op} (worker)	100 m ³ /h – 6 250 m ³ /h – 7 500 m ³ /h – 8 1000 m ³ /h – 10	Assumed
n_{wh} (h/y)	8000	Assumed

2.3 Definition of scenarios

Table 2 reflects the main assumptions imposed for each scenario. Four different biogas production plants capacities (100, 250, 500 and 1000 m³/h) were selected in agreement with different sizes described in the literature (Cucchiella and D'Adamo, 2016). These four capacities were analysed in scenarios 1-4, without considering any bio-methane subsidies. The effect of bio-methane subsidies as feed-in tariffs were analysed in scenarios 5-8, whereas the subsidies as investment percentage were studied in scenarios 9-12. Afterwards a sensitivity analysis of the main parameters was performed. These scenarios correspond to 13-15 from Table 2. Even though current values of these parameters were selected for the present study, its variation could affect considerably to the profitability of the project. Therefore electricity, natural gas and bio-methanol price were examined to predict the potential effect of their fluctuations on the profitability performance.

Table 2. Scenarios and assumptions defined.

Scenario	Bio-methane capacity (m ³ /h)	Bio-methane subsidies / Type / Values (units)	Sensitivity analysis	Parameter analyzed / Value	Purpose
1	100	No / -	No	-	Baseline case and plant size comparison
2	250	No / -	No	-	
3	500	No / -	No	-	
4	1000	No / -	No	-	
5	100	Yes / Feed-in tariffs / 10-80 (€/MW)	No	-	Quantification of bio-methane subsidies (feed-in tariffs) needed to reach profitability for each capacity
6	250	Yes / Feed-in tariffs / 10-80 (€/MW)	No	-	
7	500	Yes / Feed-in tariffs / 10-80 (€/MW)	No	-	
8	1000	Yes / Feed-in tariffs / 10-80 (€/MW)	No	-	
9	100	Yes / Investment percentage / 10-90 (%)	No	-	Quantification of bio-methane subsidies (investment percentage) needed to
10	250	Yes / Investment percentage / 10-90 (%)	No	-	

11	500	Yes / Investment percentage / 10-90 (%)	No	-	reach profitability for each capacity
12	1000	Yes / Investment percentage / 10-90 (%)	No	-	
13	500-1000	Yes / Feed-in tariffs / 20 (€/MW)	Yes	Electricity price / ± 50 % of the defined value	Effect of electricity price
14	500-1000	Yes / Feed-in tariffs / 20 (€/MW)	Yes	Natural gas price / ± 50 % of the defined value	Effect of natural gas price
15	500-1000	Yes / Feed-in tariffs / 20 (€/MW)	Yes	Bio-methanol price / ± 50 % of the defined value	Effect of bio-methanol price

3. Results

3.1 Baseline case: the importance of plant size

Figures 2 and Table 3 summarise the results of the profitability analysis performed for the four different biogas plant sizes defined in scenarios 1-4. Concerning Figure 2, the NPV results obtained are negative for all the sizes herein analysed. PI, DPBT and IRR (Table 3) confirm the poor values obtained, making fruitless the potential investment in this kind of renewable energy under the characteristics of these scenarios. These results are in agreement with the current status of bio-methane production plants in those countries where no governmental incentives are provided. Indeed, the profitability of bio-methane plants is usually linked to subsidies, as verified in previous works (Cucchiella et al., 2018; Cucchiella and D'Adamo, 2016). In agreement with PI values showed in Table 3, a bigger plant size favors the profitability as PI value increase with the size. Nevertheless, NPV values showed in Figure 2 do not progress positively along with biogas plant size. This fact is probably caused by the influence of other costs – revenues for each situation. In light of these results, we will analyze the costs and revenues leading to this unrewarding situation.

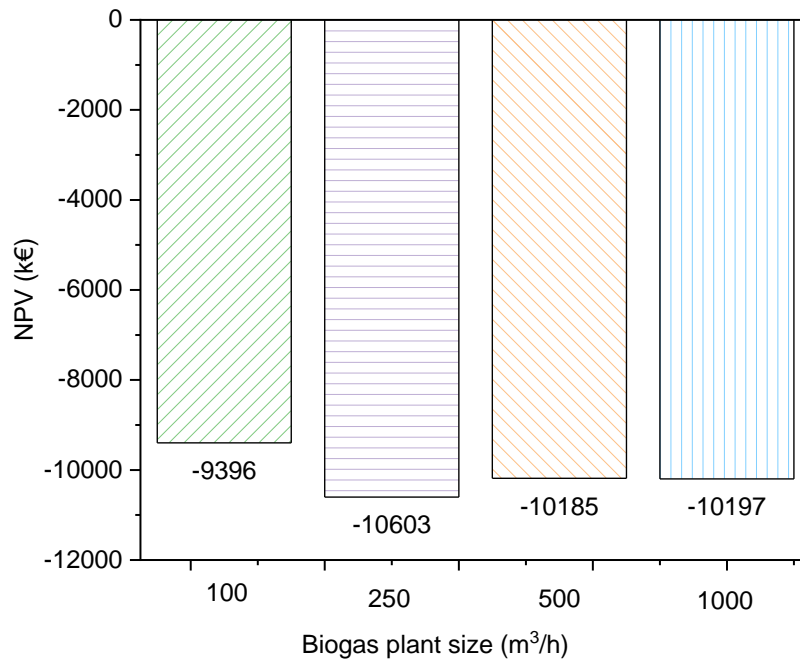


Figure 2. NPV results for scenarios 1-4.

Table 3. DPBT, IRR and PI results for scenarios 1-4.

Biogas plant size (m ³ /h)	DPBT (years)	IRR	PI
100	n.a.	n.a.	-2.74
250	n.a.	n.a.	-2.63
500	n.a.	n.a.	-2.48
1000	n.a.	n.a.	-2.21

***n.a: not available because the investment is not recovered or the NPV is never equal to zero.**

Figure 3 reveals the cost breakdown obtained for each plant size analysed. For comparison purposes, investment costs were annualized. As predicted by PI results, investment percentage decreases considerably as the biogas plant size increases. The highest investment costs are related to the bio-methanol stage, whereas biogas upgrading and electrolysis stages share the second and third position depending on the plant size. Electrolysis investment cost is higher than biogas upgrading investment cost for small sizes (100 and 250 m³/h), while this order shifts for medium and big plants. The results obtained for M&O show essentially a parallel behaviour to investment costs. On

the contrary, electricity cost clearly increases from 12% (100 m³/h) to 49% (1000 m³/h). This fact is caused by two actions: there is a higher biogas flow to be treated; and the need of producing more hydrogen in the electrolysis stage to fulfil the bio-methanol production requirements. This makes electricity costs to be higher than M&O costs for the largest capacities. It is also the reason why NPV and PI show different tendencies.

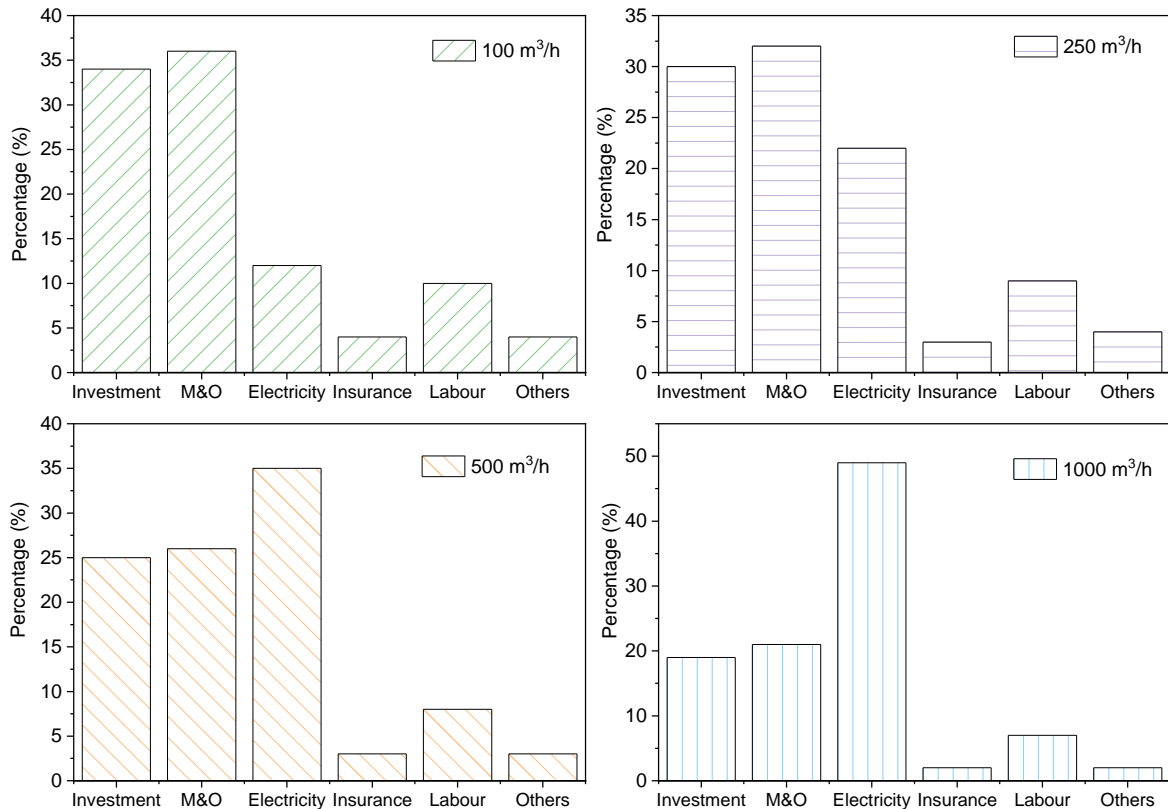


Figure 3. Cost breakdown for each biogas plant size.

Regarding the revenues, injecting bio-methane to the natural gas grid supposes the 72% of the total whereas selling the produced bio-methanol represents the 28%. The revenues for selling bio-methanol are lower than the bio-methanol production costs for a typical year. Therefore, the production of bio-methanol from the separated CO₂ does not seem to be profitable in the biogas context. Hence one may argue that there are no reasons to synergise CO₂ utilization and biogas upgrading to bio-methane under the studied circumstances. Nevertheless, as explained in the Introduction section, two kinds of governmental subsidies are typically applied. Bio-methane subsidies as feed-in tariffs

would not reduce the difference between bio-methanol revenues & costs, but bio-methane subsidies as percentage of investment can balance the benefits obtained in this stage. We will analyse these inputs in section 3.3.

3.2 Influence of governmental incentives

3.2.1 Subsidies through feed-in tariffs

Governmental incentives through feed-in tariffs are a common tool of policy-makers to boost the use of renewable energy. These policies are well-extended both in already developed countries (i.e. Germany (Baur and Uriona M., 2018; Böhringer et al., 2017) or Italy (Patrizio et al., 2017)), and in developing countries (i.e. South Africa (Eberhard and Kåberger, 2016) or Sri Lanka (Shi et al., 2018)). The reason is simple: the use of renewable energy reduces the energy dependence from big energy producers. Apropos the subsidies for bio-methane production some European countries have already implemented a strong strategy to utilise this renewable energy vector. For example, Austria bio-methane's subsidies are around 12.51–16.51 €/MW while Slovakia subsidies' are around 10.75 €/MW (Pablo-Romero et al., 2017). From the profitability analysis carried out in section 3.1 of the present work, it seems clear that the existence of subsidies is required. As discussed in the Introduction section, the value of subsidies is a topic of discussion and it depends on multiple country-dependant parameters (i.e. national salaries, natural gas price and electricity price). In this sense, this section provides an estimation of the feed-in tariffs subsidies that would be needed for reaching profitability by plant size. Figure 4 showcases the NPV evolution with subsidies value for each plant size and Table 4 collects the PI results obtained.

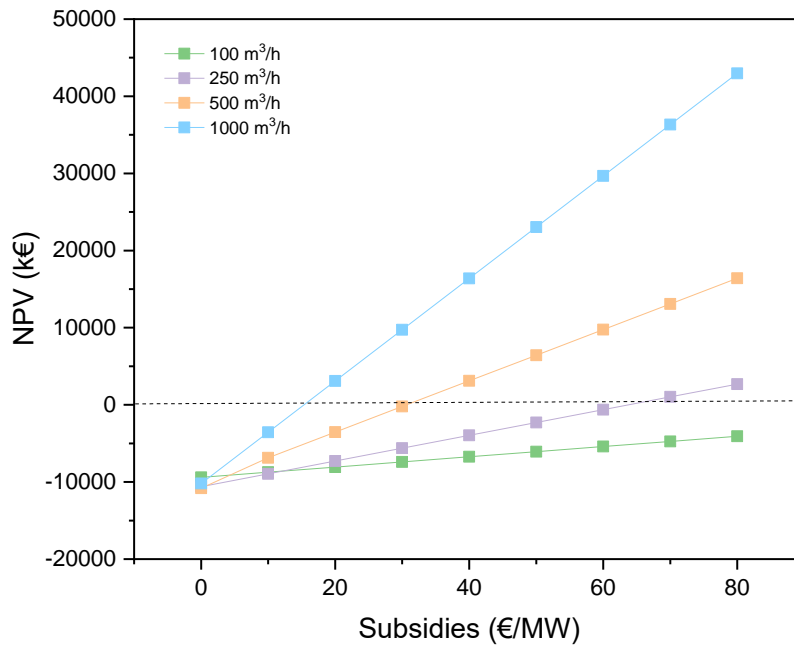


Figure 4. NPV evolution of scenarios 5-8 with bio-methane subsidies through feed-in tariffs.

Table 4. PI results obtained for bio-methane subsidies through feed-in tariffs. Scenarios 5-8.

Subsidies (€/MW)	100 m³/h	250 m³/h	500 m³/h	1000 m³/h
0	-2.74	-2.63	-2.48	-2.21
10	-2.55	-2.22	-1.67	-0.77
20	-2.35	-1.81	-0.86	0.67
30	-2.16	-1.40	-0.05	2.1
40	-1.97	-0.98	0.76	3.54
50	-1.77	-0.57	1.56	4.98
60	-1.58	-0.16	2.37	6.42
70	-1.38	0.25	3.18	7.86
80	-1.19	0.67	3.99	9.3

The subsidies values chosen for performing the analysis were in a wide range (10-80 €/MW) to provide a wider perspective. As can be seen from the results herein presented, the subsidies effect on profitability is strongly dependent on the biogas plant size. This dependence is boosted when subsidies are increased. For example Figure 4 reveals an almost null difference between small plants and big plants for the lowest subsidies,

whereas for high subsidies the difference is remarkable. Indeed, the smallest plants (100 m³/h, scenario 5) does not reach profitable results even at 80 €/MW. Increasing the size plant to 250 m³/h (scenario 6) would not solve the profitability problems since a subsidy of around 64 €/MW would be needed, which is hardly tolerable. Reasonable values for subsidies as feed-in tariffs are 10-40 €/MW, although this may depend on several factors. For these values only medium and big plants would be profitable. For 500 m³/h (scenario 7) the first NPV positive value is obtained for 30.66 €/MW of subsidie. For this value, a DPBT of 20 years would be needed to recover the investment. For the same plant size at 40 €/MW, 3106 k€ of NPV are obtained, with a PI of 0.76 and a DPBT of 5 years. These conditions are much more appealing for investors. Concerning the 1000 m³/h biogas production plant (scenario 8), 20 €/MW represents a compromise solution between investors and subsidies from governments. For this subsidies value, a PI value of 0.67 and NPV of 3095 k€ are obtained, which is both attractive and risky for the investor since a fluctuation for example in electricity price could reverse the benefits. Risky scenarios related to electricity, natural gas and bio-methanol prices are included in section 3.3.

3.2.2 Subsidies through investment percentages

The other type of governmental incentives for rewarding the production of renewable energy are subsidies through a percentage of investment. Albeit this kind of subsidies are unfrequent compared to feed-in tariffs, they could be helpful in those cases where the investment is the biggest part of the overall cost. Figure 5 and Table 5 present the profitability results of this work for the scenarios 9-12.

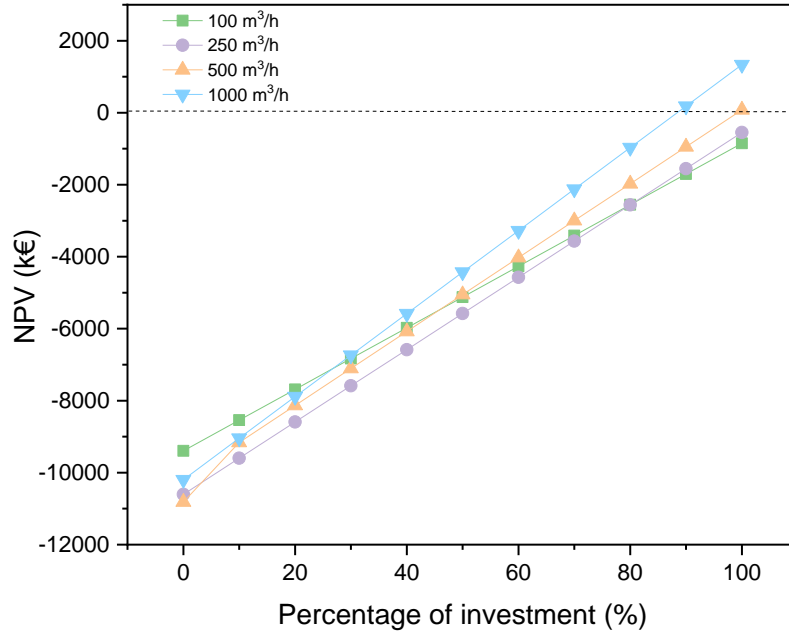


Figure 5. NPV evolution of scenarios 9-12 with bio-methane subsidies through percentage of investment.

Table 5. PI results obtained for bio-methane subsidies through percentage of investment. Scenarios 9-12.

Subsidies (%)	100 m³/h	250 m³/h	500 m³/h	1000 m³/h
0	-2.74	-2.63	-2.48	-2.21
10	-2.77	-2.65	-2.47	-2.18
20	-2.80	-2.67	-2.47	-2.13
30	-2.85	-2.69	-2.46	-2.08
40	-2.90	-2.73	-2.46	-2.01
50	-2.99	-2.77	-2.45	-1.92
60	-3.11	-2.84	-2.4	-1.77
70	-3.32	-2.94	-2.43	-1.53
80	-3.73	-3.18	-2.39	-1.05
90	-4.96	-3.86	-2.3	0.39
100	n.a.	n.a.	n.a.	n.a.

*n.a is a direct consequence of the PI formula. Please see section 2.2, Eq. (4) for a better understanding

Scenarios 9-12 (investment percentage) yield worse results than scenarios 5-8 (subsidies percentage). This observation confirms the reason why feed-in tariffs are much more frequently implemented than percentage of investment. Moreover, the use of feed-in tariffs forces the investor to run the bio-methane production plant to maintain

subsidies. Indeed, the overall efficiency of the plant is projected to be as high as possible to obtain the maximum quantity of bio-methane. This way we could substantially improve the overall performance of this production plants. Focusing on the results obtained in scenarios 9-12, NPV values (Figure 5) are only positive for the highest percentage of investment for medium and big plant sizes.

From the results obtained in Table 5 a curious discussion arises. As the percentage of investment subsidized increases, PI decreases for small and medium plant sizes (scenarios 9 and 10). This fact is due to the mathematical formula which defines PI (see Eq. (4), section 2.2). In these cases the investment decrease is higher than the NPV increase in percentage, which makes the approach less profitable at higher subsidies (according to PI indicator). For medium and bigger plants this unusual behavior is corrected as seen in Table 4.

3.3 Sensitivity analysis

Finally and to cover as many economic variables as possible, a sensitivity analysis of selected parameters was performed. The parameters studied were electricity price (scenario 13), natural gas price (scenario 14), and bio-methanol price (scenario 15). These parameters were chosen in agreement with the results obtained in the baseline scenarios (scenarios 1-4), which highlighted the importance of electricity costs and revenues. Figures 6, 7 and 8 show the NPV results obtained for scenarios 13, 14 and 15. As indicated in Table 2, the sensitivity analyses were performed on 500 m³/h and 1000 m³/h biogas production plants, assuming a feed-in tariffs subsidy of 20 €/MW. The reason is to examine cases which are close to a zero NPV value and then discuss the risk – opportunities of certain parameters.

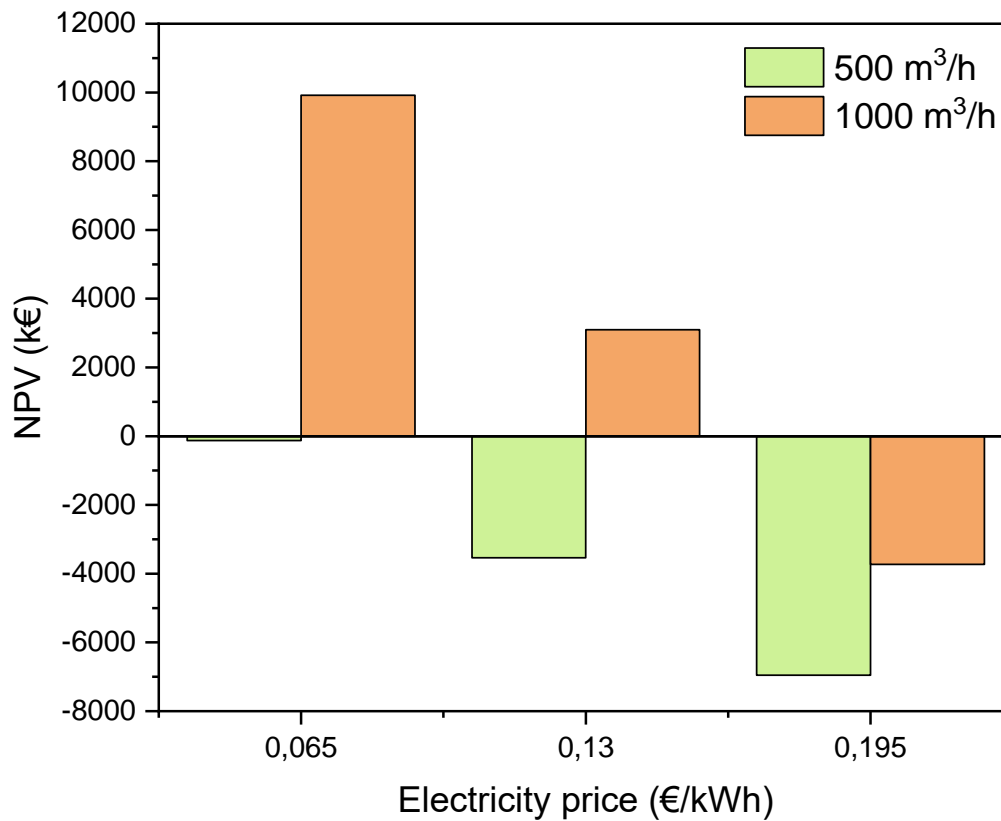


Figure 6. Influence of electricity price on NPV. Scenario 13.

Electricity costs were proved to be very important in scenarios 3 and 4 analysed in section 3.1. Inasmuch electricity price suffers important variations yearly, Figure 6 shows the effect of this parameter on the NPV in our combined bio-methane/bio-methanol production route. A reduction of 50% in the electricity price makes 500 m³/h plants almost reach profitability, whereas an increase of 50% would reverse to negative 1000 m³/h biogas production plants. Therefore, the influence of electricity price is very strong and some measures could be taken by policy-makers to prevent negative results in cases of electricity market price oscillation. Stability on electricity price would be the desirable scenario for investors to reduce risks.

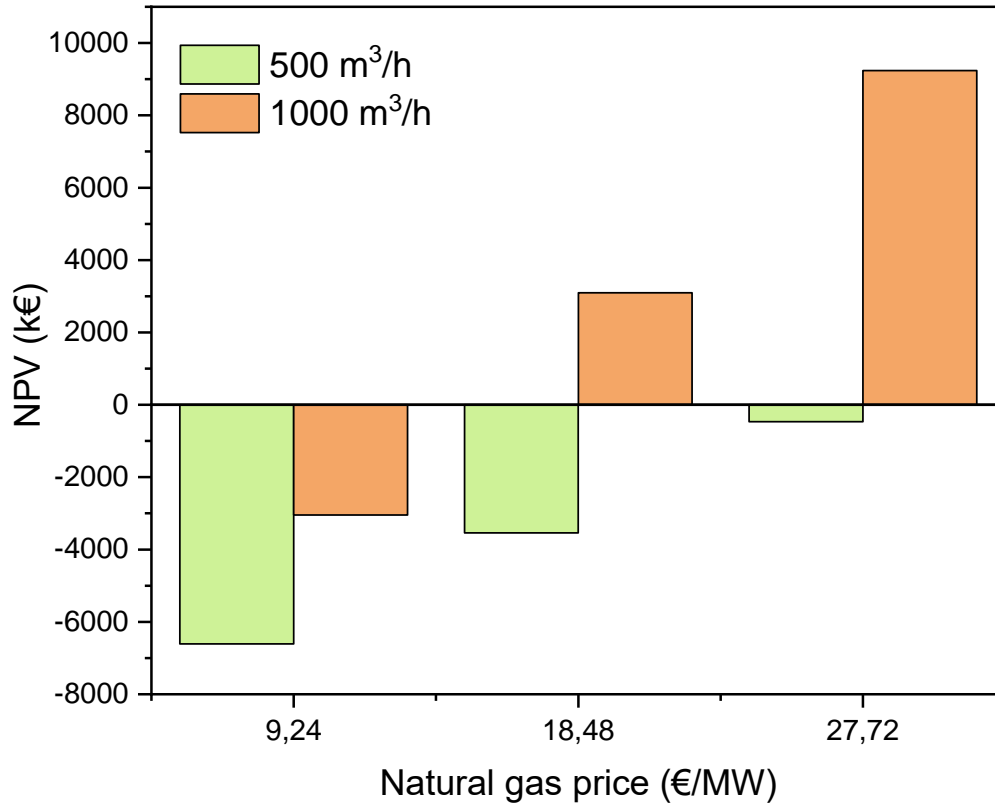


Figure 7. Influence of natural gas price on NPV. Scenario 14.

As for the influence of the natural gas price, an obvious reverse trend can be observed in Figure 7. A notable negative impact on NPV value for all the cases is observed when natural gas price is reduced. In some cases this reduction results in negative NPV as in scenario 14 depicted in Figure 7. Thereagain investors may lose or spark their apetitive for this combined bio-methane/bio-methanol technology depending on natural gas market oscilations. The policies and prices for natural gas are closely linked to international relationships and they are quite difficult to predict for a 20-year future. Moreover, the countries which lead the natural gas production (United States, Russia and Iran) have evidenced political differencies in many occasions. For intermediary countries which receive natural gas from producer countries, this is a hardly controllable factor.

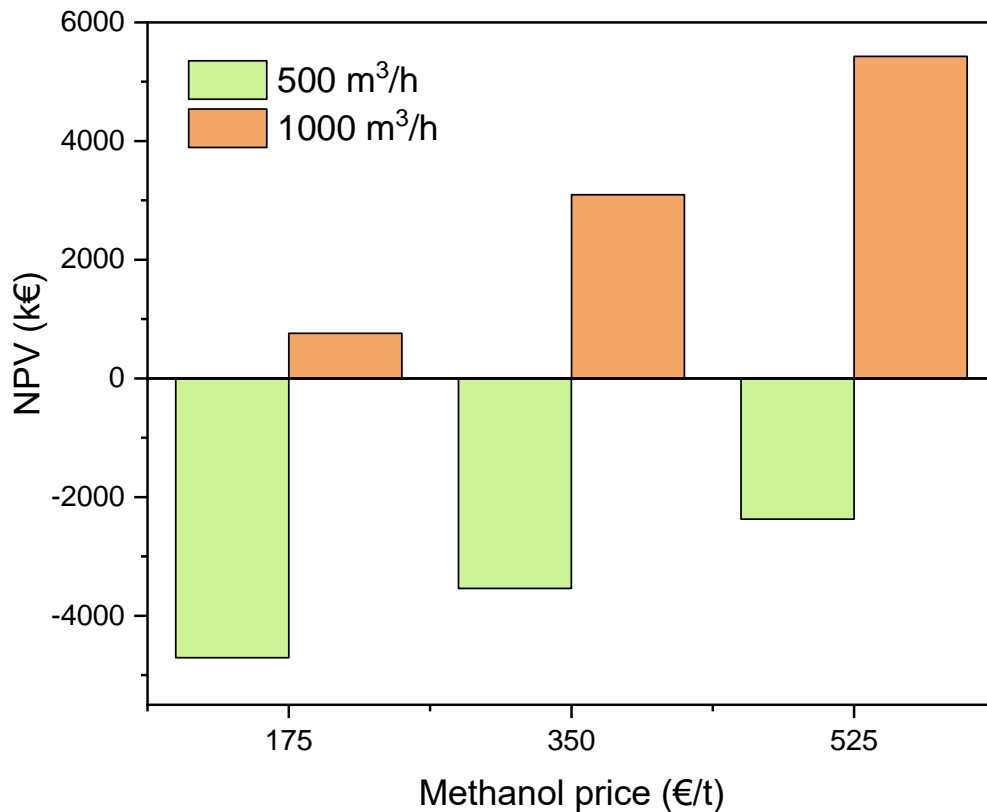


Figure 8. Influence of bio-methanol price on NPV. Scenario 15.

Methanol price has varied considerably during the last years, presenting constant fluctuations. Even though 350 €/t is a representative value, methanol price has reached 450 €/t and in some cases this value has diminished to 225 €/t (Methanex, 2019). For this very reason a sensitivity analysis of bio-methanol price was carried out in our work, which corresponds to scenario 15. The reference values were $\pm 50\%$ of 350 €/t for sake of analyzing the worst case (175 €/t) and the best case (525 €/t). As depicted in Figure 8 no profitable results are reached for a 500 m³/h plant. Even at a bio-methanol price of 525 €/t and considering 20 €/MW of subsidies as feed in tariffs, NPV is -2039 k€. A critical thought against this result can be extracted since methanol price is strongly unstable. The integrated process for biogas upgrading and bio-methanol production herein analysed may be more appropriated for the biggest capacity plants. For the previous parameters, some political actions could be taken to foster investors' appetite, but

methanol context is international and its price is linked to the raw materials. Thus, even if there are political interests on this kind of renewable energy production plants, investors would always carry a risk when supporting this initiative. Alternatively, government incentives could be linked to methanol price for medium plants. Thus, higher subsidies would be provided when methanol price falls. This fact could promote the implementation of this renewable production strategy in rural areas. On the other hand, larger biogas plants would be profitable even at the lowest methanol price.

4. Conclusions

We have performed a profitability analysis to upgrade biogas and simultaneously produce bio-methanol in order to assess the economic interest of this renewable route for potential investors. The following points summarize the conclusions of our work:

- The results obtained for the baseline scenarios are not commercially appealing and none of the biogas plant sizes studied are deemed profitable. The cost analysis showed domination of the investment cost and M&O for the smallest plants, whereas electricity cost was the highest one for medium and big plants.
- Feed-in tariffs does not seem to solve the profitability handicaps for small plants. Nevertheless, this kind of subsidy can be a valid solution for medium-large biogas plants.
- Concerning the effect of bio-methane subsidies as percentage of investment – this action is not as effective as feed-in tariffs.

Our results invite to reflect about new policies to balance the potential negative impacts that these parameters may have over the profitability of the process analysed. Overall, our approach for an integrated green process to generate bio-methane & bio-methanol would be profitable under the studied circumstances for large biogas plants when small-medium subsidies are applied. Future research will be leaded to study the influence of

biogas composition and real mixtures on profitability results (i.e. the impact of incorporating a biogas desulphurisation unit). Furthermore, alternatives for utilisation of the residual CO₂ (i.e. carbonation) will be explored. In any case, this is an encouraging result that opens new research avenues in process design, reaction engineering and low-carbon policies to explore new sustainable processes within the context of a circular economy.

Appendix I. Modelling and economic data of bio-methanol production stage

The main goal of the bio-methanol production process modelling was to estimate the investment cost corresponding to this stage, as well as the raw materials needed and the production of bio-methanol. To this end, CO₂ hydrogenation to methanol process was selected since a wide variety of data are available in the literature (Borisut and Nuchitprasittichai, 2019; Fang et al., 2019; Leonzio, 2017; Van-Dal and Bouallou, 2013). The proposed process was a simplified version of the optimization presented by Van-Dal and Bouallou (2013) (Van-Dal and Bouallou, 2013), which has also been used by other authors previously (Pérez-Fortes et al., 2016a). In their work, these authors optimised to reduce the number of compressors and heat exchangers, which considerably decrease the investment costs. Figure I.1 shows the process modelled.

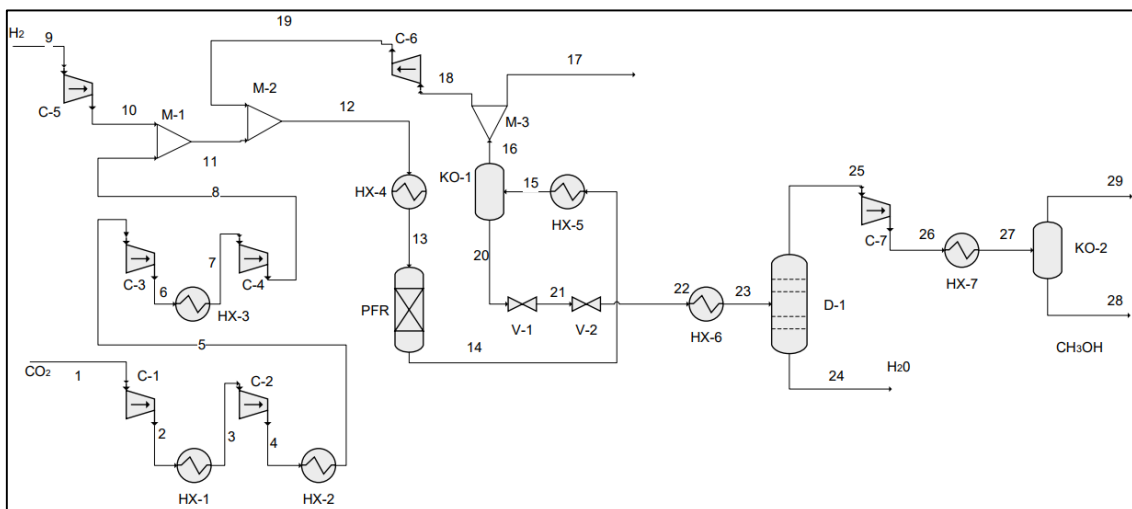


Figure I.1. CO₂ hydrogenation to bio-methanol process flowsheet. The abbreviations used for the different equipments are the following: M – Mixer; C – Compressor; HX – Heat Exchanger; PFR – Plug Flow Reactor; D – Distillation Column; KO – Knock-Out Drum;

As a brief explanation of the proposed process, first CO₂ and H₂ need to be compressed to 78 bar. CO₂ compression is carried out in four compressor stages located in serie cooling between stages, whereas H₂ is compressed in a single stage. After mixing both raw materials and the recycle stream, previous the reaction stage the mix is heated to 210 °C. The reactor is a plug flow adiabatic reactor, which consist on a packed fixed bed of Cu/ZnO/Al₂O₃ commercial catalyst. The kinetic models was implemented exactly as proposed by Van-Dal and Bouallou (2013) (Van-Dal and Bouallou, 2013). For the cost estimation of the catalysts, it was assumed to be replace each month. The mix leaving the reactor is cooled and separated to recycle the non-reacted raw materials in KO-1. The products obtained in the reactor are sent to further separation in The separation of the final water and bio-methanol is carried out in D-1 and KO-2. Please for further explanation of the process see reference Van-Dal and Bouallou (2013) (Van-Dal and Bouallou, 2013). The investment cost corresponding to this stage was estimated following the recommendations and formulas given in references (Seider et al., 2009; Sinnott and Towler, 2013). The Cu/ZnO/Al₂O₃ commercial catalyst has a market price of 154 €/kg (Alfa, 2019). For the estimation of the overall cost it was assumed a replacement of the catalyst yearly. The characteristics of the catalysts were extracted from reference Van-Dal and Bouallou (2013) (Van-Dal and Bouallou, 2013). To make the results more reliable the total purchasing equipment cost was increased a 20% as recommended in the references followed. The following formulas were used to estimate the cost of each equipment:

- Compressors: $C = 260000 + 2700 \times Q^{0.75}$; (Q: power, kW) (Sinnott and Towler, 2013).

- Heat Exchangers: $C = \exp(9.3548 - 0.3739 \times \ln Q + 0.03434 \times \ln Q^2)$; (Q: power, kW) (Seider et al., 2009).
- Distillation Column: $C = C_{\text{vessel}} + C_{\text{packing}} + C_{\text{trays}}$; $C_{\text{vessel}} = 17400 + 79 \times SM^{0.85}$; $C_{\text{packing}}(\text{raschig rings}) = 8000$; $C_{\text{trays}} = (130 + 440 \times D^{1.8}) \times TN$; (SM: Shell Mas, kg; D: Diameter, m; TN: Trays Number, units) (Sinnott and Towler, 2013).
- Knocn-Out Drums: $C = 17400 + 79 \times SM^{0.85}$; (Sinnott and Towler, 2013).
- Reactor: $C = 61500 + 32500 \times V^{0.8}$; (V: Volume, m³) (Sinnott and Towler, 2013).

Table I.1 reflects the key parameters needed for the calculation of each cost equipment as well as the equipment cost for each biogas plant size.

Table I.1. Key parameters and costs for the bio-methanol production stage equipments

Equipment	Biogas plant size (m ³ /h) – Key parameter	Biogas plant size (m ³ /h) – Cost (k€)
Compressors	100 – Q=16 KW	100 – 962
	250 – Q=40 kW	250 – 988
	500 – Q=80 kW	500 – 1024
	1000 – 161 kW	1000 – 1083
Heat Exchangers	100 – Q=93 KW	100 – 61
	250 – Q=235 kW	250 – 86
	500 – Q=470 kW	500 – 117
	1000 – Q=932 kW	1000 – 163
Distillation Column	100 – SM=2219 kg; D=0.73 m; TN=11;	100 – 78
	250 – SM=2462 kg; D=0.81 m; TN=11;	250 – 84
	500 – SM=2614 kg; D=0.86 m; TN=11;	500 – 87
	1000 – SM=2736 kg; D=0.90 m; TN=11;	1000 – 90
Knocn-Out Drums	100 – SM=1807 kg;	100 – 115
	250 – SM=1906 kg;	250 – 119
	500 – SM=1989 kg;	500 – 122
	1000 – SM=2039 kg;	1000 – 124
Reactor	100 – V=1.03 m ³	100 – 95
	250 – V=2.58 m ³	250 – 131
	500 – V=5.2 m ³	500 – 182
	1000 – V=10.32 m ³	1000 – 272

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References

- Alfa, 2019. Cu/ZnO/Al₂O₃ prices [WWW Document]. URL <https://www.alfa.com/en/catalog/045776/>
- Amran, Y.H.A., Amran, Y.H.M., Alyousef, R., Alabduljabbar, H., 2020. Renewable and sustainable energy production in Saudi Arabia according to Saudi Vision 2030; Current status and future prospects. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2019.119602>
- Baena-Moreno, Francisco Manuel, Rodríguez-Galán, M., Ramirez-Reina, T., Zhang, Z., Vilches, L., Navarrete, B., 2019. Understanding the effect of Ca and Mg ions from wastes in the solvent regeneration stage of a biogas upgrading unit. *Sci. Total Environ.* 691, 93–100. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2019.07.135>
- Baena-moreno, F.M., Rodríguez-galán, M., Vega, F., Alonso-fariñas, B., Arenas, L.F.V., Navarrete, B., 2018. Carbon capture and utilization technologies : a literature review and recent advances. *Energy Sources, Part A Recover. Util. Environ. Eff.* 00, 1–31. <https://doi.org/10.1080/15567036.2018.1548518>
- Baena-Moreno, Francisco M., Rodríguez-Galán, M., Vega, F., Reina, T.R., Vilches, L.F., Navarrete, B., 2019a. Synergizing carbon capture storage and utilization in a biogas upgrading lab-scale plant based on calcium chloride: Influence of precipitation parameters. *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2019.03.204>
- Baena-Moreno, Francisco M., Rodríguez-Galán, M., Vega, F., Reina, T.R., Vilches, L.F., Navarrete, B., 2019b. Converting CO₂ from Biogas and MgCl₂ Residues into Valuable Magnesium Carbonate: a Novel Strategy for Renewable Energy Production. *Energy.* <https://doi.org/10.1016/j.energy.2019.05.106>
- Baena-Moreno, Francisco M., Rodríguez-Galán, M., Vega, F., Vilches, L.F., Navarrete, B., 2019c. Review: recent advances in biogas purifying technologies. *Int. J. Green Energy* 00, 1–12. <https://doi.org/10.1080/15435075.2019.1572610>

- Baena-Moreno, Francisco M., Rodríguez-Galán, M., Vega, F., Vilches, L.F., Navarrete, B., Zhang, Z., 2019d. Biogas upgrading by cryogenic techniques. *Environ. Chem. Lett.* <https://doi.org/10.1007/s10311-019-00872-2>
- Baur, L., Uriona M., M., 2018. Diffusion of photovoltaic technology in Germany: A sustainable success or an illusion driven by guaranteed feed-in tariffs? *Energy.* <https://doi.org/10.1016/j.energy.2018.02.104>
- Bennett, S.J., Schroeder, D.J., Mccoy, S.T., 2014. Towards a framework for discussing and assessing CO2 utilisation in a climate context, in: *Energy Procedia.* <https://doi.org/10.1016/j.egypro.2014.11.835>
- Bilgili, F., Koçak, E., Bulut, Ü., Kuşkaya, S., 2017. Can biomass energy be an efficient policy tool for sustainable development? *Renew. Sustain. Energy Rev.* <https://doi.org/10.1016/j.rser.2016.12.109>
- BOE, 2018. Real Decreto 1462/2018.
- Böhringer, C., Cuntz, A., Harhoff, D., Asane-Otoo, E., 2017. The impact of the German feed-in tariff scheme on innovation: Evidence based on patent filings in renewable energy technologies. *Energy Econ.* <https://doi.org/10.1016/j.eneco.2017.09.001>
- Bolat, P., Thiel, C., 2014. Hydrogen supply chain architecture for bottom-up energy systems models. Part 2: Techno-economic inputs for hydrogen production pathways. *Int. J. Hydrogen Energy.* <https://doi.org/10.1016/j.ijhydene.2014.03.170>
- Borisut, P., Nuchitprasittichai, A., 2019. Methanol Production via CO2 Hydrogenation: Sensitivity Analysis and Simulation—Based Optimization. *Front. Energy Res.* <https://doi.org/10.3389/fenrg.2019.00081>
- Bose, A., Lin, R., Rajendran, K., O'Shea, R., Xia, A., Murphy, J.D., 2019. How to optimise photosynthetic biogas upgrading: a perspective on system design and microalgae selection. *Biotechnol. Adv.* <https://doi.org/10.1016/j.biotechadv.2019.107444>
- Cucchiella, F., D'Adamo, I., 2016. Technical and economic analysis of biomethane: A focus on the role of subsidies. *Energy Convers. Manag.* <https://doi.org/10.1016/j.enconman.2016.04.058>
- Cucchiella, F., D'Adamo, I., Gastaldi, M., 2019. An economic analysis of biogas-biomethane chain from animal residues in Italy. *J. Clean. Prod.*

- <https://doi.org/10.1016/j.jclepro.2019.05.116>
- Cucchiella, F., D'Adamo, I., Gastaldi, M., 2015. Financial analysis for investment and policy decisions in the renewable energy sector. *Clean Technol. Environ. Policy*. <https://doi.org/10.1007/s10098-014-0839-z>
- Cucchiella, F., D'Adamo, I., Gastaldi, M., Miliacca, M., 2018. A profitability analysis of small-scale plants for biomethane injection into the gas grid. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2018.02.243>
- D'Adamo, I., Falcone, P.M., Ferella, F., 2019. A socio-economic analysis of biomethane in the transport sector: The case of Italy. *Waste Manag.* <https://doi.org/10.1016/j.wasman.2019.06.005>
- Dalena, F., Senatore, A., Marino, A., Gordano, A., Basile, M., Basile, A., 2018. Methanol Production and Applications: An Overview, in: *Methanol: Science and Engineering*. <https://doi.org/10.1016/B978-0-444-63903-5.00001-7>
- Destek, M.A., Sinha, A., 2020. Renewable, non-renewable energy consumption, economic growth, trade openness and ecological footprint: Evidence from organisation for economic Co-operation and development countries. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2019.118537>
- Directorate-General for Energy, 2019. Quarterly Report on European Electricity Markets, European Commission.
- Eberhard, A., Kåberger, T., 2016. Renewable energy auctions in South Africa outshine feed-in tariffs. *Energy Sci. Eng.* <https://doi.org/10.1002/ese3.118>
- Fabián-Anguiano, J.A., Mendoza-Serrato, C.G., Gómez-Yáñez, C., Zeifert, B., Ma, X., Ortiz-Landeros, J., 2019. Simultaneous CO₂ and O₂ separation coupled to oxy-dry reforming of CH₄ by means of a ceramic-carbonate membrane reactor for in situ syngas production. *Chem. Eng. Sci.* <https://doi.org/10.1016/j.ces.2019.115250>
- Fang, X., Men, Y., Wu, F., Zhao, Q., Singh, R., Xiao, P., Du, T., Webley, P.A., 2019. Promoting CO₂ hydrogenation to methanol by incorporating adsorbents into catalysts: Effects of hydrotalcite. *Chem. Eng. J.* <https://doi.org/10.1016/j.cej.2019.122052>
- Ferella, F., Cucchiella, F., D'Adamo, I., Gallucci, K., 2019. A techno-economic assessment of biogas upgrading in a developed market. *J. Clean. Prod.*

<https://doi.org/10.1016/j.jclepro.2018.11.073>

Fernández-Dacosta, C., Stojcheva, V., Ramirez, A., 2018. Closing carbon cycles: Evaluating the performance of multi-product CO₂ utilisation and storage configurations in a refinery. *J. CO₂ Util.* <https://doi.org/10.1016/j.jcou.2017.11.008>

García-Gusano, D., Iribarren, D., Garraín, D., 2017. Prospective analysis of energy security: A practical life-cycle approach focused on renewable power generation and oriented towards policy-makers. *Appl. Energy.* <https://doi.org/10.1016/j.apenergy.2017.01.011>

Gong, D.C., Kao, C.W., Peters, B.A., 2019. Sustainability investments and production planning decisions based on environmental management. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2019.03.256>

le Saché, E., Johnson, S., Pastor-Pérez, L., Amini Horri, B., Reina, T., 2019. Biogas Upgrading Via Dry Reforming Over a Ni-Sn/CeO₂-Al₂O₃ Catalyst: Influence of the Biogas Source. *Energies* 12, 1007. <https://doi.org/10.3390/en12061007>

Le Saché, E., Santos, J.L., Smith, T.J., Centeno, M.A., Arellano-Garcia, H., Odriozola, J.A., Reina, T.R., 2018. Multicomponent Ni-CeO₂ nanocatalysts for syngas production from CO₂/CH₄ mixtures. *J. CO₂ Util.* <https://doi.org/10.1016/j.jcou.2018.03.012>

Lee, J., Ryu, K.H., Ha, H.Y., Jung, K.D., Lee, J.H., 2020. Techno-economic and environmental evaluation of nano calcium carbonate production utilizing the steel slag. *J. CO₂ Util.* <https://doi.org/10.1016/j.jcou.2019.12.005>

Leonzio, G., 2017. Optimization through response surface methodology of a reactor producing methanol by the hydrogenation of carbon dioxide. *Processes.* <https://doi.org/10.3390/pr5040062>

Li, J., Ma, X., Liu, H., Zhang, X., 2018. Life cycle assessment and economic analysis of methanol production from coke oven gas compared with coal and natural gas routes. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2018.02.100>

Mas'ud, A.A., Vernyuy Wirba, A., Muhammad-Sukki, F., Mas'ud, I.A., Munir, A.B., Md Yunus, N., 2015. An assessment of renewable energy readiness in Africa: Case study of Nigeria and Cameroon. *Renew. Sustain. Energy Rev.* <https://doi.org/10.1016/j.rser.2015.06.045>

- Methanex, 2019. Methanol price [WWW Document]. URL
https://www.methanex.com/sites/default/files/methanol-price/MxAvgPrice_Dec27%2C2019.pdf
- Mondal, M.A.H., Hawila, D., Kennedy, S., Mezher, T., 2016. The GCC countries RE-readiness: Strengths and gaps for development of renewable energy technologies. *Renew. Sustain. Energy Rev.*
<https://doi.org/10.1016/j.rser.2015.10.098>
- Pablo-Romero, M. del P., Sánchez-Braza, A., Salvador-Ponce, J., Sánchez-Labrador, N., 2017. An overview of feed-in tariffs, premiums and tenders to promote electricity from biogas in the EU-28. *Renew. Sustain. Energy Rev.*
<https://doi.org/10.1016/j.rser.2017.01.132>
- Patrizio, P., Leduc, S., Chinese, D., Kraxner, F., 2017. Internalizing the external costs of biogas supply chains in the Italian energy sector. *Energy.*
<https://doi.org/10.1016/j.energy.2017.01.033>
- Pérez-Fortes, M., Schöneberger, J.C., Boulamanti, A., Harrison, G., Tzimas, E., 2016a. Formic acid synthesis using CO₂ as raw material: Techno-economic and environmental evaluation and market potential. *Int. J. Hydrogen Energy.*
<https://doi.org/10.1016/j.ijhydene.2016.05.199>
- Pérez-Fortes, M., Schöneberger, J.C., Boulamanti, A., Tzimas, E., 2016b. Methanol synthesis using captured CO₂ as raw material: Techno-economic and environmental assessment. *Appl. Energy.*
<https://doi.org/10.1016/j.apenergy.2015.07.067>
- PORDATA, 2019. Electricity prices for households and industrial users (Euro/ECU) [WWW Document]. *Fund. Fr. Man. dos Santos.* URL
[https://www.pordata.pt/en/Europe/Electricity+prices+for+households+and+industrial+users+\(Euro+ECU\)-1477](https://www.pordata.pt/en/Europe/Electricity+prices+for+households+and+industrial+users+(Euro+ECU)-1477) (accessed 7.18.19).
- Price, C.A.H., Arnold, W., Pastor-Pérez, L., Amini-Horri, B., Reina, T.R., 2019. Catalytic Upgrading of a Biogas Model Mixture via Low Temperature DRM Using Multicomponent Catalysts. *Top. Catal.* <https://doi.org/10.1007/s11244-019-01216-8>
- Rivarolo, M., Bellotti, D., Magistri, L., Massardo, A.F., 2016. Feasibility study of methanol production from different renewable sources and thermo-economic analysis. *Int. J. Hydrogen Energy.* <https://doi.org/10.1016/j.ijhydene.2015.12.128>

- Samimi, F., Karimipourfard, D., Rahimpour, M.R., 2018. Green methanol synthesis process from carbon dioxide via reverse water gas shift reaction in a membrane reactor. *Chem. Eng. Res. Des.* <https://doi.org/10.1016/j.cherd.2018.10.001>
- Seider, Seader, Lewin, Widagdo, 2009. product and process Design Principles, *Journal of Chemical Information and Modeling.*
<https://doi.org/10.1017/CBO9781107415324.004>
- Shi, X., Chen, H., Yu, Y., Wen, F., 2018. Development of variable renewable energy policy in developing countries: A case study of Sri Lanka. *Int. J. Public Pol.*
<https://doi.org/10.1504/IJPP.2018.090682>
- Sinnott, R.K., Towler, G., 2013. *Chemical Engineering Design*, *Chemical Engineering Design.* <https://doi.org/10.1016/C2009-0-61216-2>
- Statista, n.d. Global production capacity of methanol 2018 & 2030 Published by M. Garside, Nov 7, 2019 The global production capacity of methanol is expected to double in the twelve years from 2018 to 2030, from approximately 140 million metric tons in 2018, to around 2 [WWW Document]. URL
<https://www.statista.com/statistics/1065891/global-methanol-production-capacity/>
- Stroud, T., Smith, T.J., Le Saché, E., Santos, J.L., Centeno, M.A., Arellano-Garcia, H., Odriozola, J.A., Reina, T.R., 2018. Chemical CO₂ recycling via dry and bi reforming of methane using Ni-Sn/Al₂O₃ and Ni-Sn/CeO₂-Al₂O₃ catalysts. *Appl. Catal. B Environ.* <https://doi.org/10.1016/j.apcatb.2017.10.047>
- Van-Dal, É.S., Bouallou, C., 2013. Design and simulation of a methanol production plant from CO₂ hydrogenation. *J. Clean. Prod.*
<https://doi.org/10.1016/j.jclepro.2013.06.008>
- Vega, F., Baena-Moreno, F.M., Gallego Fernández, L.M., Portillo, E., Navarrete, B., Zhang, Z., 2020. Current status of CO₂ chemical absorption research applied to CCS: Towards full deployment at industrial scale. *Appl. Energy.*
<https://doi.org/10.1016/j.apenergy.2019.114313>
- Wiesberg, I.L., de Medeiros, J.L., Alves, R.M.B., Coutinho, P.L.A., Araújo, O.Q.F., 2016. Carbon dioxide management by chemical conversion to methanol: HYDROGENATION and BI-REFORMING. *Energy Convers. Manag.*
<https://doi.org/10.1016/j.enconman.2016.04.041>
- Zafar, M.W., Shahbaz, M., Hou, F., Sinha, A., 2019. From nonrenewable to renewable

energy and its impact on economic growth: The role of research & development expenditures in Asia-Pacific Economic Cooperation countries. *J. Clean. Prod.* <https://doi.org/10.1016/j.jclepro.2018.12.081>

Zhang, N., Pan, Z., Zhang, Z., Zhang, W., Zhang, L., Baena-Moreno, F.M., Lichtfouse, E., 2020. CO₂ capture from coalbed methane using membranes: a review. *Environ. Chem. Lett.* <https://doi.org/10.1007/s10311-019-00919-4>

Zhang, Z., Liu, Z., Pan, Z., Baena-Moreno, F.M., Soltanian, M.R., 2020. Effect of porous media and its distribution on methane hydrate formation in the presence of surfactant. *Appl. Energy.* <https://doi.org/10.1016/j.apenergy.2019.114373>