Biogas upgrading through calcium looping: Experimental validation and study of CO$_2$ capture

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Biogas upgrading through calcium looping: Experimental validation and study of CO_2 capture

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A B S T R A C T

The calcium looping technology is one of the most promising technologies for capturing and storing CO_2. This technology has been evaluated with a variety of sorbents and conditions in previous works, but the inlet CO_2-ladden gas has typically been a flue gas from combustion, which typically has a composition of 10–20% CO_2 and 80–90% N_2. On the other side, the performance of the calcium looping process for CO_2 capture of other gases (i. e., biogas or gases resulting from hydrothermal carbonization) remains largely unstudied. In this work, this knowledge gap is assessed through evaluating the performance of the calcium looping process for biogas (synthesized as 40% CO_2, 60% CH_4) in terms of carbonation conversion. This experimental study investigates the impact of: (1) using an inlet gas composition representative for biogas instead of combustion flue gas; (2) different biogas compositions; (3) the carbonation temperature; (4) the cooling-down and heating-up of the sorbent material between the reactor and ambient temperatures within cycles; (5) the atmosphere composition during calcination; and (6) the solids particle size. The main result obtained is that the overall CO_2-capture performance of calcium looping improves when using biogas as inlet CO_2-ladden gas, in comparison with combustion flue gas. One main contribution to this improved performance is shown to be the presence of secondary reactions (i.e., dry reforming, methanation). The impact of the CH_4 to CO_2 ratio tested is not remarkable, showing that the potentialities of the process in this aspect can be adapted to several biogas producing feedstocks.

1. Introduction

1.1. Background

Global warming is one of the main challenges of our era. Carbon dioxide (CO_2) emissions, mostly produced through burning fossil fuels, are considered the main cause for this fact [1,2]. Despite the big efforts carried out to develop renewable energy technologies, power plants firing fossil fuels still amount the highest share of the energy production mix [3]. Therefore, carbon capture and storage (CCS) plays a key role to comply with the Paris Agreement [4]. Among the explored CCS technologies, the Calcium Looping (CaL) process represents a promising CCS technology. The CaL process is based on the reversible pair reaction shown by Eq. (1) [5]. Decomposition of $CaCO_3$ into CaO and CO_2 is known as calcination (endothermic reaction), while the opposite step is named carbonation (exothermic).

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \quad \Delta H_r^o = 178 kJ/mol \quad (1)$$
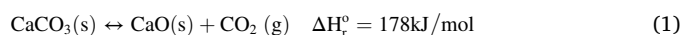
The interest in CaL lies in several advantages: (1) Relatively small energy penalty when used to capture CO_2 from power plants [6]; (2) possibility to use cheap and abundant sorbent (limestone) [7]; (3) Use of interconnected fluidized beds, which is a mature technology in comparison to other CCS technologies [5]; (4) Competitiveness in terms of costs [8]; (5) Potential to be integrated in cement production, one of the main industrial CO_2 emitters [9]; (6) it can be used for combined CO_2 capture and thermochemical energy storage (TCES), hence decreasing also the intermittency problem of variable renewable energy [10]. On the other side, CaL also has some disadvantages compared to other CCS technologies. One main drawback is the fast sorbent deactivation along the multiple carbonation/calcination cycles [7,11,12], which yields relatively large make-up flows of sorbent material, which entails increased costs [13]. Another challenge for commercial implementation is to ensure an efficient process integration, given the considerable

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high-temperature heat required for the calcination [14]. A third main drawback of CaL lies in achieving efficient solids handling, with control of high temperature solids circulation and solid-solid heat exchangers [14]. In the next section, the current research status of CaL technology is summarized.

1.2. Current status and proposal of this work

Even though the CaL technology was first proposed in the 90s [15], still many research activities on the topic are ongoing. Current CaL research tasks focus on: (1) Pilot scale demonstration; (2) Sorbent improvement; (3) Modelling for process scale-up (including combination with energy storage); (4) Integration in current industries. Examples of works within these tasks are given next.

Concerning pilot scale demonstration, Arias et al. summed up the experimental results representing more than 3100 h of operation carried out at 1.7 MW$_{th}$ CaL pilot-scale plant located in La Pereda (Spain) [16]. The results demonstrated the technical viability of CaL for CO_2 capture technology at conditions close to those expected in large scale combustion plants, with overall CO_2 capture efficiencies of over 90%. Further, a reactivation method for sorbent recarbonation was also implemented, allowing to minimize the make-up flow of limestone by approx. 50%. Previously, a similar 1.9 MW$_{th}$ pilot plant at the Industrial Technology Research Institute of Taiwan also demonstrated the technical viability of CaL, achieving 80–95% of CO_2 capture [13]. The technical viability of CO_2 capture has been evidenced, as showed in the works previously mentioned. Nonetheless, pilot scale demonstration of CaL applied for combined CO_2 capture and TCES [11] evidenced challenges linked to the calcination stage. The solar-to-electric efficiency of the integrated CaL-CSP plant is highly dependent on the performance that the solar receiver can offer. An exhaustive study for proper selection, configuration, and sizing of this one, along with a strong solar calciner design, are tasks still unsolved. Therefore, there is a knowledge gap to be covered [11].

Sorbent performance and its improvement have been studied during the last decade mostly at laboratory scale [17,18]. While there is consensus on limestone being the most suitable candidate mainly because of its wide availability and low cost [7], the fast decline of its performance with cyclic operation is an urgent issue to be solved towards commercial implementation [7]. Among the strategies developed to tackle this rapid performance decay are (1) Doping of sorbents with other materials (e.g. water hydration to synthesize calcium lignosulfonate-doped limestone): [19]; (2) Chemical pretreatment of limestone with chemical agents (e.g. acetic or pyroligneous acid) [20] (3) Incorporation of support materials (e.g., Calcium aluminate cement); to decrease sintering along cycles [7]; and (4) Manufacturing of synthetic CaO-based sorbents (incorporating e.g. ZrO_2, Al_2O_3, and CeO_2) [21]. Even though these works are advancing toward solving sorbent problems, the main gaps nowadays are on the proper utilization of fine cohesive powders. Fluidization performance is usually severely affected by particle size [22], being fine powders preferred. For fine cohesive powders, the interparticle adhesion has a stronger effect than the hydrodynamic and gravitational forces [11]. This fact can entail agglomeration, channelling and plugging phenomena, impeding uniform fluidization, and hence affecting the overall fluidization performance [11].

Regarding models for scale-up of the process and its combination with energy storage, many recent works have been published [14]. Within these, models have been presented for specific process elements (i.e., carbonator) [23], up to industrial-scale process models considering full integration with concentrated solar power plants (forecasted by Ortiz et al. to yield an overall efficiency of up to 44%) [24,25]. As explained before, the solar calciner (particle receiver) is considered to remain a major technological challenge, even though there are projects to progress from a TRL-4 (technology validated in lab) to a TRL-5 level (technology validated in a relevant environment [11,14]). The

development of advanced models to predict the solar calciner performance and obtaining robust design are still gaps to be further studied.

Integration of CaL has been studied in the framework of fuel-fired plants for carbon capture and solar plants for energy storage [26], as well as pulp and paper industry, for which a total avoided cost of 39 €/tCO_2 was estimated [27]. However, CaL could be also integrated with other CO_2-emitter industries (i.e., steel manufacturing, gaseous streams from renewable-based technologies like hydrothermal carbonization). In this sense, the integration of CaL in different industries will be key for the industrial implementation of the technology. The study of different CO_2 sources is an important research gap to be covered.

In line with the need of advancing in the integration of CaL in industrial processes, there is a need for exploring different gaseous streams containing CO_2. Further research in this line will allow for gaining knowledge on the different needs that CaL implementation might entail. Examples of these needs could be removal of minor impurities from flue gases and/or specific sorbent developments for some gaseous compounds. Literature works mentioned in this section depart from an inlet CO_2-ladden gas with a composition range representative for air-combustion flue gas, i.e. 10-20% CO_2/80–90% N_2 [28]. To the best of the authors knowledge, there is a lack of literature works investigating the application of the CaL process for other gas streams containing CO_2. Gaseous streams of great interest are those coming from renewable-based processes. Examples of these streams are biogas produced through anaerobic digestion, the gas produced from hydrothermal carbonization, or pyrolysis gas.

In this work, for the first time, we propose a combination to upgrade biogas and remove CO_2 via CaL technology, which will help to advance in the research gap explained above. The removal of CO_2 from biogas via CaL, schematized in Fig. 1, allows producing biomethane as value-added product while allowing negative emissions [29–31]. There have been works studying sorption-enhanced gasification, where carbonation is used for in-situ CH_4 reforming and removal of CO_2 from the gas in the fluidized bed reactor where raw gas is generated [32], but this entails challenges in terms of separation of the carbonated sorbent from ashes and bed material. Note that the process proposed in Fig. 1 could also be exploited from the perspective of energy storage, as it consists of a solids cycle between an exothermic and endothermic process, but commercial implementation of this aspect requires large scales.

1.3. Aim, scope and novelty

This work aims at evaluating the performance of CaL for the upgrading of biogas. More specifically, the objectives are to study: i) the impact of biogas composition vs air-combustion flue gas; ii) the performance of CaL when facing cooling down and heating up within cycles, which is characteristic of long-term thermochemical energy storage; iii) the influence of atmosphere composition during calcination (CO_2 and N_2 are used as fluidizing agents for this purpose); iv) the influence of other operational parameters: biogas composition, carbonation temperature and particle size.

To attain the stated aim, this work uses an instrumented lab-scale fluidized bed reactor. The used inlet gas streams representing biogas have been set to CO_2/CH_4 mixtures with composition of 30–50%/ 50–70% (following [33,34]). The novelty of this work relies on the fact that the performance of CaL is studied for CO_2-loaded gaseous streams not representative of air-combustion flue gas, but for much higher CO_2 concentrations representative for e.g. biogas upgrading.

2. Experimental setup

The experimental setup used is described in detail in Ref. [35] and schematically represented in Fig. 2. In brief, a quartz glass fluidized bed reactor (inner diameter of 22 mm and height of 820 mm) was placed in an electrically-heated furnace with adjustable temperature. The solids used are GranuFax $CaCO_3$ limestone (>97% purity) provided by Lhoist.
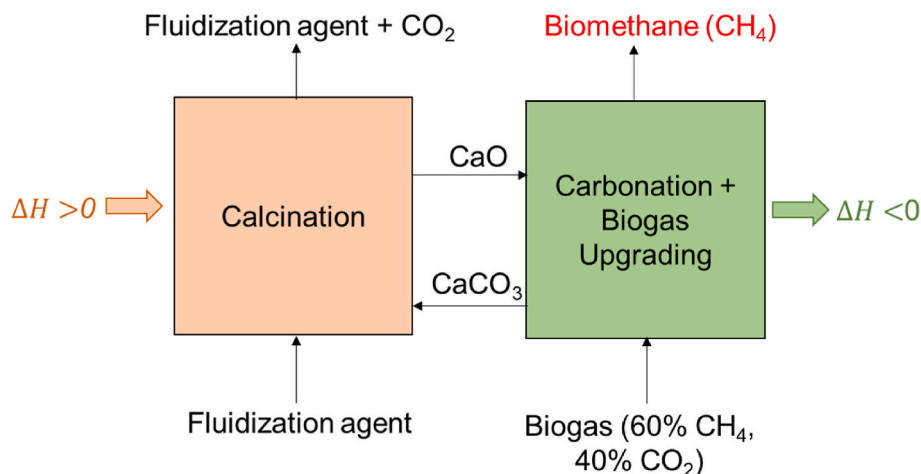
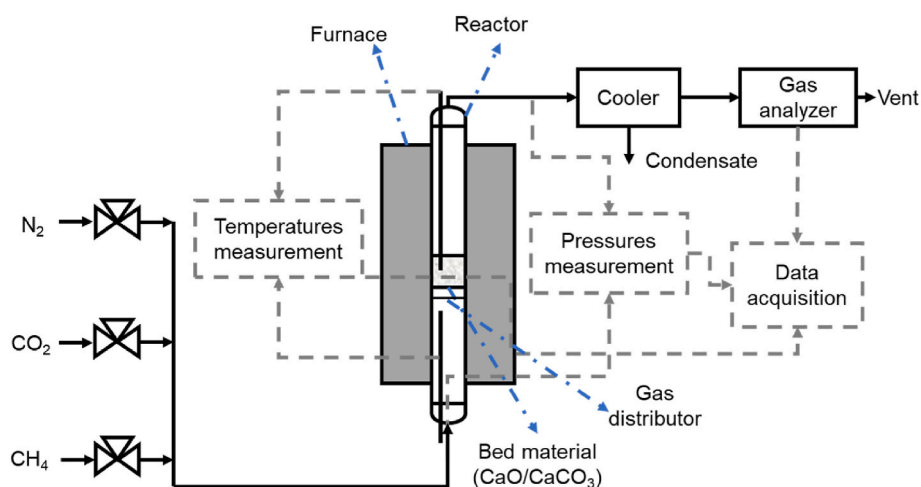**Fig. 1.** Process scheme for biogas upgrading via CaL.

Fig. 2. Scheme of the laboratory fluidized bed setup used.

The inlet gas stream is fed from the bottom with partial gas flows of its different compounds (CH_4, CO_2, and N_2, all with >99% purity, supplied by Linde) regulated through mass flow controllers. During operation, computer controlled magnetic valves could be used to control the gases fed to the reactor.

Thermocouples (type K) were used to measure temperature of (1) the

Table 1

Experimental matrix.

Test	Main purpose of the experiment	Carbonation gas composition	Carbonation temperature (°C)	Fluidization agent for calcination	Calcination temperature (°C)	Particle size range (μm)
1	Baseline	40% CO_2, 60% CH_4	700	N_2	900	355–550
2	Compare with air combustion flue gas	15% CO_2, 85% N_2	700	N_2	900	355–550
3	Evaluate the impact of increasing CO_2 composition with N_2 as accompanying gas	40% CO_2, 60% N_2	700	N_2	900	355–550
4	Evaluate the difference between CH_4 and N_2 as accompanying gas	15% CO_2, 85% CH_4	700	N_2	900	355–550
5	Study the influence of cooling down and heating up within cycles	40% CO_2, 60% CH_4	700	N_2	900	355–550
6	Study the influence of fluidization agent for calcining	40% CO_2, 60% CH_4	700	CO_2	950	355–550
7	Study the influence of fluidization agent for calcining	40% CO_2, 60% CH_4	700	N_2	950	355–550
8	Influence of biogas composition	30% CO_2, 70% CH_4	700	N_2	900	355–550
9	Influence of biogas composition	50% CO_2, 50% CH_4	700	N_2	900	355–550
10	Influence of temperature	40% CO_2, 60% CH_4	600	CO_2	900	355–550
11	Influence of temperature	40% CO_2, 60% CH_4	650	CO_2	900	355–550
12	Influence of temperature	40% CO_2, 60% CH_4	750	CO_2	900	355–550
13	Influence of temperature	40% CO_2, 60% CH_4	800	CO_2	900	355–550
14	Influence of particle size	40% CO_2, 60% CH_4	700	CO_2	900	125–355
15	Influence of particle size	40% CO_2, 60% CH_4	700	CO_2	900	550–700

inlet gas (measured in the air plenum under the porous quartz plate acting as gas distributor), and (2) the bed. The pressure drop over the reactor is measured at a frequency of 10 Hz. The outlet gas composition is studied with an on-line IR/UV/paramagnetic/thermal conductivity gas analyzer (Rosemount NGA-2000) which can measure CO_2, CO, CH_4, and SO_2. To avoid condensable components to reach this gas analyzer, the outlet gas is previously led into a cooler through a heated line.

3. Methodology

3.1. Test matrix

The experiments listed in Table 1 were carried out to test the impact of different parameters on the degree of carbonation and capture capacity. Test 1 serves as a baseline test with the following values: biogas composition (40% CO_2 and 60% CH_4), fluidization agent for calcination (N_2), calcination and carbonation temperatures (700 °C and 900 °C, respectively), and particle sizes (355–500 μm). The first group of experiments (tests 2–4 in Table 1) is aimed to study the impact of biogas composition, both in terms of CO_2 concentration (15% and 40%, representative for air-combustion flue gas and biogas, respectively) and of the gas accompanying CO_2 (CH_4 or N_2). Test 5 targets to study the influence of cooling down and heating up the sorbent material within cycles. Storing the sorbent at ambient temperature is a common procedure in sorbent cyclability studies but has also a potential interest from the perspective of CaL process if the solids are to be freighted in the case of energy storage applications (where the two reactors can be placed in different locations). The influence of fluidization agent for the calcination stage is studied through tests 6 and 7. From a process perspective, fluidizing the calcination with CO_2 would be convenient to avoid downstream separation of other gases. Nonetheless, previous works have corroborated that, for air-combustion flue gases, the selection of CO_2 entails a fast decrease of the performance [20,36,37]. Here, we intend to check if inletting biogas to the carbonator influences this fact. Tests 8 and 9 aim at disclosing the influence of biogas composition within typical composition ranges, i.e. to study the sensitivity of the process to the usual variations in biogas composition. Biogas composition can vary significantly depending on the source: higher CH_4 share is expected when producing biogas from wastewater sludge, while higher share of CO_2 is typically observed for household waste [38,39]. The impact of carbonation temperature was also examined, covering a wide range from 600 °C to 800 °C in steps of 50 °C – see tests 10–13. Finally, the influence of particle size in CaL is studied by considering tests 14 and 15 [36,40]. The size ranges investigated in this work (mean sizes of 240, 425, and 625 μm) are considerably coarser than those in previous literature studies, but there was a need to adjust them to our experimental setup by avoiding solids elutriation.

3.2. Experimental procedure and data treatment

For all tests, the reactor was charged with 15 g of bed material (yielding a fixed bed height of around 5 cm) and placed into the furnace. The analyzer was then calibrated before every experiment. As the initial bed material is carbonated, a pre-calcination stage was carried out before every experiment. This pre-calcination was always carried out in an N_2 atmosphere at 900 °C until full decarbonization was observed (<0.1% CO_2 in analyzer). After this, the first cycle starts with carbonation and, once the bed material is fully carbonated, calcination is forced by switching the inlet gas. In every cycle, enough experimental time was allowed for carbonation and calcination to ensure a steady state/equilibrium. For every test, a total of 10 cycles were completed, which was observed to be a high enough number enough for fair data interpretation. Reproducibility checks for representative cycles showed a stable value of ±2% (in relative units) for the standard deviation of the measured concentration values, which evidences satisfactory levels of robustness and accuracy.

Fig. 3 represents an example of collected and processed measurement data (in this case, CO_2 outlet concentration during test 1). As shown in Fig. 3 a, the sampled dynamic outlet CO_2 concentration reaches the saturation value as the number of cycles is increased. From this data, the instantaneous CO_2 capture rate, shown in Fig. 3 b, can be calculated by differentiation and studied – a rate decrease with the number of cycles is clearly observed from this representation. Further, the accumulated CO_2 capture can also be calculated by closure of the mass balance, which yields the data represented in Fig. 3 c. From the saturation values in such accumulated CO_2 capture curves the carbonation conversion and the CO_2 capture capacity can be calculated as:

$$\text{Carbonation conversion} = \frac{\text{CaCO}_3 \text{ at saturation (g)}}{\text{maximum stoichiometric CaCO}_3 \text{(g)}} \quad (2)$$

$$\text{CO}_2 \text{ capture capacity} = \frac{\text{CO}_2 \text{ captured at saturation (g)}}{\text{fully} - \text{calcined sorbent (CaO) (g)}} \quad (3)$$

4. Results

Fig. 4 showcases the impact on carbonation conversion of using biogas-like inlet gas instead of air-combustion flue gas. As seen, the sorption ability decreases over cycles for all four tests represented, with carbonation conversion decreasing from 0.7 to 0.85 to 0.19–0.26. This drop has been previously seen and studied in many works [11,40,41], and is mainly attributed to two different phenomena: (1) sintering of the sorbent at high temperatures; and (2) formation of a pore-plugging layer of $CaCO_3$ on CaO [40,42,43]. As seen, this decrease impacts higher for earlier cycles, eventually achieving somehow stable residual conversions. According to Ref. [11], the values of these residual conversion can for decarbonation of air-combustion flue gas be in a very wide range (0.07–0.82, within which our experimental values with other inlet gases are contained). Focusing on the influence of the inlet gas composition, higher sorption ability is observed when using synthetic biogas (test 1, baseline) than for air-combustion flue gas. To gain insight about the causes of this difference, two more experiments were performed where only the CO_2-accompanying gas (test 3), or the CO_2 concentration (test 4) were varied in comparison to the baseline test. In general, it is seen that the CO_2 concentration in the inlet gas plays a stronger and clearer role than the choice of accompanying gas. While a higher CO_2 concentration in the inlet gas yields improved sorption ability (as the driving force for the mechanism is increased), it is also seen that the impact of switching the accompanying gas from N_2 to CH_4 gains importance (improving the sorption ability) at higher CO_2 concentration levels.

A potential explanation for the improved sorption ability in presence of CH_4 could be the existence of secondary reactions, like dry reforming of CH_4 (Eq. (4)). This reaction, which produces CO and H_2 happens at temperatures around 700 °C [44], is usually carried out in the presence of a catalyst to maximize yields but can still play a considerable role in the absence of catalysts. At the operating temperatures the CO and H_2 produced can react to form CH_4 and H_2O (methanation reaction, Eq. (5) and Eq. (6)) [45]. Furthermore, reverse carbon gasification could also happen (Eq. (7)) further producing H_2O [46].

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (4)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (5)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (6)$$

$$CO + H_2 \leftrightarrow H_2O + C \quad (7)$$

The resulting presence of H_2O could thus be the reason behind higher sorption ability when using CH_4 as accompanying gas, since it has been proved that the presence of H_2O enhances the sorbent performance in CaL [36,47–49]. This hypothesis is also aligned with the observed increase sorption at higher levels of CO_2 concentration, as the latter acts as
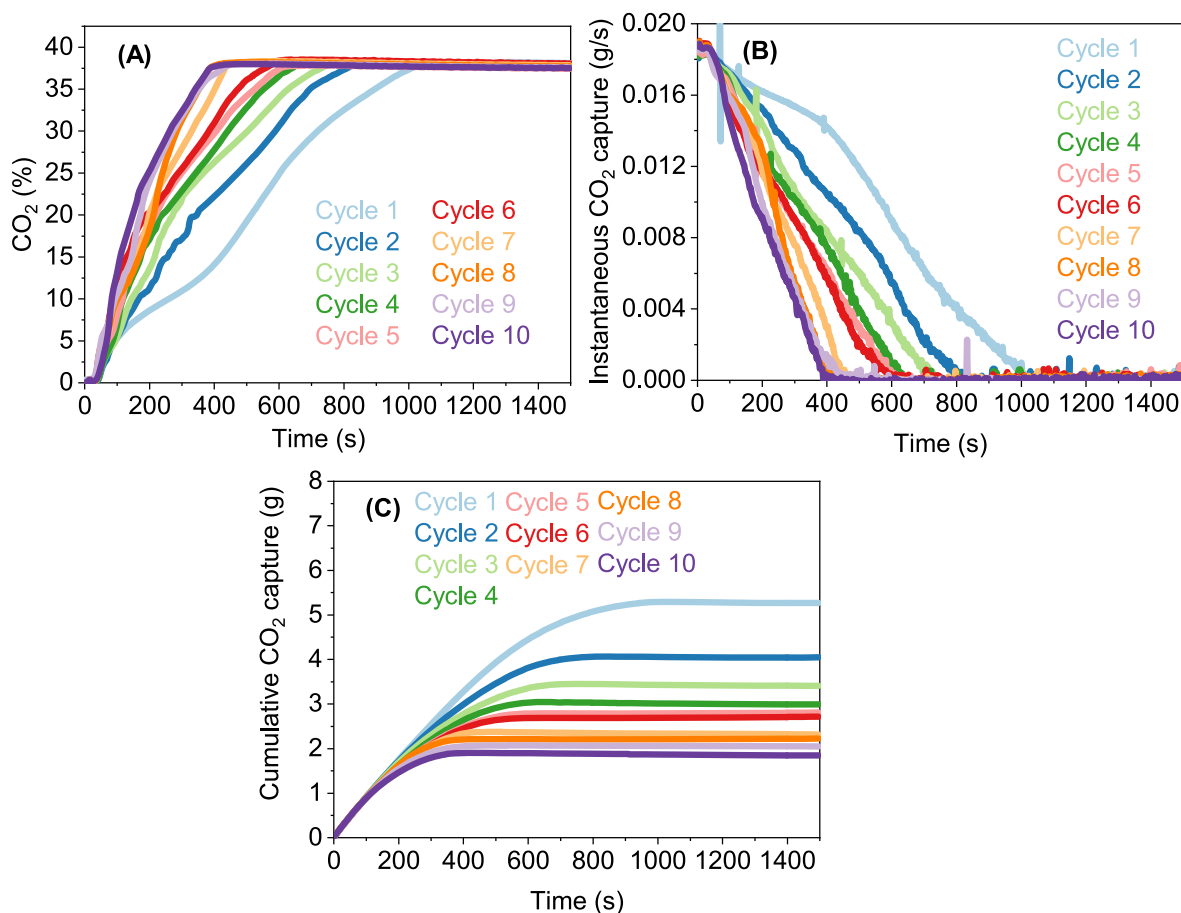
Fig. 3. Example of CO_2 concentration data obtained from measurements (Fig. 3a) and subsequent data processing (Fig. 3b–c). Data taken from Test 1.
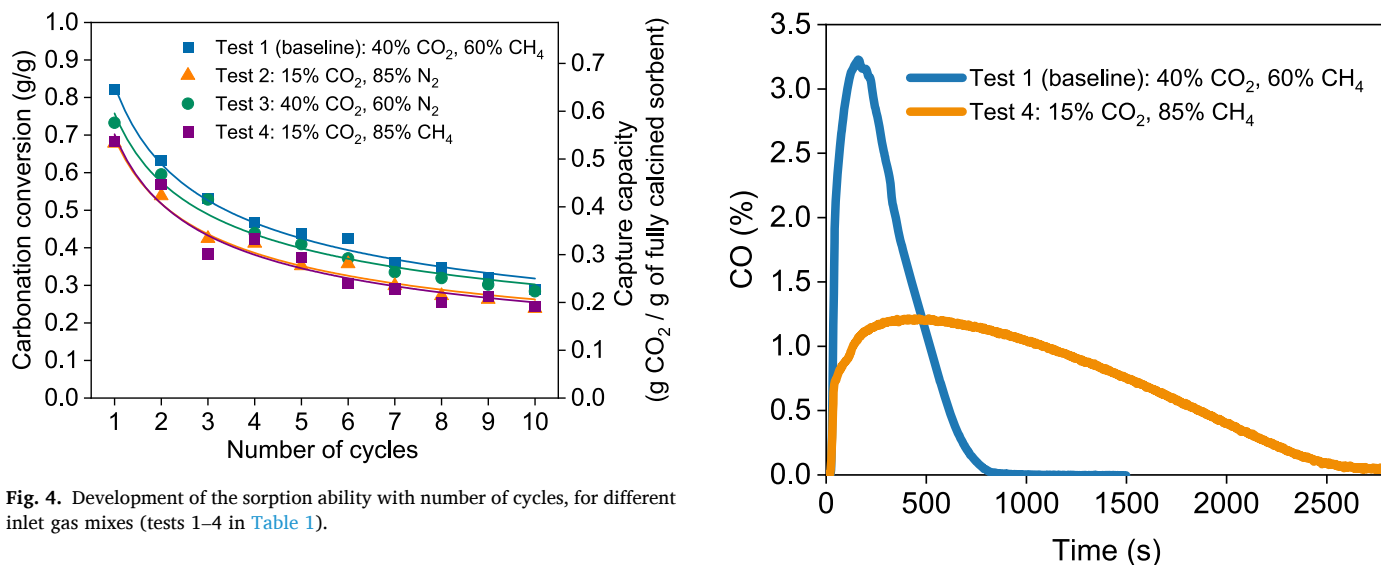

Fig. 4. Development of the sorption ability with number of cycles, for different inlet gas mixes (tests 1–4 in Table 1).

Fig. 5. CO concentration over time for the first cycle of tests 1 and 4.

source for H_2O production. To check the validity of the hypothesis, CO concentration data was studied. Fig. 5 shows CO concentration for the first cycle in tests 1 and 4 – the CO concentration was null for the tests using N_2 as accompanying gas, i.e. tests 2 and 3. The disappearance of CO over time indicates the production of H_2O (i.e. via Eq. (5)). As seen from Fig. 5, the CO concentration reaches 3 times higher values for the high-CO_2 case (test 1) compared to the low-CO_2 one (test 4), hence boosting H_2O production as indicated by the fast decrease of the CO peak.

The influence of cooling down and heating up the sorbent material within cycles, was also evaluated to assess the impact of storing sorbent at ambient conditions. This is related to energy storage applications, and other off-site calcination scenarios and longer lab characterization tests on in which the sorbent is cooled in-between cycles. Intermediate ambient storage of the active solids has shown to impact on the reaction rates in other processes (e.g. slowing them for char gasification [50]).

However, for the studied cycle, the results obtained (Fig. 6) show that the conversion and capture capacity along the cycles is not severely affected by cooling down and heating up within cycles. Thus, implementation of the CaL cycle with intermediate ambient storage will not yield a considerable modified need for make-up sorbent flow.

Previous literature studying decarbonation of air-combustion flue gas reports that calcining with CO_2 as fluidizing agent leads to a fast decrease of the calcination conversion with the number of cycles [40, 51]. The main reasons are the significantly high temperature needed (950 °C, according to equilibrium [52]) to have a relatively fast reaction [53], hence causing sintering of the bed material and thus entailing the loss of available reactive surface [54]. These occur to a less extent when fluidizing calcination with other inert gases (e.g. N_2, H_2O or He [51]), as the temperature needed is usually lower (e.g., 900 °C for N_2). However, the use of such inert gases will require an extra stage, such as membrane separation, to separate the CO_2 released from the inert gas [51]. Fig. 7 shows the results from the experiments carried out to study the impact of calcination conditions (varying fluidization gas and temperature) on sorbent sorption ability. Results show that the drop in sorption ability is amplified by both the use of CO_2 as fluidizing agent for calcination and the higher temperature needed.

A comparison evaluating the impact of the expected variations in biogas composition (tests 1, 8 and 9) is shown in Fig. 8. As seen, there are not considerable differences among the three compositions studied in comparison with other analyses of this work. Thus, the process is robust to the expected range of variation in biogas composition.

According to previous works using air-combustion flue gas as carbonator agent, lower carbonation temperatures lead to lower overall carbonation conversions [47,55,56]. The reason behind is the formation of a high density $CaCO_3$ product layer over the CaO particles at lower temperatures [55]. This fact is caused by the lower diffusion at lower temperatures, resulting in high-density $CaCO_3$ spots that cover the CaO surface. Consequently, a bigger $CaCO_3$ layer thickness is formed, which reduces the sorbent carrying capacity [55]. Furthermore, the effect of the temperature on CH_4 concentration needs to be considered, as it is known that the sorption reaction rate is slower at higher temperatures due to equilibrium limitations [57], entailing higher CO_2 and lower CH_4 concentrations in the outlet gas. However, there is a significant knowledge gap concerning the use of other gases as carbonator agents. As shown in Fig. 9, the effect of the carbonation temperature on the sorption ability is the same for biogas as for the air-combustion flue gas studied in previous works [55,57], i.e. higher temperatures yield improved sorption ability. A closer look at the dynamic concentrations of CO_2 and CH_4 in the outlet gas during carbonation (Fig. 10A and 10B, respectively) reveals the slower absorption rate resulting from higher

Fig. 7. Sorption ability with number of cycles for different calcining gases (tests 1, 6 and 7 in Table 1).

Fig. 8. Sorption ability with number of cycles for different biogas compositions (tests 1, 8 and 9 in Table 1).

Fig. 9. Impact of temperature on sorption ability with number of cycles (tests 1, 10–13 in Table 1).
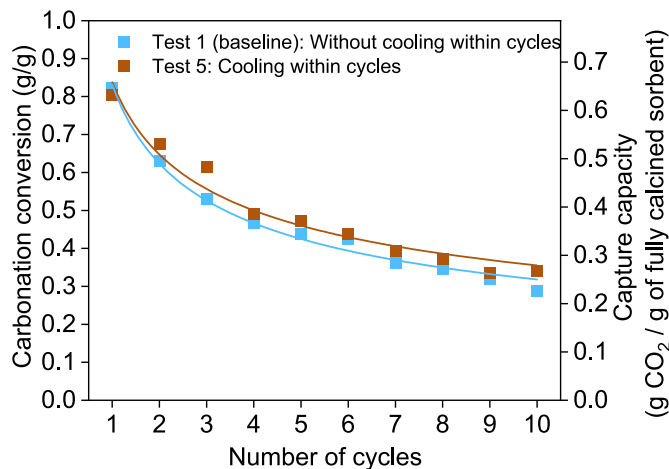

Fig. 6. Development of the sorption ability with number of cycles, with and without intermediate ambient storage of the sorbent (tests 1 and 5 Table 1).
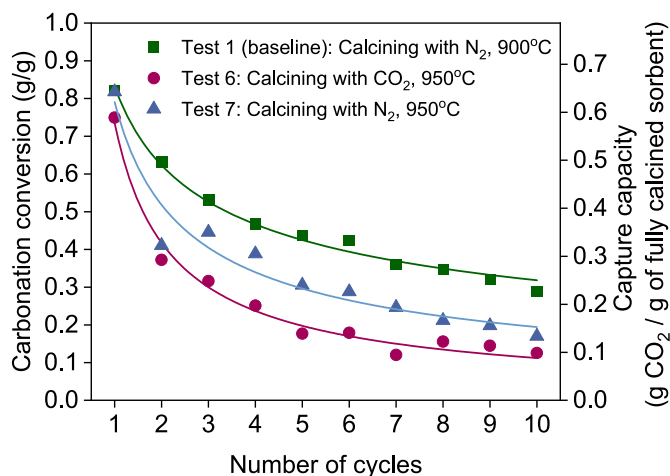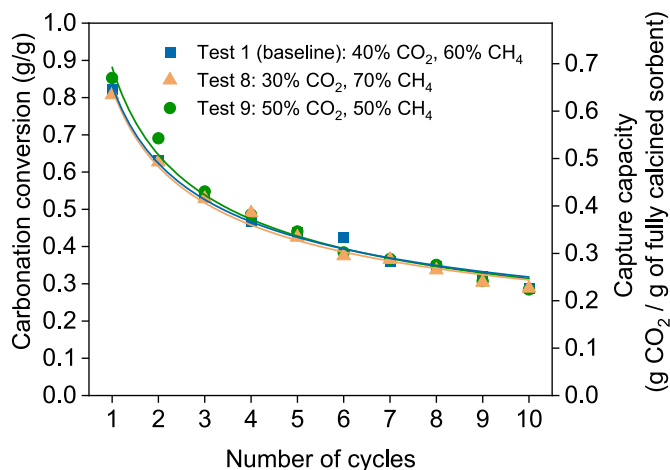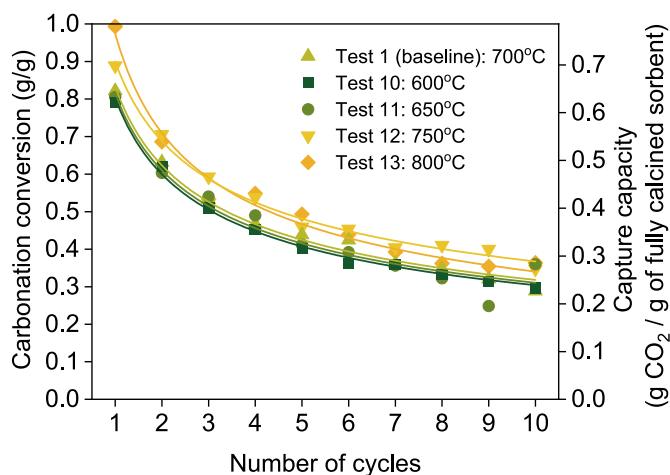
temperatures. This fact calls for higher sorbent-to-gas stoichiometric ratio and larger sorbent inventories in the carbonator, which in its turn represents a need for economic optimization. Please note that in
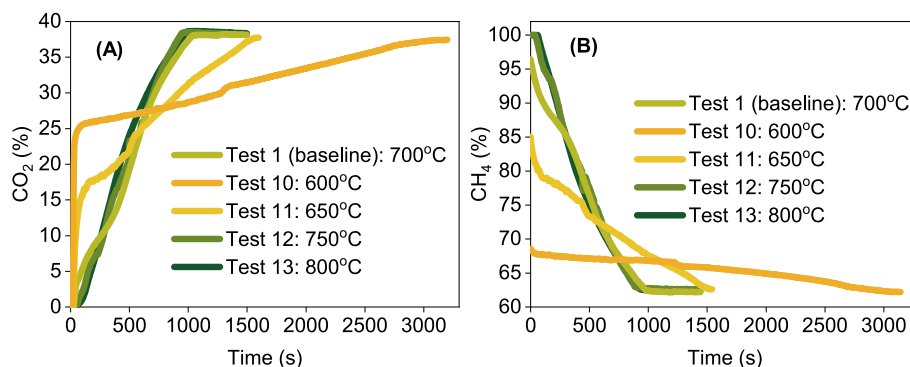
Fig. 10. Dynamic evolution of the carbonator outlet concentrations of (A) CO_2 and (B) CH_4 (tests 1, 10–13 in Table 1).

Fig. 10A and 10B the concentration values reach approximately 62/38%, i.e. a difference of ($\pm$2%) to the 60/40% ratio, which corresponds to the experimental error of the analyzer.

Finally, the effect of particle size was examined. Results in previous literature do not show a clear general trend. Some works claim that overall cycle performance of CaL is more stable when using finer sorbent particles [36,40], while others do not report any considerable difference in sorption ability [58]. According to these previous works, there could be many factors influencing the eventual effect of particle size on the sorption ability over cycles (i.e., impurities in the flue gas or atmosphere for calcination). As depicted in Fig. 11, lower sorption ability was obtained for the first cycles with the finest range of particle size tested, while mid- and coarse-sized particles show roughly similar results, with coarse ones yielding slightly higher levels. A potential reason for this fact could be again the presence of H_2O due to secondary reactions (c.f. Fig. 5). In relation to this [36], found that addition of H_2O to the CaL process was found to enhance multicycle performance, with a higher impact on larger particles [36,40]. The CO concentration measured for the different particles sizes presents similar trends to those in Fig. 5, reaching the following maximum values: 4.2% for 550–700 μm; 3.2% for 355–550 μm; and 1.7% for 125–355 μm. Thus, the CO measured - and hence the potential H_2O produced - is highest for coarse particles and lowest for fine ones.

5. Conclusions and future works

In this work we studied the CaL process for biogas upgrading by experimentally evaluating the impact of several parameters on the sorption capacity along cycles. As main general finding, the sorption ability is found to improve when feeding biogas instead of combustion flue gas, which is caused by small productions of H_2O due to secondary reactions such as dry reforming or methanation. Indeed, the carbonation conversion reaches 0.82 for biogas, while it was 0.69 for typical air-combustion flue gas (for the first cycle). The impact of CH_4 to CO_2 ratio was also examined, revealing that biogas with different CH_4 to CO_2 ratio of can be used without highly impacting the carbonation conversion. This opens this process idea for biogas producing feedstocks with large deviation in CH_4 to CO_2 ratio. Further, a positive impact concerning carbonation conversion is observed when increasing the temperature. Nonetheless, for higher temperatures, lower CH_4 compositions were obtained in the outlet gas. Finally, the study suggests a slight improvement of the carbonation performance for larger particle sizes due to the production of H_2O generated through secondary reactions.

Our study also tackles down two main challenges: (1) the use of CaL for other gaseous streams gases than those coming from air-combustion is possible, evidencing the potential of CaL to be used at different industrial processes. In this line, the results of this work could be expanded to other flue gases from renewable-based technologies like hydrothermal carbonization or gasification; (2) the results also indicate that CaL overcomes a current main challenge in many energy storage
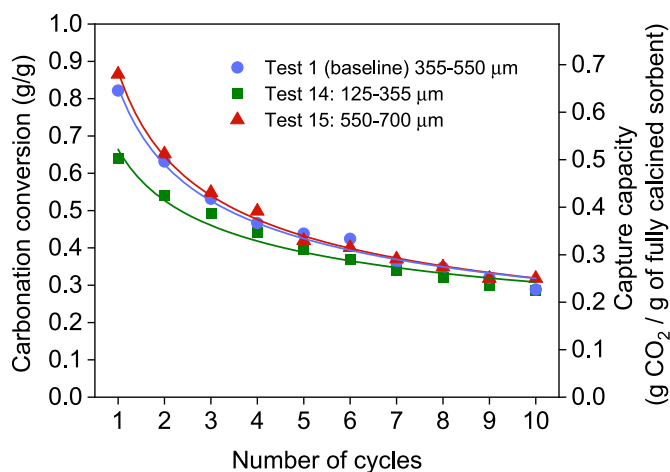

Fig. 11. Impact of particle size on sorption ability with number of cycles (tests 1, 14–15 in Table 1).

applications using solids cycles: the fact that storage of the solids at ambient conditions in between cycles reduces their reactivity compared to continuous cycling. This is shown not to be the case for CaL under the conditions here tested.

This work not only answers to the research gaps and challenges identified, but also opens new research questions. In the path towards the industrial implementation of CaL for biogas upgrading, the following points need to be addressed: (1) study on how minor impurities contained in biogas streams affects the sorbent cyclability (2) study on how the utilization of other gases (i.e., steam); in the calcination stage impact the sorption ability; (3) design of specific advanced sorbents to improve the sorption ability over cycles for biogas upgrading; (4) equipment sizing and mass and energy balances; (5) development of trustable models for this process, allowing to obtain robust design of the equipment involved; (6) techno-economic and life cycle analysis of the process.

Data availability

All data used are included in the manuscript.

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