



CHALMERS
UNIVERSITY OF TECHNOLOGY

Biogas upgrading through calcium looping: Experimental validation and study of CO₂ capture

Downloaded from: <https://research.chalmers.se>, 2023-09-08 04:42 UTC

Citation for the original published paper (version of record):

Baena-Moreno, F., Mei, D., Leion, H. et al (2023). Biogas upgrading through calcium looping: Experimental validation and study of CO₂ capture. *Biomass and Bioenergy*, 176. <http://dx.doi.org/10.1016/j.biombioe.2023.106918>

N.B. When citing this work, cite the original published paper.



Biogas upgrading through calcium looping: Experimental validation and study of CO₂ capture

Francisco M. Baena-Moreno^{a,*}, Daofeng Mei^a, Henrik Leion^b, David Pallarès^a

^a Department of Space, Earth and Environment, Division of Energy Technology, Chalmers University of Technology, 412 96, Göteborg, Sweden

^b Department of Chemical and Biological Engineering, Division of Energy and Material, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden

ARTICLE INFO

Keywords:

Calcium looping
Biogas upgrading
Calcination-carbonation
Biomethane
CO₂ capture

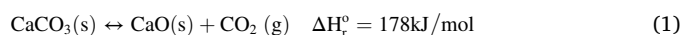
ABSTRACT

The calcium looping technology is one of the most promising technologies for capturing and storing CO₂. This technology has been evaluated with a variety of sorbents and conditions in previous works, but the inlet CO₂-laden gas has typically been a flue gas from combustion, which typically has a composition of 10–20% CO₂ and 80–90% N₂. On the other side, the performance of the calcium looping process for CO₂ 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% CO₂, 60% CH₄) 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 CO₂-capture performance of calcium looping improves when using biogas as inlet CO₂-laden 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 CH₄ to CO₂ 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 (CO₂) 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 CaCO₃ into CaO and CO₂ is known as calcination (endothermic reaction), while the opposite step is named carbonation (exothermic).



The interest in CaL lies in several advantages: (1) Relatively small energy penalty when used to capture CO₂ 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 CO₂ emitters [9]; (6) it can be used for combined CO₂ 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

* Corresponding author.

E-mail address: francisco.baena@chalmers.se (F.M. Baena-Moreno).

<https://doi.org/10.1016/j.biombioe.2023.106918>

Received 20 February 2023; Received in revised form 22 March 2023; Accepted 27 July 2023

Available online 30 July 2023

0961-9534/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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 CO₂ capture technology at conditions close to those expected in large scale combustion plants, with overall CO₂ 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 CO₂ capture [13]. The technical viability of CO₂ capture has been evidenced, as showed in the works previously mentioned. Nonetheless, pilot scale demonstration of CaL applied for combined CO₂ 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 pyrolygneous 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. ZrO₂, Al₂O₃, and CeO₂) [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 €/tCO₂ was estimated [27]. However, CaL could be also integrated with other CO₂-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 CO₂ 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 CO₂. 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 CO₂-laden gas with a composition range representative for air-combustion flue gas, i.e. 10–20% CO₂/80–90% N₂ [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 CO₂. 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 CO₂ via CaL technology, which will help to advance in the research gap explained above. The removal of CO₂ 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 CH₄ reforming and removal of CO₂ 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 (CO₂ and N₂ 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 CO₂/CH₄ 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 CO₂-loaded gaseous streams not representative of air-combustion flue gas, but for much higher CO₂ 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 CaCO₃ limestone (>97% purity) provided by Lhoist.

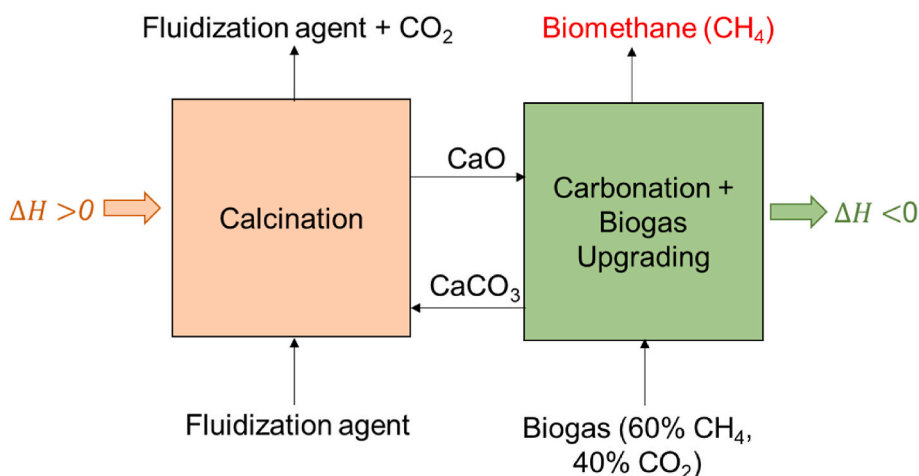


Fig. 1. Process scheme for biogas upgrading via CaL.

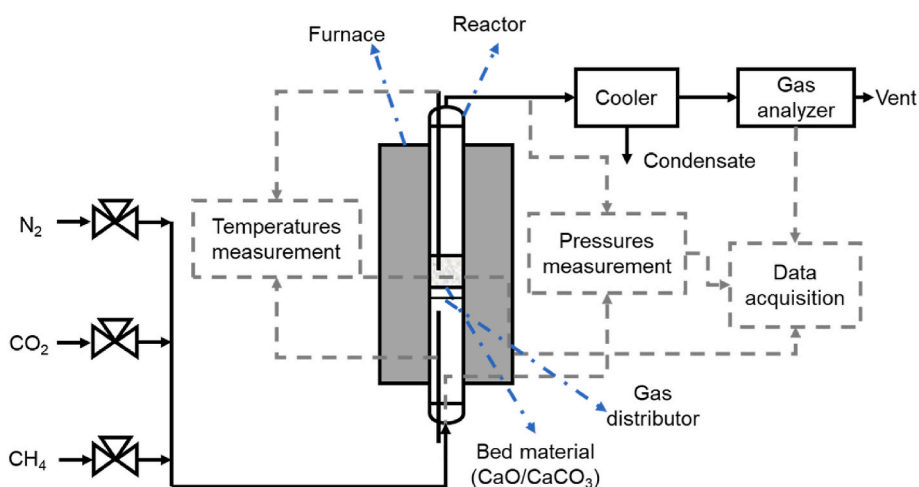


Fig. 2. Scheme of the laboratory fluidized bed setup used.

The inlet gas stream is fed from the bottom with partial gas flows of its different compounds (CH₄, CO₂, and N₂, 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 CO₂, CO, CH₄, and SO₂. 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% CO₂ and 60% CH₄), fluidization agent for calcination (N₂), 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 CO₂ concentration (15% and 40%, representative for air-combustion flue gas and biogas, respectively) and of the gas accompanying CO₂ (CH₄ or N₂). 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 CO₂ would be convenient to avoid downstream separation of other gases. Nonetheless, previous works have corroborated that, for air-combustion flue gases, the selection of CO₂ 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 CH₄ share is expected when producing biogas from wastewater sludge, while higher share of CO₂ 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 N₂ atmosphere at 900 °C until full decarbonization was observed (<0.1% CO₂ 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, CO₂ outlet concentration during test 1). As shown in Fig. 3 a, the sampled dynamic outlet CO₂ concentration reaches the saturation value as the number of cycles is increased. From this data, the instantaneous CO₂ 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 CO₂ 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 CO₂ capture curves the carbonation conversion and the CO₂ capture capacity can be calculated as:

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

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

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 CaCO₃ 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 CO₂-accompanying gas (test 3), or the CO₂ concentration (test 4) were varied in comparison to the baseline test. In general, it is seen that the CO₂ concentration in the inlet gas plays a stronger and clearer role than the choice of accompanying gas. While a higher CO₂ 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 N₂ to CH₄ gains importance (improving the sorption ability) at higher CO₂ concentration levels.

A potential explanation for the improved sorption ability in presence of CH₄ could be the existence of secondary reactions, like dry reforming of CH₄ (Eq. (4)). This reaction, which produces CO and H₂ 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 H₂ produced can react to form CH₄ and H₂O (methanation reaction, Eq. (5) and Eq. (6)) [45]. Furthermore, reverse carbon gasification could also happen (Eq. (7)) further producing H₂O [46].



The resulting presence of H₂O could thus be the reason behind higher sorption ability when using CH₄ as accompanying gas, since it has been proved that the presence of H₂O enhances the sorbent performance in CaL [36,47–49]. This hypothesis is also aligned with the observed increase sorption at higher levels of CO₂ concentration, as the latter acts as

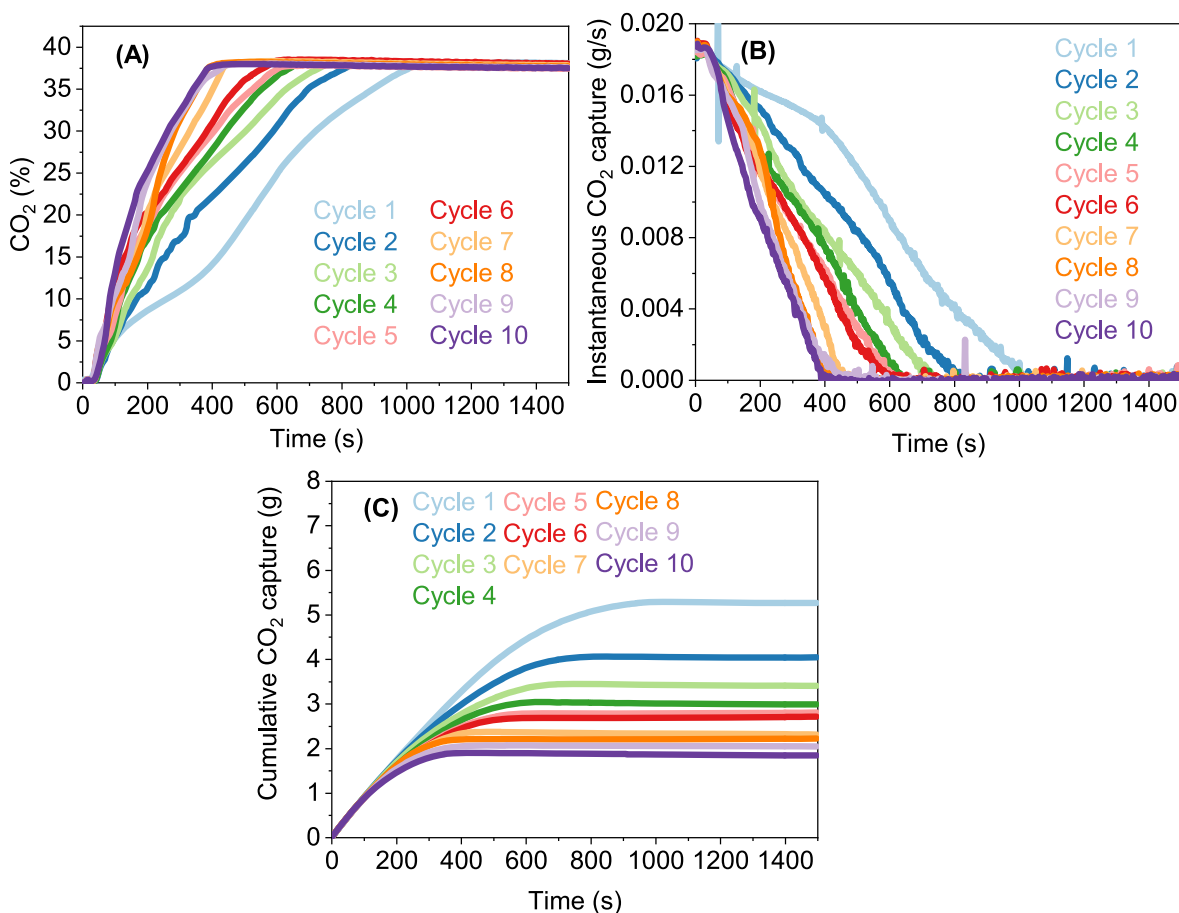


Fig. 3. Example of CO₂ concentration data obtained from measurements (Fig. 3a) and subsequent data processing (Fig. 3b–c). Data taken from Test 1.

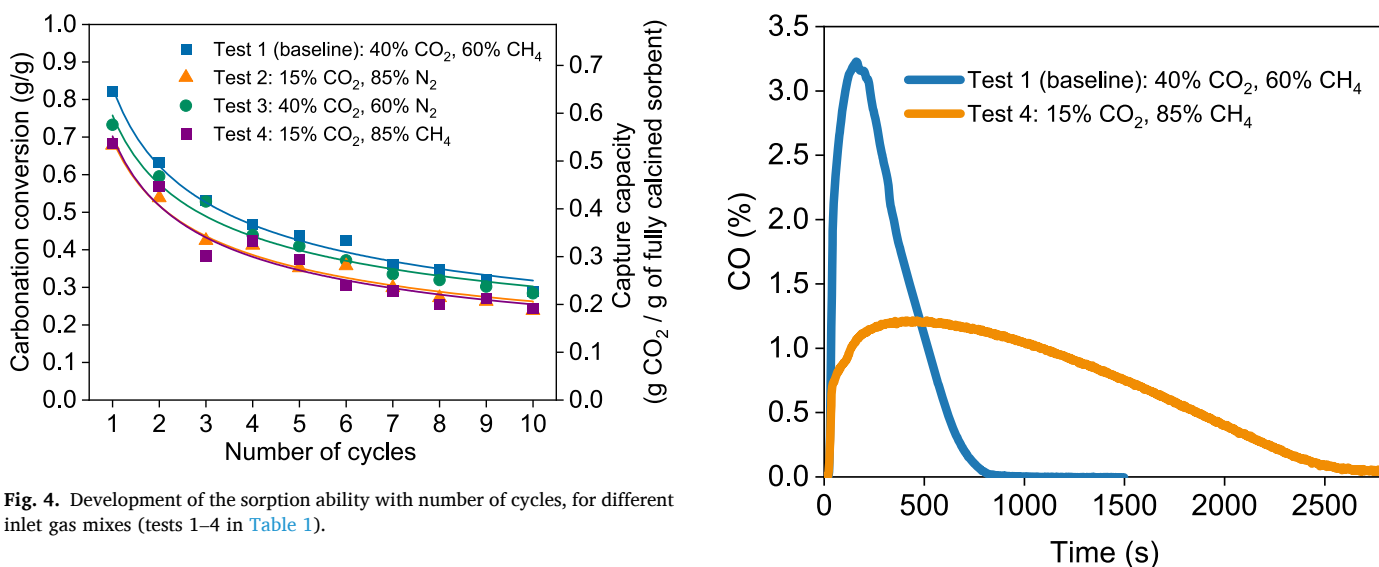


Fig. 4. Development of the sorption ability with number of cycles, for different inlet gas mixes (tests 1–4 in Table 1).

source for H₂O 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 N₂ as accompanying gas, i.e. tests 2 and 3. The disappearance of CO over time indicates the production of H₂O (i.e. via Eq. (5)). As seen from Fig. 5, the CO concentration reaches 3 times higher values for the high-CO₂ case (test 1) compared to the low-CO₂ one (test 4), hence boosting H₂O production as indicated by the fast decrease of the CO peak.

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

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 CO₂ 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. N₂, H₂O or He [51]), as the temperature needed is usually lower (e.g., 900 °C for N₂). However, the use of such inert gases will require an extra stage, such as membrane separation, to separate the CO₂ 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 CO₂ 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 CaCO₃ 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 CaCO₃ spots that cover the CaO surface. Consequently, a bigger CaCO₃ layer thickness is formed, which reduces the sorbent carrying capacity [55]. Furthermore, the effect of the temperature on CH₄ 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 CO₂ and lower CH₄ 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 CO₂ and CH₄ in the outlet gas during carbonation (Fig. 10A and 10B, respectively) reveals the slower absorption rate resulting from higher

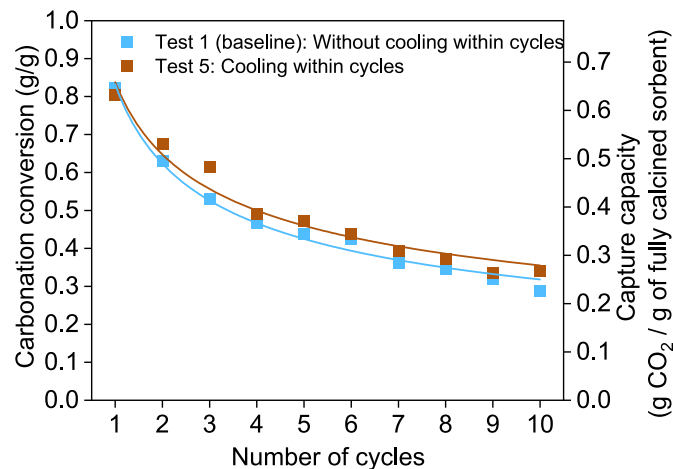


Fig. 6. Development of the sorption ability with number of cycles, with and without intermediate ambient storage of the sorbent (tests 1 and 5 Table 1).

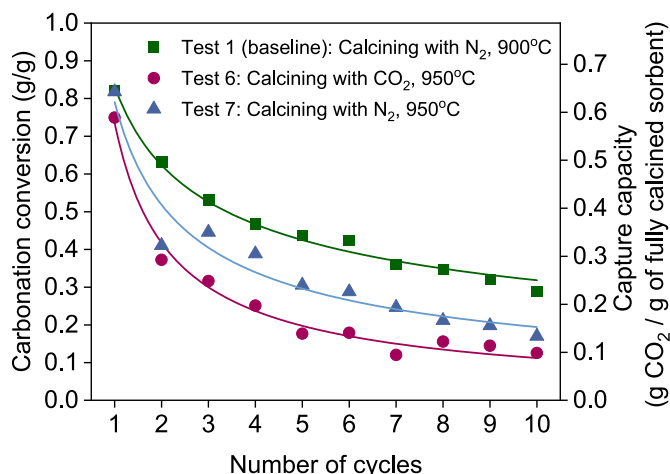


Fig. 7. Sorption ability with number of cycles for different calcining gases (tests 1, 6 and 7 in Table 1).

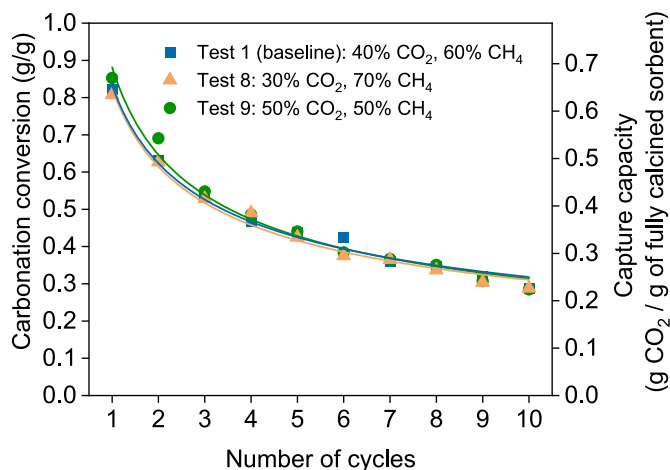


Fig. 8. Sorption ability with number of cycles for different biogas compositions (tests 1, 8 and 9 in Table 1).

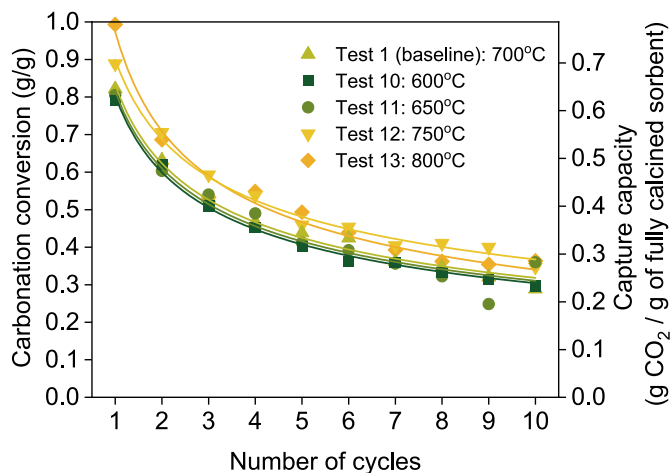


Fig. 9. Impact of temperature on sorption ability with number of cycles (tests 1, 10–13 in Table 1).

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

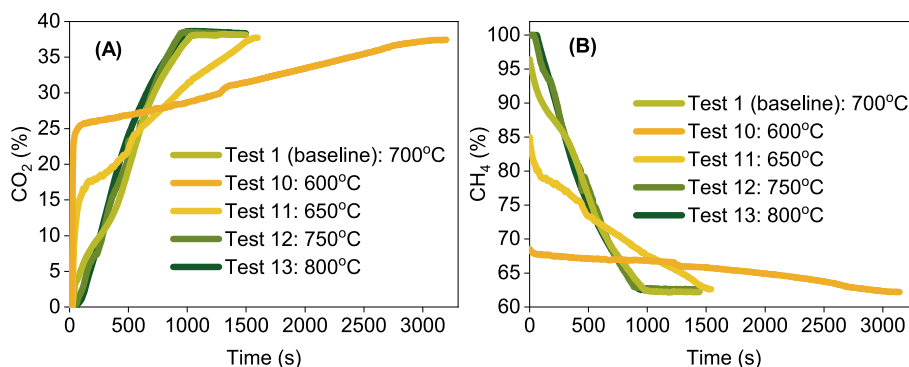


Fig. 10. Dynamic evolution of the carbonator outlet concentrations of (A) CO₂ and (B) CH₄ (tests 1, 10–13 in Table 1).

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 H₂O due to secondary reactions (c.f. Fig. 5). In relation to this [36], found that addition of H₂O 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 H₂O 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 H₂O 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 CH₄ to CO₂ ratio was also examined, revealing that biogas with different CH₄ to CO₂ ratio of can be used without highly impacting the carbonation conversion. This opens this process idea for biogas producing feedstocks with large deviation in CH₄ to CO₂ ratio. Further, a positive impact concerning carbonation conversion is observed when increasing the temperature. Nonetheless, for higher temperatures, lower CH₄ 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 H₂O 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

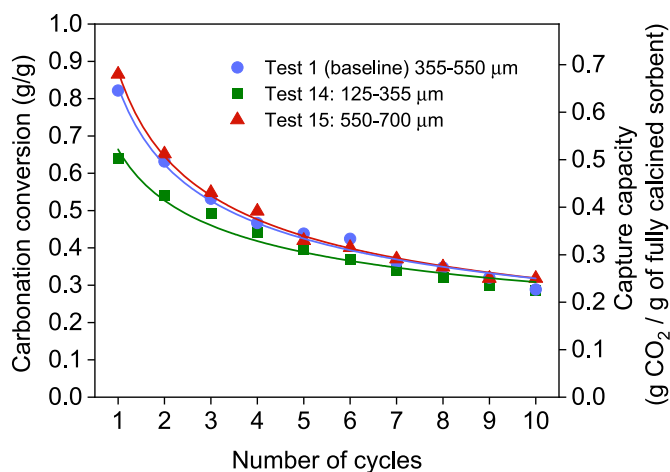


Fig. 11. Impact of particle size on sorption ability with number of cycles (tests 1, 14–15 in Table 1).

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.

References

- [1] D. Garraín, C. de la Rúa, Y. Lechón, Consequential effects of increased biofuel demand in Spain: global crop area and CO₂ emissions from indirect land use change, *Biomass Bioenergy* 85 (2016) 187–197, <https://doi.org/10.1016/j.biombioe.2015.12.009>.
- [2] A. Almena, P. Thornley, K. Chong, M. Röder, Carbon dioxide removal potential from decentralised bioenergy with carbon capture and storage (BECCS) and the relevance of operational choices, *Biomass Bioenergy* 159 (2022), 106406, <https://doi.org/10.1016/j.biombioe.2022.106406>.

- [3] H.R.M.R.P. Ritchie, Our World in Data, Energy Mix, 2022. <https://ourworldindata.org/energy-mix#citation>. (Accessed 9 February 2023).
- [4] IEA, CCUS in Clean Energy Transitions, 2020. Paris, <https://www.iea.org/reports/ccus-in-clean-energy-transitions>. (Accessed 9 February 2023).
- [5] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, The calcium looping cycle for large-scale CO₂ capture, *Prog. Energy Combust. Sci.* 36 (2010) 260–279, <https://doi.org/10.1016/j.pecs.2009.10.001>.
- [6] X. Zhang, P. Song, L. Jiang, Performance evaluation of an integrated redesigned coal fired power plant with CO₂ capture by calcium looping process, *Appl. Therm. Eng.* 170 (2020), 115027, <https://doi.org/10.1016/j.applthermaleng.2020.115027>.
- [7] J. Chen, L. Duan, Z. Sun, Review on the development of sorbents for calcium looping, *Energy Fuels* 34 (2020) 7806–7836, <https://doi.org/10.1021/acs.energyfuels.0c00682>.
- [8] M. Zhao, A.I. Minett, A.T. Harris, A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO₂, *Energy Environ. Sci.* 6 (2013) 25–40, <https://doi.org/10.1039/C2EE22890D>.
- [9] C.C. Dean, J. Blamey, N.H. Florin, M.J. Al-Jeboori, P.S. Fennell, The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production, *Chem. Eng. Res. Des.* 89 (2011) 836–855, <https://doi.org/10.1016/j.cherd.2010.10.013>.
- [10] G. Martínez Castilla, D.C. Guío-Pérez, S. Papadokostantakis, D. Pallarès, F. Johnsson, Techno-economic assessment of calcium looping for thermochemical energy storage with CO₂ capture, *Energies* 14 (2021) 3211, <https://doi.org/10.3390/en14113211>.
- [11] C. Ortiz, J.M. Valverde, R. Chacartegui, L.A. Pérez-Maqueda, P. Giménez, The Calcium-Looping (CaCO₃/CaO) process for thermochemical energy storage in Concentrating Solar Power plants, *Renew. Sustain. Energy Rev.* 113 (2019), 109252, <https://doi.org/10.1016/j.rser.2019.109252>.
- [12] C. Prieto, P. Cooper, A.I. Fernández, L.F. Cabeza, Review of technology: thermochemical energy storage for concentrated solar power plants, *Renew. Sustain. Energy Rev.* 60 (2016) 909–929, <https://doi.org/10.1016/j.rser.2015.12.364>.
- [13] D.P. Hanak, E.J. Anthony, V. Manovic, A review of developments in pilot-plant testing and modelling of calcium looping process for CO₂ capture from power generation systems, *Energy Environ. Sci.* 8 (2015) 2199–2249, <https://doi.org/10.1039/C5EE01228G>.
- [14] C. Ortiz, J.M. Valverde, R. Chacartegui, L.A. Pérez-Maqueda, P. Gimenez-Gavarrill, Scaling-up the calcium-looping process for CO₂ capture and energy storage, *KONA Powder and Particle Journal* 38 (2021) 189–208, <https://doi.org/10.14356/kona.2021005>.
- [15] T. Maparanyanga, D. Lokhat, Modelling of a calcium-looping fluidized bed reactor system for carbon dioxide removal from flue gas, *Int. J. Low Carbon Technol.* 16 (2021) 691–703, <https://doi.org/10.1093/ijlct/ctaa102>.
- [16] B. Arias, M.E. Diego, A. Méndez, J.C. Abanades, L. Díaz, M. Lorenzo, A. Sanchez-Biezma, Operating experience in la Pereda 1.7 MWh calcium looping pilot, *Energy Proc.* 114 (2017) 149–157, <https://doi.org/10.1016/j.egypro.2017.03.1157>.
- [17] Y. Yan, K. Wang, P.T. Clough, E.J. Anthony, Developments in calcium/chemical looping and metal oxide redox cycles for high-temperature thermochemical energy storage: a review, *Fuel Process. Technol.* 199 (2020), 106280, <https://doi.org/10.1016/j.fuproc.2019.106280>.
- [18] V. Moreno, J. Arcenegui-Troya, P. Enrique Sánchez-Jiménez, A. Perejón, R. Chacartegui, J. Manuel Valverde, L. Allan Pérez-Maqueda, Albero, An alternative natural material for solar energy storage by the calcium-looping process, *Chem. Eng. J.* 440 (2022), 135707, <https://doi.org/10.1016/j.cej.2022.135707>.
- [19] H. Chen, C. Zhao, L. Duan, C. Liang, D. Liu, X. Chen, Enhancement of reactivity in surfactant-modified sorbent for CO₂ capture in pressurized carbonation, *Fuel Process. Technol.* 92 (2011) 493–499, <https://doi.org/10.1016/j.fuproc.2010.11.002>.
- [20] M. Erans, V. Manovic, E.J. Anthony, Calcium looping sorbents for CO₂ capture, *Appl. Energy* 180 (2016) 722–742, <https://doi.org/10.1016/j.apenergy.2016.07.074>.
- [21] M. Heidari, M. Tahmasebpoor, S.B. Mousavi, C. Pevida, CO₂ capture activity of a novel CaO adsorbent stabilized with (ZrO₂+Al₂O₃+CeO₂)-based additive under mild and realistic calcium looping conditions, *J. CO₂ Util.* 53 (2021), 101747, <https://doi.org/10.1016/j.jcou.2021.101747>.
- [22] F. Raganati, R. Chirone, P. Ammendola, Gas–solid fluidization of cohesive powders, *Chem. Eng. Res. Des.* 133 (2018) 347–387, <https://doi.org/10.1016/j.cherd.2018.03.034>.
- [23] M. Bailera, P. Lisbona, L.M. Romeo, L.I. Díez, Calcium looping as chemical energy storage in concentrated solar power plants: carbonator modelling and configuration assessment, *Appl. Therm. Eng.* 172 (2020), 115186, <https://doi.org/10.1016/j.applthermaleng.2020.115186>.
- [24] M. Bailera, S. Pascual, P. Lisbona, L.M. Romeo, Modelling calcium looping at industrial scale for energy storage in concentrating solar power plants, *Energy* 225 (2021), 120306, <https://doi.org/10.1016/j.energy.2021.120306>.
- [25] C. Ortiz, M.C. Romano, J.M. Valverde, M. Binotti, R. Chacartegui, Process integration of Calcium-Looping thermochemical energy storage system in concentrating solar power plants, *Energy* 155 (2018) 535–551, <https://doi.org/10.1016/j.energy.2018.04.180>.
- [26] D.P. Hanak, C. Bilyok, V. Manovic, Calcium looping with inherent energy storage for decarbonisation of coal-fired power plant, *Energy Environ. Sci.* 9 (2016) 971–983, <https://doi.org/10.1039/C5EE02950C>.
- [27] M.P.S. Santos, V. Manovic, D.P. Hanak, Unlocking the potential of pulp and paper industry to achieve carbon-negative emissions via calcium looping retrofit, *J. Clean. Prod.* 280 (2021), 124431, <https://doi.org/10.1016/j.jclepro.2020.124431>.
- [28] Z. Li, H. Sun, N. Cai, Rate equation theory for the carbonation reaction of CaO with CO₂, *Energy Fuels* 26 (2012) 4607–4616, <https://doi.org/10.1021/ef300607z>.
- [29] G. Pasini, A. Baccioli, L. Ferrari, M. Antonelli, S. Frigo, U. Desideri, Biomethane grid injection or biomethane liquefaction: a technical-economic analysis, *Biomass Bioenergy* 127 (2019), 105264, <https://doi.org/10.1016/j.biombioe.2019.105264>.
- [30] G. Valenti, A. Arcidiacono, J.A. Nieto Ruiz, Assessment of membrane plants for biogas upgrading to biomethane at zero methane emission, *Biomass Bioenergy* 85 (2016) 35–47, <https://doi.org/10.1016/j.biombioe.2015.11.020>.
- [31] U.K. Roy, T. Radu, J.L. Wagner, Carbon-negative biomethane fuel production: integrating anaerobic digestion with algae-assisted biogas purification and hydrothermal carbonisation of digestate, *Biomass Bioenergy* 148 (2021), 106029, <https://doi.org/10.1016/j.biombioe.2021.106029>.
- [32] D.P. Harrison, Sorption-enhanced hydrogen production: a review, *Ind. Eng. Chem. Res.* 47 (2008) 6486–6501, <https://doi.org/10.1021/ie800298z>.
- [33] G. Piechota, B. Igliński, Biomethane in Poland—current status, potential, perspective and development, *Energies* 14 (2021) 1517, <https://doi.org/10.3390/en14061517>.
- [34] G. Piechota, Removal of siloxanes from biogas upgraded to biomethane by cryogenic temperature condensation system, *J. Clean. Prod.* 308 (2021), 127404, <https://doi.org/10.1016/j.jclepro.2021.127404>.
- [35] H. Leion, V. Frick, F. Hildor, Experimental method and setup for laboratory fluidized bed reactor testing, *Energies* 11 (2018) 2505, <https://doi.org/10.3390/en11102505>.
- [36] J. Arcenegui-Troya, P.E. Sánchez-Jiménez, A. Perejón, J.M. Valverde, L.A. Pérez-Maqueda, Steam-enhanced calcium-looping performance of limestone for thermochemical energy storage: the role of particle size, *J. Energy Storage* 51 (2022), 104305, <https://doi.org/10.1016/j.est.2022.104305>.
- [37] J. Chen, L. Duan, Z. Sun, Review on the development of sorbents for calcium looping, *Energy Fuels* 34 (2020) 7806–7836, <https://doi.org/10.1021/acs.energyfuels.0c00682>.
- [38] Y. Li, C.P. Alaimo, M. Kim, N.Y. Kado, J. Peppers, J. Xue, C. Wan, P.G. Green, R. Zhang, B.M. Jenkins, C.F.A. Vogel, S. Wuertz, T.M. Young, M.J. Kleeman, Composition and toxicity of biogas produced from different feedstocks in California, *Environ. Sci. Technol.* 53 (2019) 11569–11579, <https://doi.org/10.1021/acs.est.9b03003>.
- [39] F.M. Baena-Moreno, M. Rodríguez-Galán, T.R. Reina, Z. Zhang, L.F. Vilches, B. Navarrete, Understanding the effect of Ca and Mg ions from wastes in the solvent regeneration stage of a biogas upgrading unit, *Sci. Total Environ.* 691 (2019) 93–100, <https://doi.org/10.1016/j.scitotenv.2019.07.135>.
- [40] J.D. Durán-Martín, P.E. Sánchez Jimenez, J.M. Valverde, A. Perejón, J. Arcenegui-Troya, P. García Triñanes, L.A. Pérez Maqueda, Role of particle size on the multicyclic calcium looping activity of limestone for thermochemical energy storage, *J. Adv. Res.* 22 (2020) 67–76, <https://doi.org/10.1016/j.jare.2019.10.008>.
- [41] S.A. Salaudeen, B. Acharya, A. Dutta, CaO-based CO₂ sorbents: a review on screening, enhancement, cyclic stability, regeneration and kinetics modelling, *J. CO₂ Util.* 23 (2018) 179–199, <https://doi.org/10.1016/j.jcou.2017.11.012>.
- [42] D. Alvarez, J.C. Abanades, Pore-size and shape effects on the recarbonation performance of calcium oxide submitted to repeated calcination/recarbonation cycles, *Energy Fuels* 19 (2005) 270–278, <https://doi.org/10.1021/ef049864m>.
- [43] D. Alvarez, J.C. Abanades, Determination of the critical product layer thickness in the reaction of CaO with CO₂, *Ind. Eng. Chem. Res.* 44 (2005) 5608–5615, <https://doi.org/10.1021/ie050305s>.
- [44] J. Shen, A.A.C. Reule, N. Semagina, Ni/MgAl₂O₄ catalyst for low-temperature oxidative dry methane reforming with CO₂, *Int. J. Hydrogen Energy* 44 (2019) 4616–4629, <https://doi.org/10.1016/j.ijhydene.2019.01.027>.
- [45] J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, Recent advances in methanation catalysts for the production of synthetic natural gas, *RSC Adv.* 5 (2015) 22759–22776, <https://doi.org/10.1039/C4RA16114A>.
- [46] C. Tanios, M. Labaki, Catalytic reforming: a sustainable technology for hydrogen production, in: *Recent Advances in Renewable Energy Technologies*, Elsevier, 2022, pp. 199–247, <https://doi.org/10.1016/B978-0-12-823532-4.00008-2>.
- [47] V. Manovic, E.J. Anthony, Carbonation of CaO-based sorbents enhanced by steam addition, *Ind. Eng. Chem. Res.* 49 (2010) 9105–9110, <https://doi.org/10.1021/ie101352s>.
- [48] J.J. Arcenegui Troya, V. Moreno, P.E. Sanchez-Jiménez, A. Perejón, J.M. Valverde, L.A. Pérez-Maqueda, Effect of steam injection during carbonation on the multicyclic performance of limestone (CaCO₃) under different calcium looping conditions: a comparative study, *ACS Sustain. Chem. Eng.* 10 (2022) 850–859, <https://doi.org/10.1021/acssuschemeng.1c06314>.
- [49] J. Arcenegui-Troya, P.E. Sánchez-Jiménez, A. Perejón, V. Moreno, J.M. Valverde, L.A. Pérez-Maqueda, Kinetics and cyclability of limestone (CaCO₃) in presence of steam during calcination in the CaL scheme for thermochemical energy storage, *Chem. Eng. J.* 417 (2021), 129194, <https://doi.org/10.1016/j.cej.2021.129194>.
- [50] L. Lundberg, P.A. Tchhoffor, D. Pallarès, R. Johansson, H. Thunman, K. Davidsson, Influence of surrounding conditions and fuel size on the gasification rate of biomass char in a fluidized bed, *Fuel Process. Technol.* 144 (2016) 323–333, <https://doi.org/10.1016/j.fuproc.2016.01.002>.
- [51] B. Sarrión, A. Perejón, P.E. Sánchez-Jiménez, N. Amghar, R. Chacartegui, J. Manuel Valverde, L.A. Pérez-Maqueda, Calcination under low CO₂ pressure enhances the calcium Looping performance of limestone for thermochemical

- energy storage, *Chem. Eng. J.* 417 (2021), 127922, <https://doi.org/10.1016/j.cej.2020.127922>.
- [52] I. Barin, *Thermochemical Data of Pure Substances*, Wiley, 1995, <https://doi.org/10.1002/9783527619825>.
- [53] J.M. Valverde, S. Medina, Crystallographic transformation of limestone during calcination under CO₂, *Phys. Chem. Chem. Phys.* 17 (2015) 21912–21926, <https://doi.org/10.1039/C5CP02715B>.
- [54] R.H. Borgwardt, Calcium oxide sintering in atmospheres containing water and carbon dioxide, *Ind. Eng. Chem. Res.* 28 (1989) 493–500, <https://doi.org/10.1021/ie00088a019>.
- [55] Z. Li, F. Fang, X. Tang, N. Cai, Effect of temperature on the carbonation reaction of CaO with CO₂, *Energy Fuels* 26 (2012) 2473–2482, <https://doi.org/10.1021/ef201543n>.
- [56] P. Sun, J.R. Grace, C.J. Lim, E.J. Anthony, A discrete-pore-size-distribution-based gas–solid model and its application to the CaO + CO₂ reaction, *Chem. Eng. Sci.* 63 (2008) 57–70, <https://doi.org/10.1016/j.ces.2007.08.054>.
- [57] Y.A. Criado, B. Arias, J.C. Abanades, Effect of the carbonation temperature on the CO₂ carrying capacity of CaO, *Ind. Eng. Chem. Res.* 57 (2018) 12595–12599, <https://doi.org/10.1021/acs.iecr.8b02111>.
- [58] S. Chen, C. Qin, J. Yin, X. Zhou, S. Chen, J. Ran, Understanding sulfation effect on the kinetics of carbonation reaction in calcium looping for CO₂ capture, *Fuel Process. Technol.* 221 (2021), 106913, <https://doi.org/10.1016/j.fuproc.2021.106913>.