Synergizing carbon capture and utilization in a biogas upgrading plant based on calcium chloride: Scaling-up and profitability analysis

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Abstract

Herein we analyse the profitability of a novel regenerative process to synergize biogas upgrading and carbon dioxide utilization. Our proposal is a promising alternative which allows to obtain calcium carbonate as added value product while going beyond traditional biogas upgrading methods with high thermal energy consumption. Recently we have demonstrated the experimental viability of this route. In this work, both the scale-up and the profitability of the process are presented. Furthermore, we analyse three representative scenarios to undertake a techno-economic study of the proposed circular economy process. The scale-up results demonstrate the technical viability of our proposal. The precipitation efficiency and the product quality are still remarkable with the increase of the reactor size. The techno-economic analysis reveals that the implementation of this circular economy strategy is unprofitable without subsidies. Nonetheless, the results are somehow encouraging as the subsides needed to reach profitability are lower than in other biogas upgrading and carbon dioxide utilization proposals. Indeed, for the best-case scenario, a feed-in tariff incentive of 4.3 €/MWh makes the approach profitable. A sensitivity study through tornado analysis is also presented, revealing the importance of reducing bipolar membrane electrodialysis energy consumption. Overall our study envisages the big challenge that the EU faces during the forthcoming years. The evolution towards bio-based and circular economies requires the availability of economic resources and progress on engineering technologies.

Keywords

Carbon Capture and Utilization; Biogas Upgrading; Biomethane Circular Economy; Green Process;

1. Introduction

The increase of Greenhouse Gases (GHG) emissions and the forthcoming scarcity of fossil fuels are dilemmas of our era that need effective countermeasures (Sarkodie and Strezov, 2019; Sun et al., 2019). In this line, the European Union (EU) frames a strategic plan known as Horizon Europe (HE), aimed to enhance both the European industrial competitiveness and the current environmental conditions (Europe Union, 2019). Through HE, the EU will lead global efforts to decarbonise industries and to evolve towards circular economy policies (Europe Union, 2019). One of the main challenges relays on producing renewable chemicals and fuels (Danish et al., 2019; Jacob et al., 2020). The use of biomass and waste to produce these materials have the potential to reduce the dependence of fossil resources (Ferreira et al., 2020; Wang et al., 2020). Furthermore, biomass – waste utilization contributes to institute the circular economy philosophy as well as its utilization reduces the amount of waste treatment (Atia et al., 2019; Theuerl et al., 2019). A widely recognized method to valorise biomass is the production of biogas. Biogas is basically composed by 60% CH_4 and 40% CO_2 (le Saché et al., 2019), although other impurities (i.e. H_2S or siloxanes) can be found in its composition (Vilardi et al., 2020). Biogas upgrading enables to obtain a high purity biomethane (Chin et al., 2020), which can substitute traditional natural gas. On the other hand, the separated CO_2 must be used to fulfill the circular economy concept (Bassano et al., 2020).

In this sense, our research team has recently proposed and experimentally validate a regenerative process for CO_2 valorisation, as shown in Figure 1 (Baena-Moreno et al., 2019a). In this process, biogas is firstly upgraded in a packed tower using NaOH as solvent (Eq. (1)). Afterwards, the produced Na_2CO_3 must be regenerated to keep the process affordable. Two alternatives are available for these purpose, either thermal or chemical regeneration (Baena-Moreno et al., 2020b). The first alternative entails a high energy consumption (Vega et al., 2017). The chemical regeneration path needs to use a precipitant such as $CaCl_2$, producing $CaCO_3$ as a side added value product (Eq. (2)) (Baciocchi et al., 2012). Indeed, the major advantage of NaOH in comparison with other traditional CO_2 solvents (i.e. MEA or piperazine) is that it can be chemically regenerated, hence avoiding the high energy penalty of thermal regeneration. In our previous works, we have intensively studied the chemical regeneration route in order to obtain a valuable by-product, which could balance the overall economic performance of the process. Thus, the analysis of both precipitation efficiencies and product quality have been the objective of our seminal studies. Among the main conclusions obtained, we can highlight that the use of $CaCl_2$ as precipitant results in an enhanced product quality than using $Ca(OH)_2$

(Baena-Moreno et al., 2019c). The regeneration reaction between Na_2CO_3 and $CaCl_2$ is represented in Eq. (2). As indicated in the equation, NaCl is obtained as by-product. Implementing a 100% circular economy requires regeneration of NaCl to NaOH. For this purpose, bipolar membrane electrodialysis (BMED) has been successfully employed (Ye et al., 2015). The main problem of this technology is the high cost related to both investment and energy consumption. Thus, its implementation to comply with the circular economy philosophy of our process depends on the economic performance.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (1)$$

$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3 \quad (2)$$

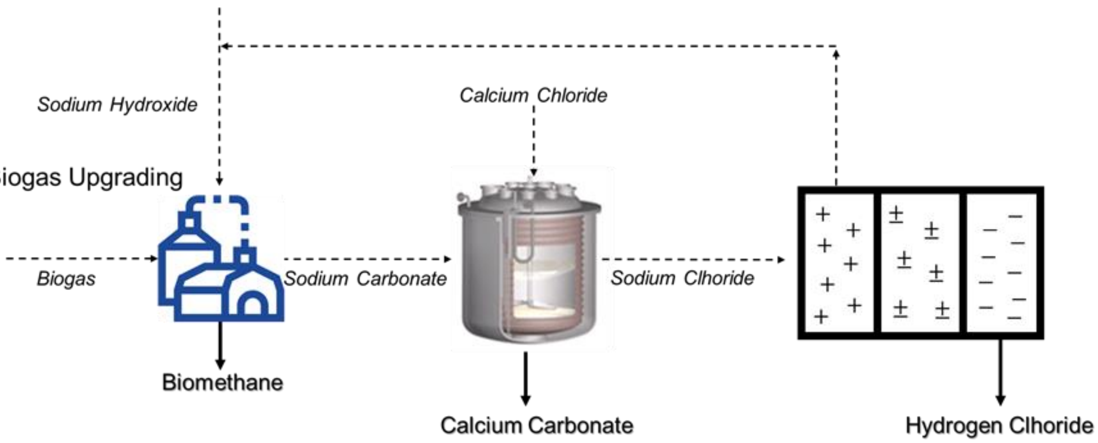
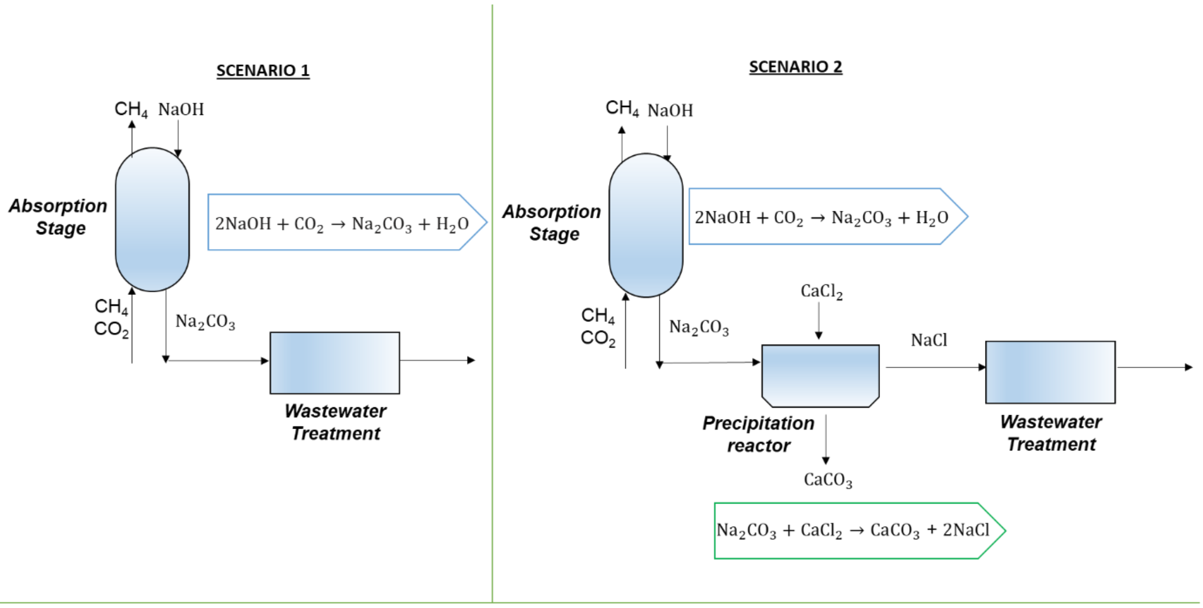


Figure 1. Regenerative process for biogas upgrading and CO_2 utilization.

The chemical aspects of the regenerative route proposed in Fig. 1 including physicochemical properties of the $CaCO_3$ obtained and the precipitation efficiency has been the subject of our pioneering works (Baena-Moreno et al., 2019d). Despite the lab-scale validation has been confirmed the applicability of this process at large scale remains an open quest. In order to address this quest this work goes a step forward in the conceptual design – modelling of the process and its economic performance through a profitability analysis. Furthermore, we propose this study as a tool to assess the readiness of circular economy approaches. To this end, we come up with three different scenarios, as depicted in Figure 2. These scenarios correspond to the complete absence of circular economy (Fig. 2.A); partial circular economy (Fig. 2.B); and full circular economy (Fig. 2.C). In scenario 1, only the upgrading of biogas is performed, yielding biomethane and a sodium carbonate as end products. Such carbonate cannot be further valorised, hence it must be treated in a wastewater treatment stage. In scenario 2, we propose the valorisation of sodium carbonate via calcium carbonate production, as explained above. Thus, a precipitation reactor is needed. In this scenario, the resulting NaCl solution is sent to the wastewater treatment stage to keep a partial circular economy. Finally, in scenario 3, we include the regeneration of this NaCl solution to NaOH through BMED. Some pre-treatments are needed before BMED can work with NaCl. Those pre-treatments are: softening, to remove all the calcium carbonates remaining; and membrane distillation (MD). The three scenarios were evaluated for 100, 250, 500 and 1000 m^3/h of biogas, in agreement with standard sizes defined in previous works (Cucchiella and D'Adamo, 2016). The stages were modelled theoretically, with the exception of the precipitation stage. To define a realistic precipitation efficiency value, scale-up experiments were performed. These experiments were carried out at higher volumes than previous works to check the behaviour of the precipitation efficiency.



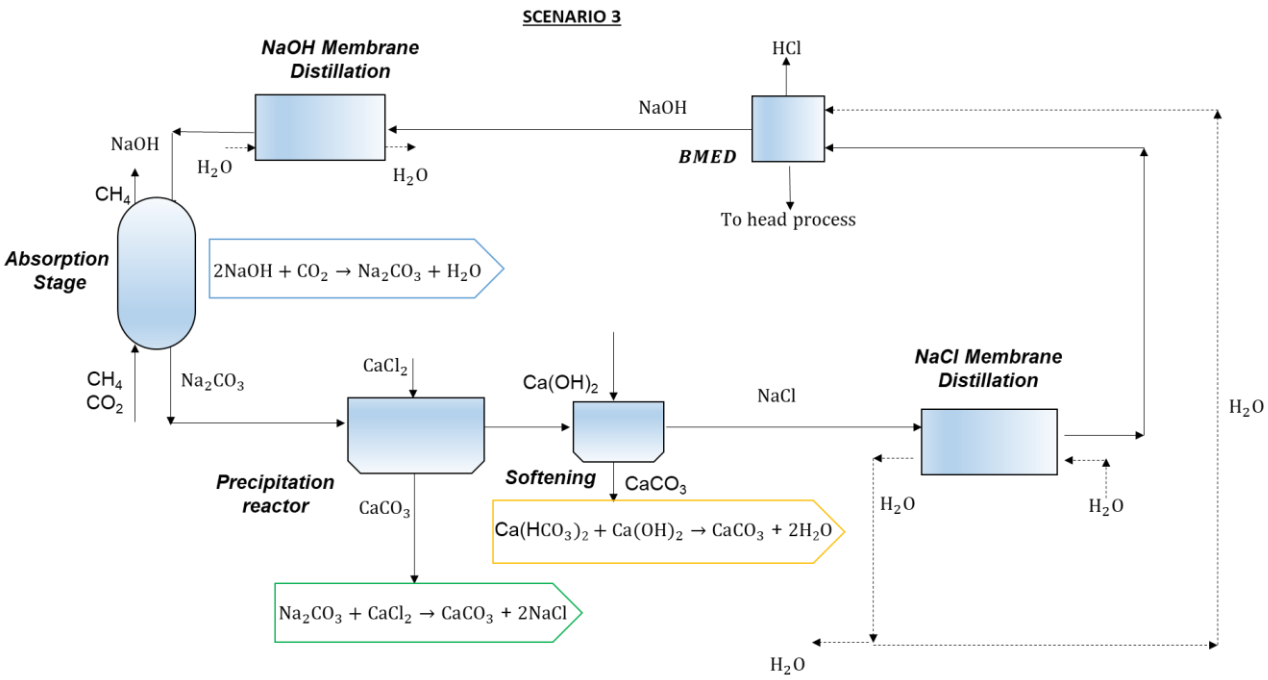


Figure 2. Scenarios proposed: Absence of circular economy (scenario 1); Partial circular economy (scenario 2); Full circular economy (scenario 3).

To achieve the explained objectives, this work is organized as follow. First, the experimental scale-up of the precipitation reactor is analysed. This first step serves to select a precipitation efficiency value for the modelling of the precipitation reactor. Moreover, the powders obtained are physicochemical characterized to corroborate that scaling-up does not affect the product quality. Afterwards, the equipment are modelled for the three different scenarios and for all the plant sizes. This modelling is required to perform the economic analysis. The economic performance is analysed through a profitability analysis based on the discount cash flow (DCF) method. Thus, the results obtained for each scenario – plant size can be directly compared. In the economic analysis, the influence of potential subsidies is considered. Furthermore, we propose a wide sensitivity analysis to study the influence of each parameter for each plant size – scenario.

2. Methodology

2.1 Experimental

Materials

NaOH, Na_2CO_3, $CaCl_2$ and $CaCO_3$ employed in this work were provided by PanReac-AppliChem (pure-grade or pharma-grade, 99% purity).

Methods

The experimental methodology used is analogous to that reported elsewhere (Baena-Moreno et al., 2019a). For all the experiments, the initial concentration of the Na_2CO_3 – NaOH solution coming from the packed tower was set at 20 g/100 mL Na_2CO_3 and 6 g/100 mL NaOH. The values for the reaction parameters were chosen in agreement with the most appropriated results obtained previously (Baena-Moreno et al., 2019a). Thus, temperature was set at 30ºC; the molar ratio used was 1.2 mol/mol; and the reaction time chosen was 45 minutes. Five reactor volumes were tested: 200, 500, 1000, 2000 and 5000 mL. These five tests allow to check the influence of the reactor volume on the precipitation efficiency, hence defining a more realistic precipitation efficiency than that the obtained in our previous work. The maximum reactor volume tested was limited by the vessels availability volume in our laboratory. The tests were performed duplicated, resulting in an overall experimental error of ±2%. Further information concerning the experimental methodology is available elsewhere (Baena-Moreno et al., 2019a).

PCC Physicochemical Characterization

The powders obtained were physicochemical analysed by means of Raman and scanning electron microscopy (SEM) in order to study the influence of the reactor volume on the product quality. The powders obtained were first dried at 105°C during 24 hours. Raman measurements of the powders samples were recorded using a Thermo DXR2 spectrometer equipped with a Leica DMLM microscope. The wavelength of applied excitation line was 532nm ion laser and 50x objective of 8-mm optical was used to focus the depolarized laser beam on a spot of about 3 µm in diameter. On the other hand, a JEOL JSM6400 operated at 20 KV equipped with energy dispersive X-ray spectroscopy (EDX) and a wavelength dispersive X-ray spectroscopy (WDS) systems was used for the microstructural/chemical characterization (SEM with EDX and WDS). The powders were coated with a thin layer of gold and positioned on a slide coated in colloidal graphite paint.

2.2 Profitability analysis

Process description and modelling

As aforementioned, three scenarios were considered in our study. The three scenarios studied were modelled as explained in Appendix I. The characteristics of each scenario and the most important equipment are briefly explained here. For the scenario 1, the packed tower is the most important equipment. In this packed tower biogas upgrading is carried out, producing the absorption of CO_2 and Na_2CO_3 as by-product. The aqueous Na_2CO_3 solution does not meet the quality standards for market selling and hence we assumed that this stream is directly treated in a wastewater treatment stage. Scenario 2 defines a partial circular economy in which $CaCO_3$ is produced from the CO_2 absorbed in the packed tower. To this end, a precipitation reactor is included in comparison with scenario 1. As explained before, this precipitation reactor uses $CaCl_2$ as precipitant agent. The NaCl aqueous solution is not valorised in this scenario and hence a wastewater treatment stage is needed. Finally, scenario 3 entails the recovery and transformation of NaCl into NaOH in a BMED stage. Adjusting the NaCl aqueous solution to suitable conditions for BMED requires some pre-treatments. The first pre-treatment is the removal of Ca^{2+} and CO_3^{2-} ions which have not reacted in the precipitation stage. To this end, a softening with $Ca(OH)_2$ is conducted, obtaining a low-quality $CaCO_3$ as by-product (Baena-Moreno et al., 2019c). This low-quality $CaCO_3$ can be sold at a moderate price. Afterwards NaCl concentration must be increased to obtain a concentrated NaOH in the BMED. MD was selected for this purpose for two main reasons: it can work with waste energy streams (available for example in wastewater treatment plants); and the water recovered presents high purity. This allows to employ the water recovered in the subsequent BMED stage, where water is needed to transform NaCl into NaOH and HCl. Once NaOH has been obtained from NaCl, a new MD stage is needed to adjust the concentration previous recycling to the packed tower. Moreover, HCl produced as by-product in the BMED possesses a market value, enhancing the economic performance of the process. Other equipment considered in the modelling of the process include for instance the pumps needed to impulse the fluids. For specific information of the modelling the reader is referred to Appendix I.

Economic model

The DCF method was employed in our work, choosing as indicators net present value (NPV) and profitability index (PI). NPV is aimed to estimate the economic outputs of the project. PI allows to quantify the value created per unit of investment, which is interesting for investors. Eqs. (3) and (4) define the parameters needed to calculate NPV and PI, respectively.

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

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

Cash inflows (I_t) and cash outflows (O_t) depends on the scenario analyzed. The discount rate parameter (r_d) includes the time effect and the lifetime of the project (n) was set in

20 years. Generally, I_t can be calculated as indicated in Eq. (5). The revenues for selling biomethane ($R_{biomethane}$) are common to all the scenarios. Eq. (6) indicated how to calculate them, based on the amount of biomethane produced ($Q_{biomethane}$) and the natural gas price (p_{NG}). The revenues obtained for potential subsidies ($R_{subsidies}$) are calculated through Eq. (7), where the value of subsidies ($p_{subsidies}$) is the key parameter. The pondered revenues for selling the other products ($R_{products}$) depends on the scenario. For scenario 1, there are no other products. For scenario 2, the revenues for selling the produced $CaCO_3$ (R_{CaCO_3}) is included through Eq. (8), which depends on the amount produced (Q_{CaCO_3}) and the price (p_{CaCO_3}). For scenario 3, apart from the previous revenues, the low-quality $CaCO_3$ obtained in the softening and the HCl co-produced in the BMED can be sold. The revenues for these by-products are included in Eq. (9) and (10).

$$I_t = R_{biomethane} + R_{subsidies} + R_{products} \tag{5}$$

$$R_{biomethane} = Q_{biomethane} * p_{NG} \tag{6}$$

$$R_{subsidies} = Q_{biomethane} * p_{subsidies} \tag{7}$$

$$R_{CaCO_3} = Q_{CaCO_3} * p_{CaCO_3} \tag{8}$$

$$R_{low-quality\ CaCO_3} = Q_{low-quality\ CaCO_3} * p_{low-quality\ CaCO_3} \tag{9}$$

$$R_{HCl} = Q_{HCl} * p_{HCl} \tag{10}$$

As for the cost side, O_t is calculated through Eq. (11). The loan necessary for the investment (C_{inv}) was assumed to be covered by a third party. Thus, an annual cost of the loan (C_{loan}) (Eq. (12)), and the interest (C_{il}) (Eq. (13)) are included. The years of the loan (n_l) and the interest rate (r_{int}) are other parameters which influence in Eq. (12) and (13). C_{inv} is different for each scenario. The calculation of this value for each scenario is described in Appendix I. Other costs included in the profitability analysis and collected in Eqs. (14)-(19) are maintenance and overhead (M&O) (C_{mo}); depreciation (C_{df}); insurance (C_{ins}); installation (C_{inst}); electricity (C_e); and labour (C_{lab}). C_e depends on unitary electricity consumption (C_{ue}), which is different for each scenario, and includes the energy consumption of all the parameters. The specific calculation of this parameter for each is included in Appendix I. For the selection of parameters whose value depends of the country (i.e. electricity price or natural gas price), it was assumed that the plant would be installed in Spain. Table 1 collects all the economic inputs needed for the calculations.

$$O_t = C_{loan} + C_{il} + C_{mo} + C_{df} + C_{ins} + C_{inst} + C_e + C_{consumables} + C_{lab} \quad (11)$$

$$C_{loan} = \frac{C_{inv}}{n_l} \quad (12)$$

$$C_{il} = [C_{inv} - C_{loan} * (t+1)] * r_{int} \quad (13)$$

$$C_{mo} = C_{inv} * p_{mo} \quad (14)$$

$$C_{df} = C_{loan} * p_{df} \quad (15)$$

$$C_{ins} = C_{inv} * p_{ins} \quad (16)$$

$$C_{inst} = C_{inv} * p_{inst} \quad (17)$$

$$C_e = C_{ue} * p_e \quad (18)$$

$$C_{lab} = C_{labu} * n_{op} \quad (19)$$

Table 1. Economic inputs for the profitability study.

Data	Value	Reference
p_{NG} (€/MWh)	21.5	(Directorate-General for Energy, 2019)

p_{CaCO_3} (€/t)	High quality – 300 Low quality – 80	Suppliers
p_{HCl} (€/t)	100	Suppliers
p_{CaCl_2} (€/t)	120	Suppliers
p_{NaOH} (€/t)	100	Suppliers
$p_{Ca(OH)_2}$ (€/t)	100	Suppliers
p_{H_2O} (€/m^3)	1	Suppliers
C_{inv} (k€)	Scenario 1: 100 m^3/h – 202; 250 m^3/h – 363; 500 m^3/h – 565; 1000 m^3/h – 881 Scenario 2: 100 m^3/h – 538; 250 m^3/h – 853; 500 m^3/h – 1252; 1000 m^3/h – 1878 Scenario 3: 100 m^3/h – 417; 250 m^3/h – 601; 500 m^3/h – 902; 1000 m^3/h – 1494	Appendix I
r_{int} (%)	6	(Ferella et al., 2019)
n_l (a)	15	(Baena-Moreno et al., 2020a)
n (a)	20	Assumed
r_d (%)	5	(Ferella et al., 2019)
p_{mo} (%)	10	(Cucchiella et al., 2018; Pérez-Fortes et al., 2016a)
p_{df} (%)	20	(Cucchiella et al., 2018; Ferella et al., 2019)
p_{ins} (%)	1	(Cucchiella et al., 2019)
p_{inst} (%)	20	(Pérez-Fortes et al., 2016b)
p_e (€/kWh)	0.08	(Martínez et al., 2020)
C_{labu} (€/a/worker)	22857	(Government of Spain, 2019)
C_{ue} (€/a)	Scenario 1: 100 m^3/h – 589; 250 m^3/h – 1473; 500 m^3/h – 2945; 1000 m^3/h – 5890 Scenario 2: 100 m^3/h – 9794; 250 m^3/h – 12110; 500 m^3/h – 15971; 1000 m^3/h – 23692 Scenario 3: 100 m^3/h – 253556; 250 m^3/h – 614604; 500 m^3/h – 1216350; 1000 m^3/h – 2419843	Appendix I
n_{op} (worker)	Scenario 1 – 5 Scenario 2 – 15 Scenario 3 – 25	Assumed
n_{wh} (h/a)	8000	Assumed

3. Results

3.1 Experimental

Figure 3 shows the results obtained for the precipitation experiments. Indeed, scaling-up the reactor volume causes an efficiency decrease. This fact is probably caused by diffusion phenomena, which have a higher impact at higher volumes. Nonetheless, the decrease percentage is above 2% when scaling-up from 200 mL to 5000 mL (scaling factor of 25). Thus, it is reasonable to predict that the precipitation efficiency value of an industrial reactor with higher volume would be around 80%. For the economic analysis, we have used the value obtained for the highest reactor volume tested (79.96% for 5000 mL).

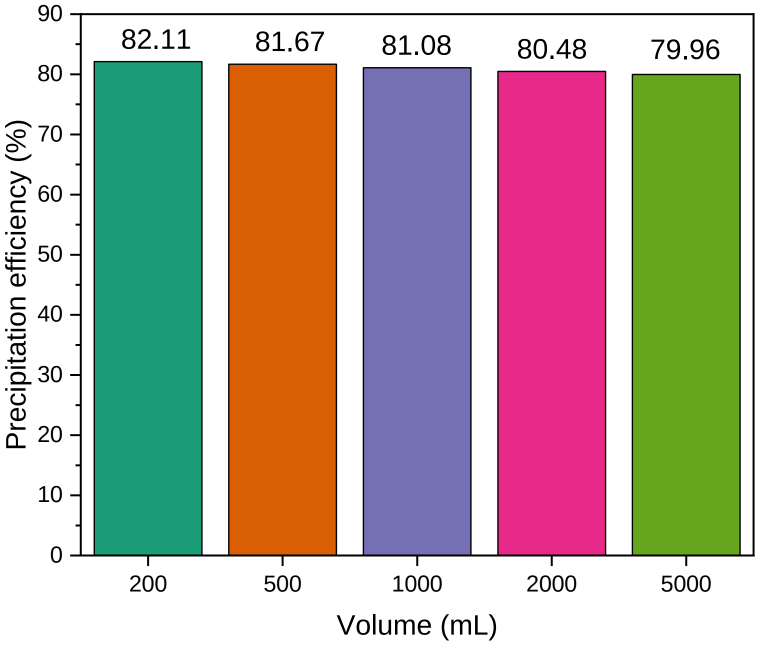


Figure 3. Influence of reactor volume on the precipitation efficiency. Tests carried out at 30ºC, 1.2 molar ratio and 45 minutes.

To corroborate that the quality of the product is not affected by the increase of the reactor volume, Raman and SEM analysis were performed. As Figure 4 reveals, the obtained $CaCO_3$ powders have still the same physicochemical characteristics that pure calcite, even at the greater reactor volume tested. Calcite is recognized for presenting a strong Raman vibration mode at 1100 cm^{-1}. Another characteristic Raman band for calcite is showed at 1100 cm^{-1} (Dandeu et al., 2006). Our sample spectrum shows both typical bands. Indeed, the high quality of the solid samples can be confirmed, as the Raman spectra does not show any other residual impurities indicating we have a pure compound.

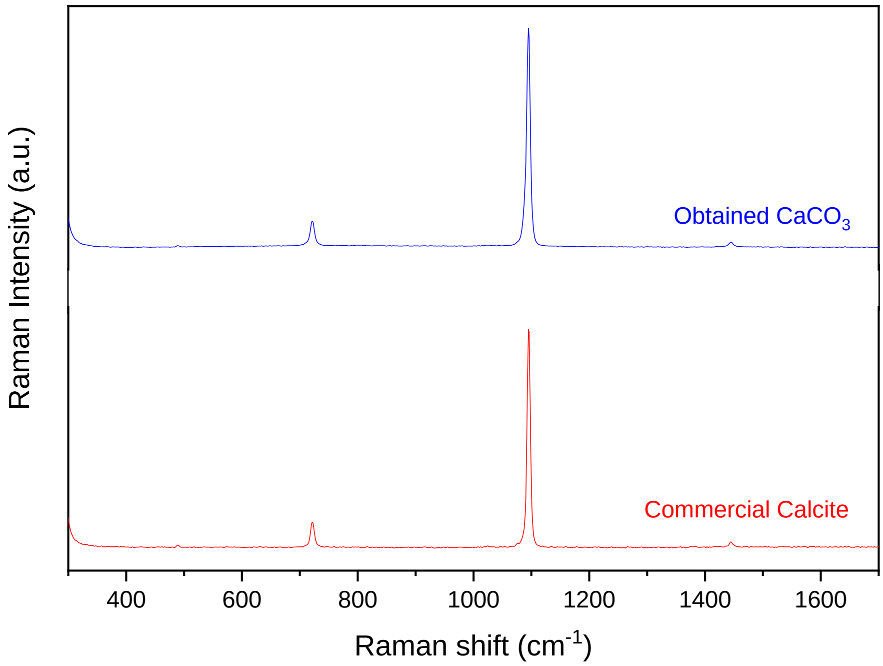


Figure 4. Raman spectra for $CaCO_3$ obtained for 5000 mL reactor volume.

Further confirmation of the quality of the solid samples was obtained through SEM images. As shown in Figure 5, rhombohedral structure is found in the $CaCO_3$ powders. The rhombohedral form of calcite allows its use for applications such as paper industry or pharmacy components, as the properties needed are very specific (Baena-Moreno et al., 2019c). This fact again highlights the high purity of the product obtained, reinforcing its wide commercial end-uses.

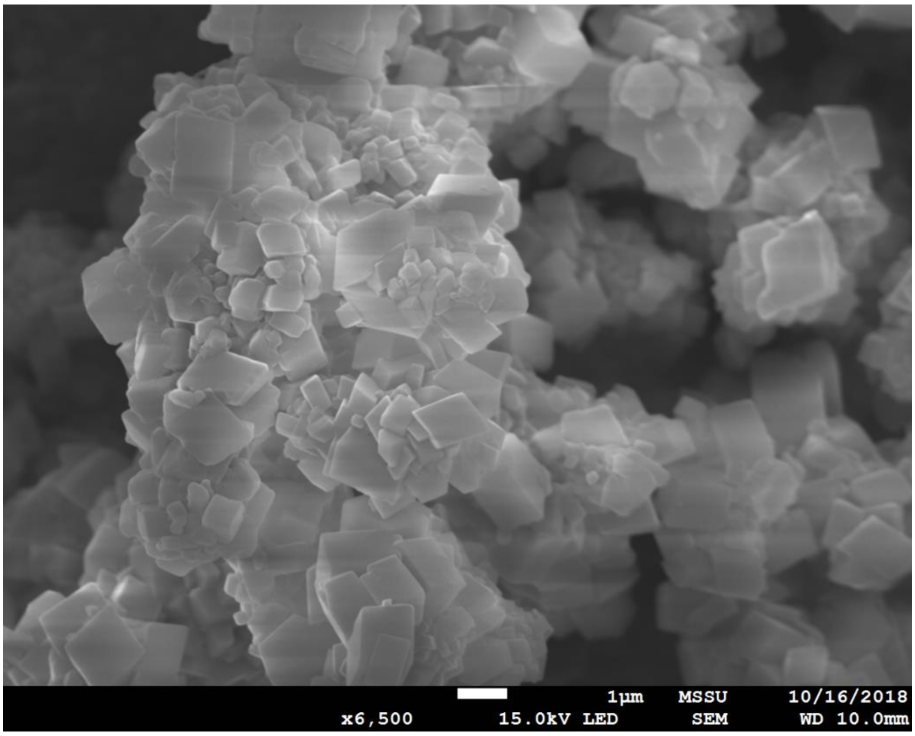


Figure 5. SEM image for $CaCO_3$ obtained for 5000 mL reactor volume.

3.2 Profitability analysis results

In view of the successful precipitation experiments and corroborated product quality, the profitability analysis was carried out. Figure 6 showcases the economic outputs of the three scenarios and plant sizes, in terms of NPV. These results are considered as baseline cases, as potential subsidies for biomethane production are not included. As shown, the NPVs are far from being positive and hence the approach is unprofitable under the current casuistic. However, an interesting discussion emerges from the results. As shown in Figure 6, for a fixed plant size (i.e. 100 m^3/h), the economic outputs worsen as we sequentially evolve towards a full circular economy situation. Indeed, scenario 1 is much more profitable than scenarios 2 and 3. This fact claims the importance of potential subsidies to promote the circular economy philosophy aimed by the EU. On the other hand, Figure 7 reveals the PI results obtained. As shown the best PI results are obtained for scenario 2. This result highlights the advantages of including a precipitation reactor, as the revenues for obtaining $CaCO_3$ are outweighs the extra-investment needed.

Even though the economic outputs of the presented approach are negative, some positive conclusions can be drawn from the results. In comparison with previous works which synergize biogas upgrading and CO_2 utilization, the NPV here obtained is greater. For example, in a previous work of our team where we analyzed the production of biomethane and formic acid, the results of the baseline scenario were around ten times worse than here (Baena-Moreno et al., 2020b). In another work in which bio-methanol was obtained from biogas, the economic results of the baseline scenario were also two to five times worse than the results obtained here (Baena-Moreno et al., 2020c). This comparison somehow indicates the potentiality of producing biomethane and $CaCO_3$ from biogas following the process scheme here proposed in scenario 2. In fact, this way of producing $CaCO_3$ may have other potential benefits when compared to other renewable-based products. $CaCO_3$ is widely used in cement manufacturing, which is a major CO_2 emitter industry. If the $CaCO_3$ used in this industry is bio-origin based, the CO_2 later release would not count as net carbon emission due to its biogenic origin. This opens new opportunities for future works to analyze the environmental advantages of this bio-economy path.

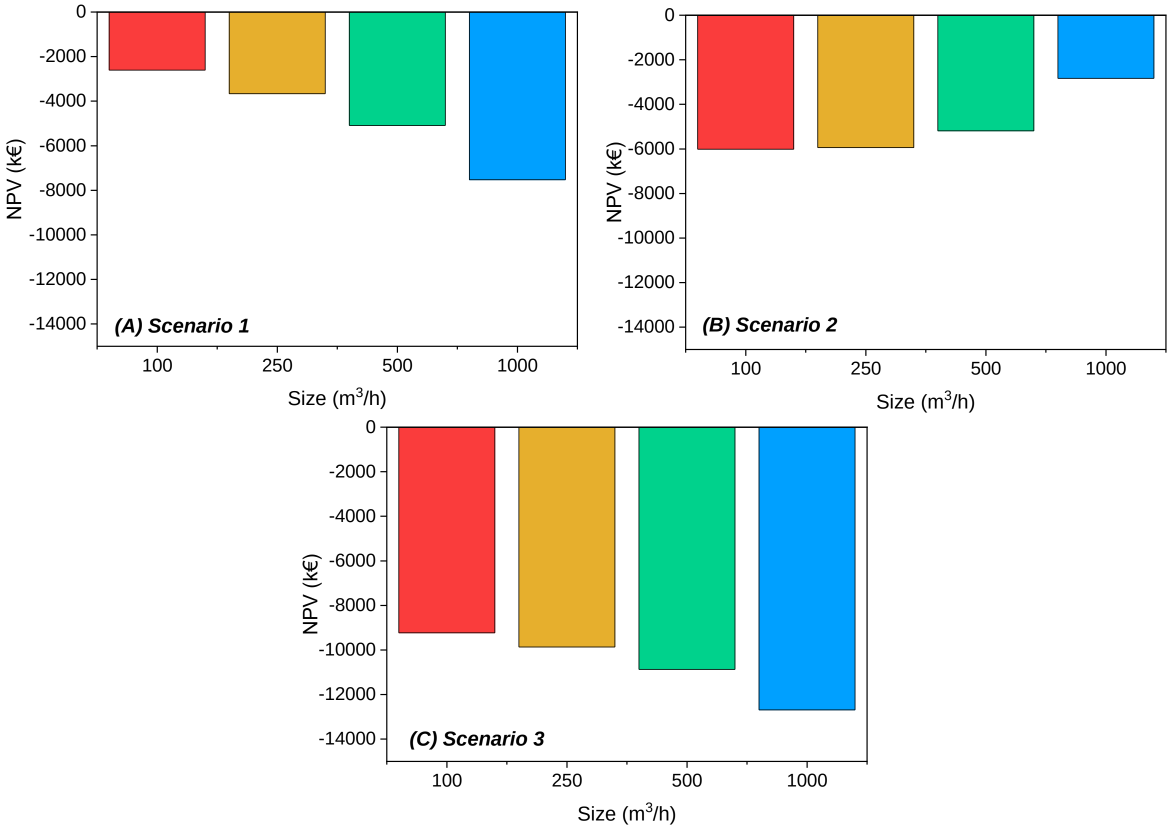


Figure 6. NPV results for the scenarios proposed

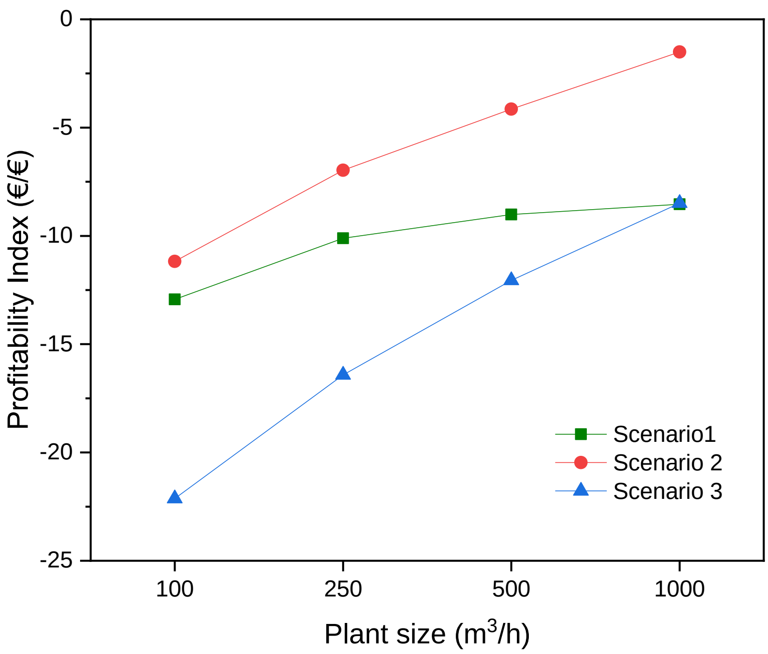


Figure 7. PI results for the scenarios proposed

Another curiosity of the results obtained is the positive evolution of NPV with plant size for scenario 2. In contrast with scenarios 1 and 3, in which NPV worsen as the plant size increases, Figure 6.A shows the different tendency for scenario 2. This fact is caused by the differences between revenues and costs for each scenario – plant sizes, as showcased in Figure 8. Figure 8 shows the revenues and costs obtained for the year 1 and 16 for all the plant sizes – scenarios. Years 1 and 16 have different overall costs as the loan duration was assumed to be 15 years. As a matter of fact, the differences between cost and revenues in scenario 2 for the year 16 are almost null for 1000 m^3/h plant size. Therefore, the greater NPV obtained is reasonable. Indeed, probably positive economic results would be obtained for higher biogas plant sizes. This again is a good opportunity which will be pondered in future works since herein we analyze standard biogas plant sizes.

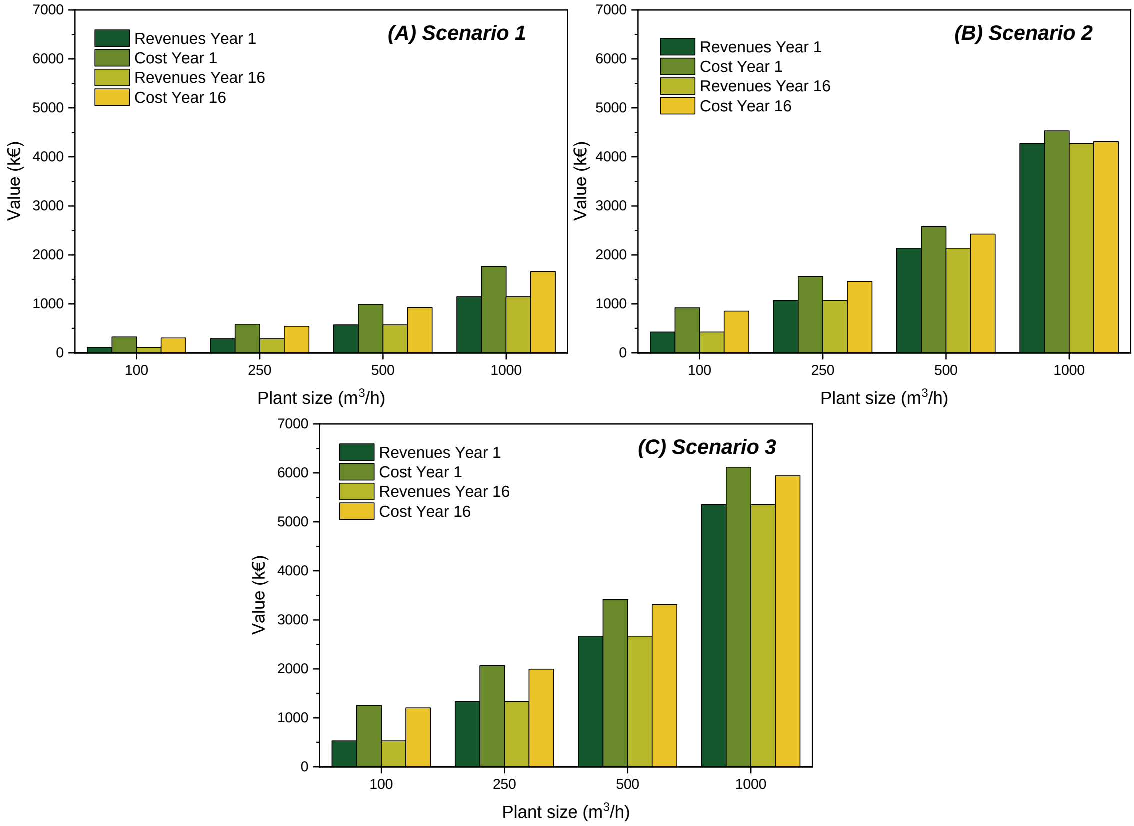


Figure 8. Revenues – costs comparison for the different scenarios – biogas plant sizes. Year 1 and 16.

The natural gas prices needed to reach NPV equal to zero was analyzed for all the scenarios – plant sizes. Figure 9 showcases the results obtained. Clearly the largest plant size in scenario 2 is quite promising. This option could be profitable at a natural gas price of 25.8 €/MWh, which could be achieved with minimal efforts. Indeed, in comparison with the current natural gas price (21.5 €/MWh), the difference is only 4.3 €/MWh. This result somehow indicates that scenario 2 is an important alternative to be considered in the short – medium term. For the largest plant size, scenario 1 and 3 need a natural gas price of 32.9 and 40.6 MWh are respectively estimated. The difference from the current price can be saved either increasing natural gas prices or through subsidies as feed-in tariffs. The first alternative could lead to customer disappointment and the search of alternative energy sources. However, the second alternative is already implemented in some countries such as Austria or Slovakia, which are fostering a substantial development of the biomethane market in the last years (Pablo-Romero et al., 2017). The subsidies offered are around 12.51–16.51 €/MWh in Austria and 10.75 €/MWh in Slovakia. Under these incentives, the largest plant size for scenario 1 would reach profitability. However, scenario 3 still would be unprofitable. This fact deserves some pondering as these results demonstrate the long path we have ahead to implement a complete circular economy scheme. A general comparison of all presented scenarios indicates that scenario 2 merits further consideration as it would be highly profitable even at the subsidy offered in Slovakia. Moreover, 500 m^3/h plant size of this scenario would be also profitable with a subsidy of 15.7 €/MWh. This value is achievable through political efforts as demonstrated in Austria or Slovakia. Italy is another country with a strong policy to favour biomethane production (Marc and Carole, 2019). Indeed, a new incentives scheme has been launched recently (Marc and Carole, 2019). In this new proposal, 61 €/MWh are offered as feed-in tariffs. Under these circumstances, the plant sizes from 250 to 1000 m^3/h of all the scenarios here proposed would be profitable. In comparison with other alternatives to synergize biogas upgrading and CO_2 utilization, our process generally needs lower subsidies. For example, the 500 m^3/h biogas plant size within our proposal, would be profitable with modest subsidies such as: 15.4 €/MWh for scenario 1; 15.7 €/MWh for scenario 2; and 32.7 €/MWh for scenario 3. At the same plant size, subsidies needed in other proposal are the following: 139.7 €/MWh for biomethane and formic acid production (Baena-Moreno et al., 2020b); 30.6 €/MWh for biomethane and methanol production (Baena-Moreno et al., 2020c); and 41 €/MWh for biomethane and urea production (Baena-Moreno et al., 2020d). Comparing the results of other approaches with our scenario 2, it seems that the implementation of a partial circular economy is without a doubt more profitable.

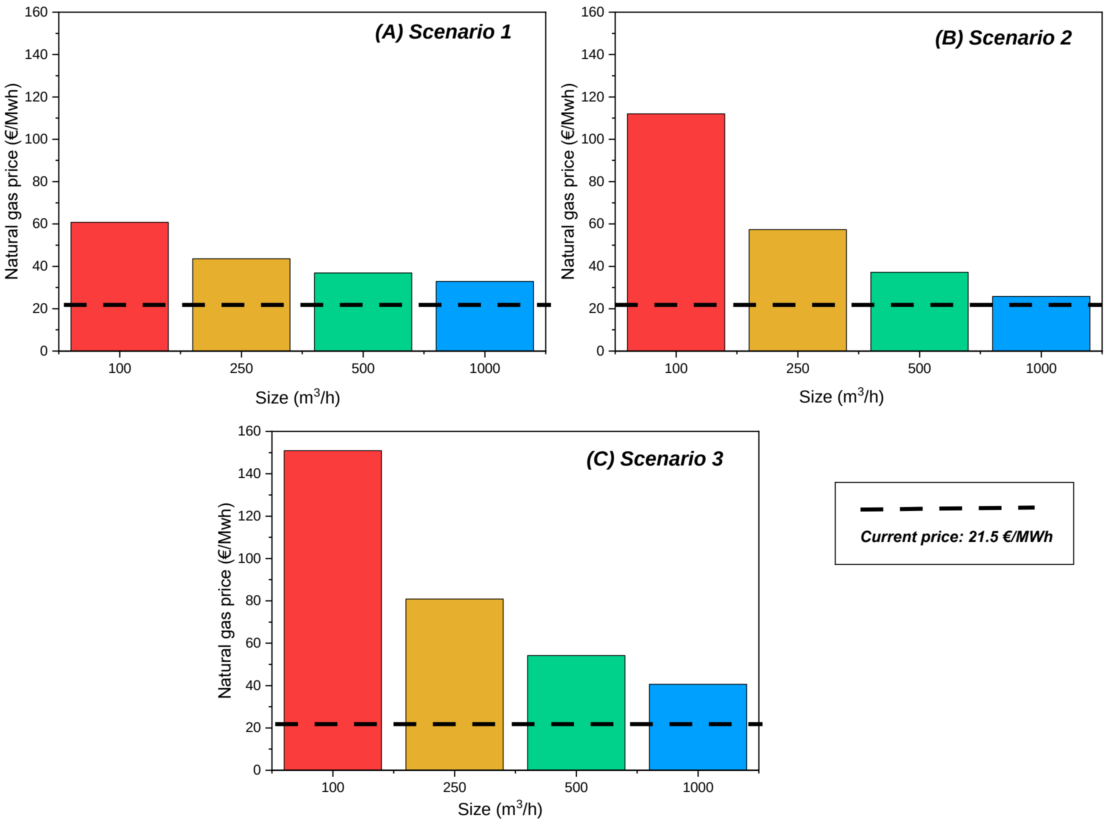


Figure 9. Natural gas price for NPV equal to zero.

Finally, as there may be some uncertainties regarding the used data, a sensitivity analysis of the majority of parameters is performed. Tornado analysis is the tool chosen for this purpose, as it provides a clear overview of the most impacting parameters. Those parameters are different for each scenario but we can summarize them as follow: NaOH price; total investment; labour cost; $CaCO_3$ price; $CaCl_2$ price; HCl price; $Ca(OH)_2$ price; and energy consumption employed in BMED. These parameters are varied in agreement with the percentages indicated in Table 2. The uncertainty of the selected parameters was evaluated from the NPV results obtained for each plant size – scenario. Figures 10, 11 and 12 collect the results obtained for scenario 1, 2 and 3, respectively. The results represented are the variation of the NPV respect to the baseline case NPV.

Parameter (units)	**Original value**	**Variation**
NaOH (€/t)	100	±20%
Investment (k€)	Scenario 1: 100 m^3/h – 202 k€; 250 m^3/h – 363k€; 500 m^3/h – 565 k€; 1000 m^3/h – 881 k€ Scenario 2: 100 m^3/h – 538 k€; 250 m^3/h – 853 k€; 500 m^3/h – 1252 k€; 1000 m^3/h – 1878 k€ Scenario 3: 100 m^3/h – 417 k€; 250 m^3/h – 601 k€; 500 m^3/h – 902 k€; 1000 m^3/h – 1494 k€	±10%
Labour (workers)	Scenario 1: 5 Scenario 2: 15 Scenario 3: 25	Scenario 1: ±1 Scenario 2: ±3 Scenario 3: ±6
$CaCO_3$ high quality (€/t)	300	±20%
$CaCO_3$ low quality (€/t)	80	±20%
$CaCl_2$ (€/t)	120	±20%
HCl (€/t)	100	±20%
$Ca(OH)_2$ (€/t)	100	±20%
BMED energy consumption (kWh/m^3)	2713	±30%

Beginning for scenario 1, as Figure 10 reveals, the most influencing parameters are labour and NaOH price. For the lowest biogas plant size (100 m^3/h), labour cost plays a key role. On the other hand, for the rest of sizes, NaOH is the most important parameter to be controlled. Therefore, this parameter must be optimized in order to achieve better economic outputs. This result is reasonable since the raw material consumption of 100 m^3/h plant size is considerably lower than the rest of capacities. The investment variation within the selected range does not considerably affect the overall economic performance. Indeed, for the small plant sizes (100 and 250 m^3/h), this parameter is the less impacting.

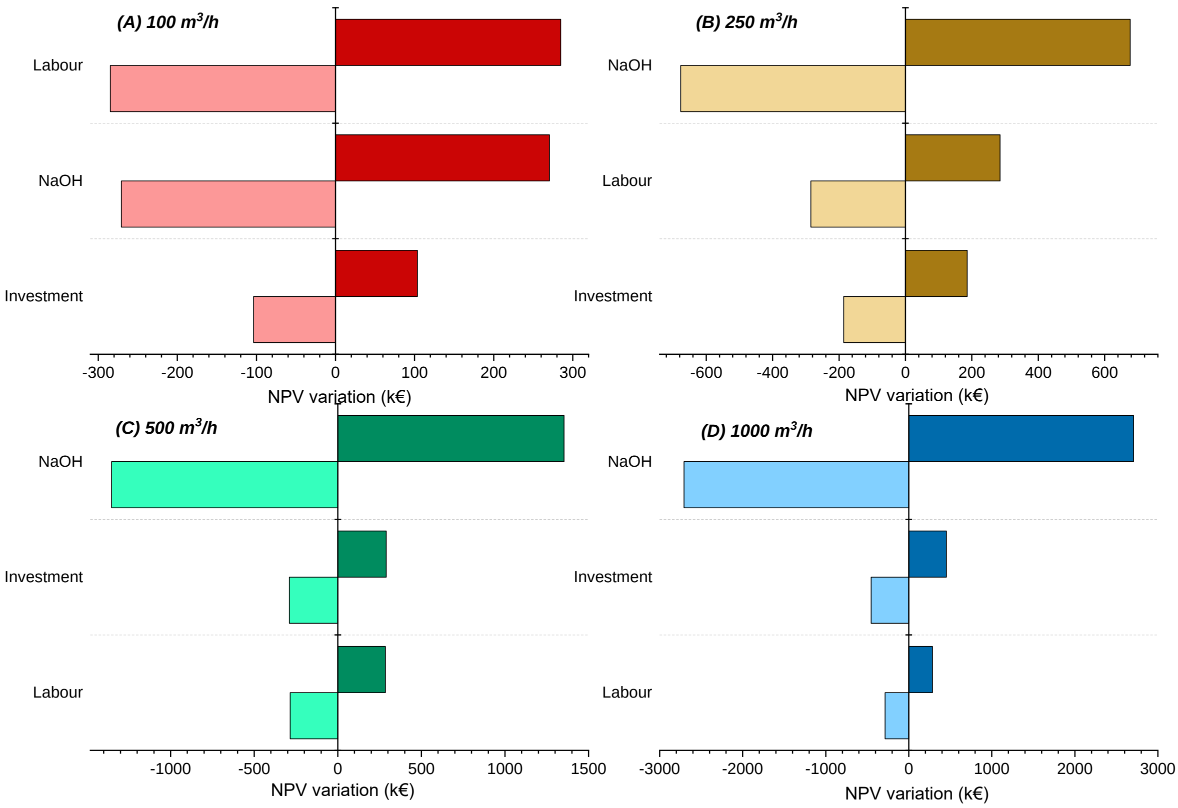


Figure 10. Tornado analysis for scenario 1

Figure 11 showcases the sensitivity analysis performed for scenario 2. Differently from scenario 1, here the effect of each parameter varies for each biogas plant size. For example, labour cost is the most influencing parameter for 100 m^3/h whereas it ranks in the last position for 1000 m^3/h. Another example is NaOH price. This case coincides with the analysis of the first scenario for the same reason. The effect of $CaCO_3$ price is one of the most important for all the sizes. Indeed, its variation can cause an impact of ±8000 k€ for 1000 m^3/h plant size. This variation can even revert the sign of the NPV, as for the largest plant the original NPV was -2833 k€. Thus, controlling the $CaCO_3$ can turn positive the profitability of the project even suppressing subsidies. On the other hand, an important cost to be considered is the $CaCl_2$ price. As shown, its variation can severely affect the profitability of all the plant sizes.

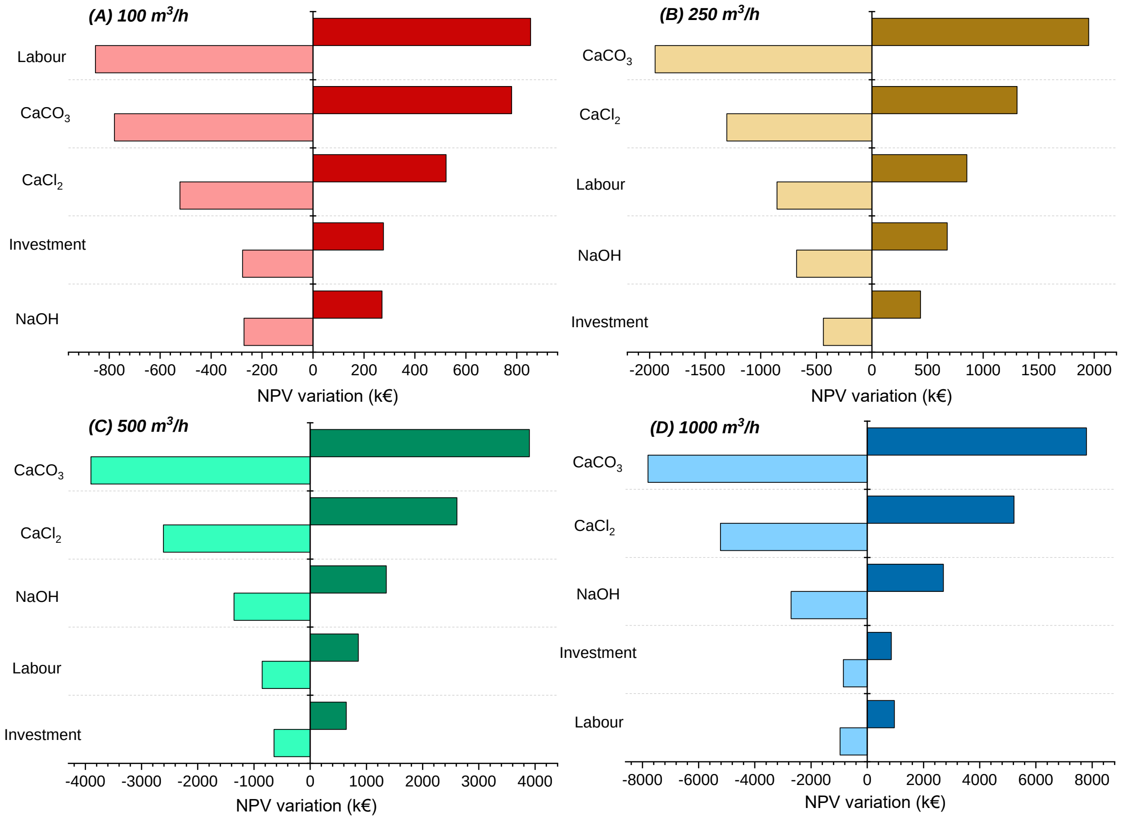


Figure 11. Tornado analysis for scenario 2

Finally, Figure 12 depicts the tornado analysis results for scenario 3. Apart from the results previously discussed for scenarios 1 and 2, the most impacting parameter here is the energy consumption of the BMED stage. Indeed, in agreement with several studies, decreasing the energy consumption of BMED is the main challenge of this technology towards full commercialization (Jaime-Ferrer et al., 2008; Wilhelm et al., 2001). Therefore, the stabilization at a lower value can be potentially beneficial for the interests of this circular economy approach. Saving a 30% of energy consumption for this stage entails a NPV improvement of 8917 k€ for 1000 m^3/h. Considering that the NPV of the baseline case for the largest plant was -12687 k€, this improvement would be about 70%.

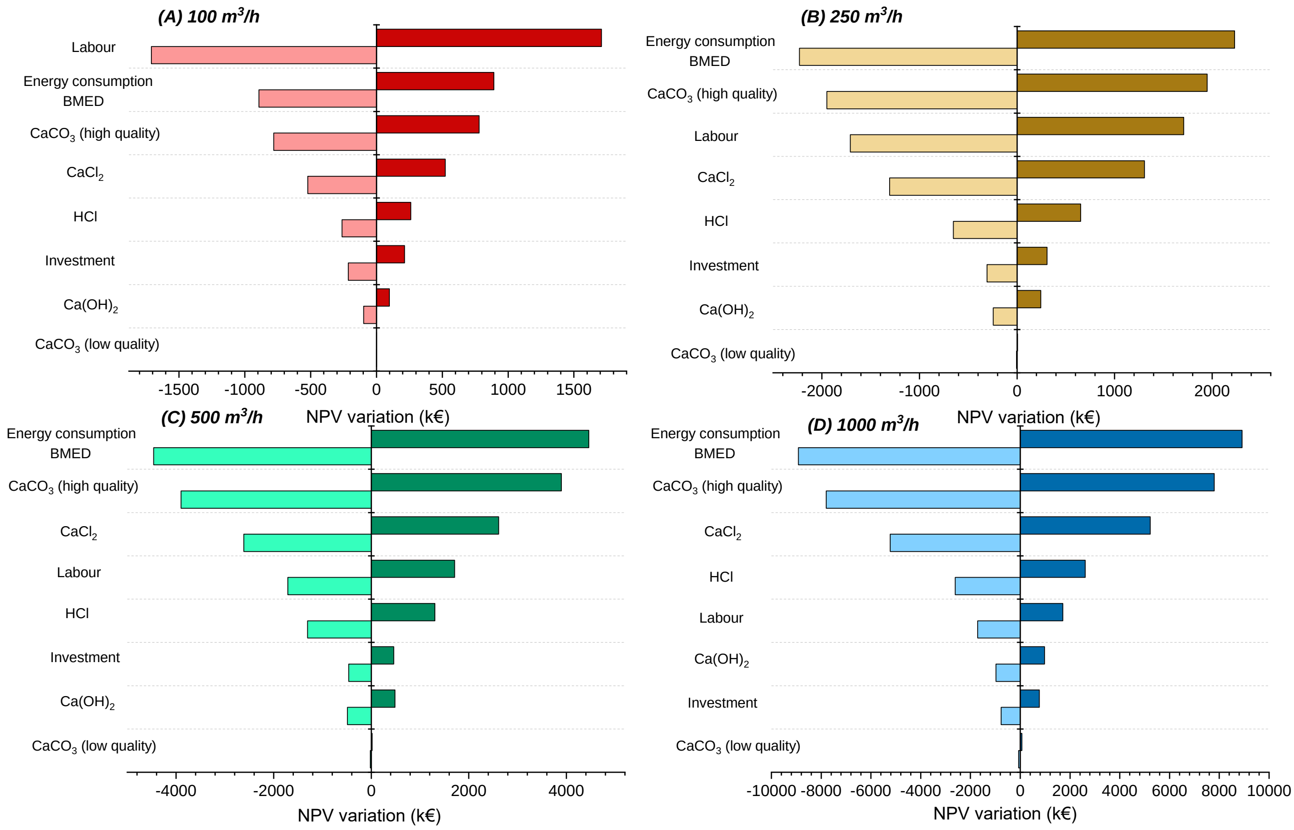


Figure 12. Tornado analysis for scenario 3

4. Conclusions

Our paper thoroughly analyses the profitability of a novel regenerative process to synergize biogas upgrading and CO_2 utilization. This path is a promising alternative to promote the circular economy concept and a “waste to fuels – chemicals” philosophy. Indeed, our study serves as an example of the economic appealing of circular economy implementation. To this end, we compare the absence of circular economy, partial circular economy and full circular economy implementation. Precipitation experiments validated at the laboratory in previous studies are scale-up for the first time. The results show the technical viability of our proposal, as both the precipitation efficiency and the product quality are not significantly affected by the reactor size. Regrettably, the profitability analysis envisages that the full implementation of circular economy is economically unfeasible under the current circumstances. However, the proposal herein studied is more profitable than previous works which synergize biogas upgrading and CO_2 utilization. As example, for the best case studied (scenario 2 – 1000 m^3h), our configuration could be profitable at a natural gas price of 25.8 €/MWh or with a feed-in tariff incentive of 4.3 €/MWh. The sensitivity analysis shows room for improvement. For example, for scenario 3, a reduction of 30% in BMED energy consumption could entail savings of up to 10000 k€.

Generally, our work reveals that the implementation of circular economy processes in the short – medium term is not profitable in the context of biomethane production. Initiatives aiming for a hybrid biogas and CO_2 utilization route must be initially subsidized to ensure their economic competitiveness. Otherwise, the evolution towards low-carbon societies will not be economically appealing in the coming years. Obviously, further scientific efforts must be done to decrease the overall energy consumption – process costs and certainly the scientific community is determined to work on the right direction to pursue a low-carbon future.

Appendix I: Techno-economic modelling of the scenarios proposed

The modelling of the different scenarios studied was carried out by equipment. Thus allowed to stablish a mass balance as can be seen at the end of this Appendix. First, the packed tower for biogas upgrading was modelled following two methods for sake of comparison. The first method is an estimation from previous published data whereas the second method follows a theoretical path. The parameters needed to obtain the economic estimation of the packed tower are the height and the diameter. The first method was proposed in reference (Turton, 2001), consisting on estimating the values for our cases (subscript tower) from a previous reference (subscript ref). The diameter can be estimated through Eq. (I.1), whereas the height is estimated with Eq. (I.2).

$$\frac{G_{ref}}{A_{ref}} = \frac{G_{tower}}{A_{tower}} \qquad (I.1)$$

$$H_{tower} = H_{ref} * \left(\frac{\eta_{tower}}{\eta_{ref}}\right) * \left(\frac{[CO_2]_{tower}}{[CO_2]_{ref}}\right)^{0.6} \qquad (I.2)$$

Where G_i is the molar gas flow rate (mol/m^{2}s); A_i is the area of the packed tower (m^2), which depends on the packed tower diameter, D (m); H_i is the height of the packed tower (m); η_i is the absorption efficiency (%); and $[CO_2]_i$ is the inlet CO_2 concentration (%). The references values were obtained from reference (Tontiwachwuthikul et al., 1992): 14.8 mol/m^{2}s; 0.1 m; 99%; and 19.5%, respectively. The G_{tower} depends on the plant size, whereas 99% absorption efficiency and 40% inlet CO_2 concentration were assumed for our design. The results obtained following this method are collected in Table I.1. The height of the tower is the same as it depends of fixed parameters for all the plant sizes.

The second method used to estimate both diameter and height of the tower is explained in deep in references (Afkhamipour and Mofarahi, 2017; Aroonwilas et al., 2001; Iizuka et al., 2012). Briefly, the diameter was calculated following Eqs. (8), (9) and (10) of reference (Iizuka et al., 2012). For height estimation, Eq. (12) of the same reference was used. Previously, gas-phase volumetric overall mass transfer coefficient was estimated following Eq. (5) of reference (Afkhamipour and Mofarahi, 2017), and the liquid load was estimated with Figure 5 of reference (Aroonwilas et al., 2001). The results obtained can be seen in Table I.1. As can be seen the result differences are small, hence we used an average to estimate the investment for the packed tower (Eq. (I.3)) and for the packing (Eq. (I.4)), both on them depending on the volume (Turton, 2001).

$$C_{invtower} = 10^{3.4974+0.4485x\log_{10}(V)+0.1074x\log_{10}(V)^2} \quad (I.3)$$

$$C_{invpacking} = 10^{2.4493+0.9744x\log_{10}(V)+0.0055x\log_{10}(V)^2} \quad (I.4)$$

Table I.1. Dimensions of the packed tower.

Plant size (m^3/h)	Diameter (m)		Height (m)		Diameter used (m)	Height used (m)	Volume (m^3)
	Method 1	Method 2	Method 1	Method 2			
100	0.23	0.27	9.04	10.96	0.25	10	0.49
250	0.34	0.44			0.39		1.19
500	0.48	0.62			0.55		2.38
1000	0.68	0.88			0.78		4.78

The precipitation reactor cost was obtained in agreement with Eq. (I.5), (Sinnott and Towler, 2013), where the reactor volume (V) was calculated as indicated in Eq. (I.6). The volumetric flow (Q) depends on the biogas plant size and the time used (45 minutes) was discussed in our precipitation experiments (Baena-Moreno et al., 2019a). The cost of the agitator was estimated using Eq. (I.7), where the power (W=12.89 kW) was calculated using the software given in reference (CheCalc, 2020) (assuming pitched bladed, and scale of agitation 4). The energy consumption of the agitator was calculated with Eq. (I.8), where C_e is the electricity cost. The same equations were used to design the softening stage, assuming here a reaction time of 20 minutes in agreement with previous works (Baena-Moreno et al., 2019c). Moreover, W value for the agitator is 7.2 kW.

$$C_{prep.react} = 113000 + 3250xV^{0.65} \quad (I.5)$$

$$V = \frac{Q}{t} \quad (I.6)$$

$$C_{prep.agit} = 17000 + 1130xW^{1.05} \quad (I.7)$$

$$C_{cons.agit} = W\ x\ C_e x\ 8000 \quad (I.8)$$

For the estimation of membrane distillation costs, Eq. (I.9) was used, in which the investment is the direct multiplication of membrane area (A) and the membrane cost per unit of area (C_{membMD}). C_{membMD} value was 53.4 in agreement with previous published data (Tavakkoli et al., 2017). These membranes were assumed to be changed each 6.5 years (Martínez et al., 2020). The calculation of the membrane area was done following Eq. (I.10), where Q is the volumetric flow of permeate (depending on the biogas plant size) and J_w the water flux characteristic of the solution treated (20 L/m^{2}h) (Shahzad et al., 2019; Ye et al., 2016). The thermal energy requirements were not included in this work since waste energy streams are available in WWTP which could be used for this purpose. Electrical consumption was calculated following Eq. (11), where unitary electricity consumption ($E_{cons.MD}$) was fixed at 1 kWh/m^3 (Mezher et al., 2011).

$$C_{inv.MD} = A\ x\ C_{membMD} \quad (I.9)$$

$$A = \frac{Q}{J_w} \quad (I.10)$$

$$C_{cons.MD} = E_{cons.MD}\ x\ Q\ x\ C_e x\ 8000/1000 \quad (I.11)$$

The design of the BMED stage was done in agreement with reference (Strathmann, 2004). For sake of clarity and conciseness, here we include the most important equations followed. Please for more information see the reference indicated. The BMED cost (Eq. (I.12)) is the sum of membrane costs ($C_{membBMED}$), the stack costs ($C_{stackBMED}$) and the peripheral equipment costs ($C_{peripheralBMED}$). These costs are calculated with Eqs. (I.13) – (I.15). The unitary cost of BMED membrane ($C_{unitary,membBMED}$) was 89 €/m^2 for Ion-exchange membrane costs and 445 €/m^2 for BMED membrane (Strathmann, 2004). The area of the membrane (A) was calculated with the procedure indicated in reference (Strathmann, 2004). The membrane replacement was assumed each 2 years in agreement with reference (Strathmann, 2004). The energy costs ($C_{cons.BMED}$) (Eq. (I.16)) depends mainly on the energy consumption ($E_{cons.BMED}$), which was estimated based on previous literature data to get NaOH at 2M (Reig et al., 2016), and on the volumetric flow of the product (P).

$$C_{inv.BMED} = C_{membBMED} + C_{stackBMED} + C_{peripheralBMED} \quad \text{(I.12)}$$

$$C_{membBMED} = C_{unitary,membBMED} \text{ x } A \quad \text{(I.13)}$$

$$C_{stackBMED} = 1.5 \text{ x } C_{membBMED} \quad \text{(I.14)}$$

$$C_{peripheralBMED} = 0.5 \text{ x } C_{tackBMED} \quad \text{(I.15)}$$

$$C_{cons.BMED} = E_{cons.BMED} \text{ x } P \text{ x } C_e \text{x } 8000 \quad \text{(I.16)}$$

Pumping costs were estimated as indicated in Eq. (I.17) (Martínez et al., 2020), where the volumetric flow (Q) depends on the biogas plant size. Finally, the wastewater treatment stage was calculated following Eq. (I.18) (Turton, 2001), which mainly depends on the total volumetric flow to be treated (Q_w).

$$C_{inv.pumping} = 2103.5 \text{ x } Q^{0.831} \quad \text{(I.17)}$$

$$C_{inv.WWTP} = 69000 \text{ x } 0.89 \text{ x } {Q_w}^{0.64} \quad \text{(I.18)}$$

Summing all the costs previously indicated, the total investment costs (C_{inv}) was obtained for each scenario and biogas plant size. These investment costs are collected in Table I.2. On the other hand, Table I.3 includes the main inputs and outputs by scenario and size.

Table I.2. Key parameters and equipment costs.

Scenario	Biogas plant size (m^3/h)	C_{inv} (k€)
1	100	202
	250	363
	500	565
	1000	881
2	100	538
	250	853
	500	1252
	1000	1878
3	100	417
	250	601
	500	902
	1000	1494

Table I.3. Inputs and outputs by size.

Scenario 1								
	Inputs				**Outputs**			
	100 m^3/h	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**	**100 m^3/h**	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**
CO_2 (kg/h)	72	180	361	721	0	0	0	0
CH_4 (m^3/h)	60	150	300	600	60	150	300	600
NaOH (kg/h)	136	340	680	1360	0	0	0	0
To wastewater treatment (m^3/h)	0	0	0	0	214	535	1070	2140
Scenario 2								
	Inputs				**Outputs**			
	100 m^3/h	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**	**100 m^3/h**	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**
CO_2 (kg/h)	72.14	180.36	360.72	721.44	0	0	0	0
CH_4 (m^3/h)	60	150	300	600	60	150	300	600
NaOH (kg/h)	136	340	680	1360	0	0	0	0
$CaCl_2$ (kg/h)	218	545	1090	2180	0	0	0	0
$CaCO_3$ (kg/h)	0	0	0	0	130	325	650	1300
To wastewater treatment (m^3/h)	0	0	0	0	569	1423	2845	5690
Scenario 3								
	Inputs	**Outputs**						
	100 m^3/h	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**	**100 m^3/h**	**250 m^3/h**	**500 m^3/h**	**1000 m^3/h**
CO_2 (kg/h)	72.14	180.36	360.72	721.44	0	0	0	0
CH_4 (m^3/h)	60	150	300	600	60	150	300	600
$CaCl_2$ (kg/h)	218	545	1090	2180	0	0	0	0
$CaCO_3$ high quality (kg/h)	0	0	0	0	130	325	650	1300
$CaCO_3$ low quality (kg/h)	0	0	0	0	66	165	330	660
$Ca(OH)_2$ (kg/h)	49	123	245	490	0	0	0	0
HCl (kg/h)	0	0	0	0	131	328	655	1310

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