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OVERVIEW ON THE CALCIUM LOOPING PROCESS (CaL) AND REACTOR DESIGN

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Abstract. *The calcium looping reaction (CaL) is a reversible reaction between CaO and CO_2, this reaction is an promising method for the removal of CO_2 from exhaust gases, due to the low energy penalties imposed on power plants. Current studies indicate the CaL process is being inserted to improve syngas, to increase energy content of fuel gases, therefore its study is necessary worldwide. However, little is known about Brazil's participation in this research area. The objective of the article is to carry out a bibliometric review, to observe the role and position of Brazil in this research area. For that the database "scopus" was used and connectors and keywords were used, such as: "Calcium Looping" OR "Ca Looping" AND "Fluidized bed" AND "Reactor design". The results indicate that in the last 5 years (2019-2023), 20 articles have been published, and the three countries that most published were: China, United States and Germany. Although the subject CaL is a current topic, articles considering reactor design are restricted. The annual average of publications is 3 articles, and the impact of articles measured by their citations, indicate that they have an average of 13 citations per year. For the other side, that reactor design began to have more impact from 2020, because its was associated with issues such as: 1) the use of heat stores for solar energy and 2) calcium looping processes associated with the use of biomass for energy improvement of fuel gases using biomass. Although the study of calcium looping is associated with the use of biomass in the energy sector and considering the potential of Brazil in the use of biomass, it has scarce studies about this matter, being a field to be greatly explored in the coming years.*

Keywords: *Calcium Looping, carbon dioxide, biomass, fuel gases, bibliometric review, reactor design*

1. INTRODUCTION

Global warming is being accelerated by anthropogenic CO_2 emissions. According to Blamey et al. (2010), they indicated that there is a change in the global climate system due to anthropogenic CO_2 emissions. According to the IPCC (2022) and Toledo et al. (2023), anthropogenic CO_2 emissions for the years 1850-2019 were 2400 ± 240 $GtCO_2$, with 58% emitted between 1850 and 1989 and 48% between 1990 and 2019. On the other hand, the IPCC report (2022) indicates that to limit a temperature increase to a maximum of 1.5°C, a total carbon load of 500 $GtCO_2$ can be added to the atmosphere, and if this increase is limited to 2°C, this load could be 1500 $GtCO_2$. However, the report by the International Energy Agency (IEA) in 2014 showed that expectations for 2035 already projected a 20% increase in CO_2 emissions, causing a temperature rise of 3.6°C on the planet.

According to Tobias et al. (2021), it was indicated that the largest consumer of natural resources is the energy sector. Therefore, it is considered the main cause of environmental impacts, as 68% of the energy produced is derived from fossil fuels. Consequently, there is an urgent need to mitigate these impacts, which is continually growing. As a result, the world has invested in conferences, research, and the establishment of goals through treaties to reduce the concentration of anthropogenic CO_2 in the atmosphere. Initiatives like the Paris Agreement, defined by global bodies such as the Intergovernmental Panel on Climate Change (IPCC), and leadership meetings held by organizations like the International Energy Agency (IEA) and the UNFCCC (United Nations Framework Convention on Climate Change) have played pivotal roles in addressing this challenge (Chen et al, 2020).

In this context, the concept of mitigation is defined as the reduction of greenhouse gas (GHG) emissions. This reduction encompasses changes in the utilization of natural resources, the adoption of alternative energy sources, improvements in energy efficiency, and a shift towards lower carbon intensity (Magalhães, 2010). Reports and treaties issued by various global agencies identify carbon capture technologies as the most cost-effective solutions for mitigating emissions in large-scale processes (IEA, 2022).

According to Spigarelli and Kawatra (2013), there are three categories of carbon capture and sequestration technology (CCS) for the energy sector, which differ based on the combustion approach employed: Post-combustion, Pre-combustion, and Oxy-combustion. In both post-combustion and pre-combustion methods, CO_2 separation processes are necessary. Among these separation processes, chemical absorption using MEA (Monoethanolamine) and Calcium Looping (CaL) stand out as the most prominent (Tobias et al., 2021).

The Calcium Looping (CaL) process offers several advantages, including: 1) The use of natural limestone or dolomite for the preparation of CaO, which has a relatively high CO_2 absorption capacity, reaching 0.786 $gCO_2/gCaO$. 2) Low energy consumption, with only a 6–8% efficiency penalty. For example, as reported by Han et al. (2022), applying the CaL process to a 100 MW thermal power plant with a reference efficiency of 46% results in a total net efficiency of 38.8%, including CO_2 compression. 3)The ability to repurpose the deactivated CaO sorbents as raw materials in other industrial processes, such as the cement and steel industry. 4) A relatively low cost of CO_2 capture using CaL technology, approximately $24 per ton, which is about half the cost of amine scrubbing technology (Han et al., 2022). However, it's important to note that the efficiency of the CaL process decreases with the number of cycles, primarily due to sorbent sintering, as highlighted in the literature. This sintering leads to changes in pore shape, pore shrinkage, and grain growth, resulting in significant volumetric changes during repeated calcination and carbonation reactions (Chen et al , 2020).

As a solution to the decreasing efficiency observed in the Calcium Looping (CaL) process, various alternatives have been studied. These include: 1) Pre-thermal treatment of sorbents; 2) Material modification and incorporation of inerts into the structure (e.g., SiO_2, Al_2O_3, MgO); 3) Doping of CaO sorbents with alkali metal salts (e.g., Li, Na, K); 4) The development of synthetic sorbents; 5) CaO hydration. These alternatives, as discussed by Erans et al. (2016) and Santos (2022), aim to address the primary obstacle to the use of CaL technology, which is the decreasing efficiency over multiple cycles.

In response to the increasing demand for technologies that mitigate global warming and the continuous technological advancements in Calcium Looping to address efficiency decline resulting from material sintering, this article seeks to analyze the latest findings regarding this technology. We have utilized two publication databases to gather comprehensive information on this subject. Furthermore, this analysis examines Brazil's involvement in research related to this topic.

2. METHODOLOGY

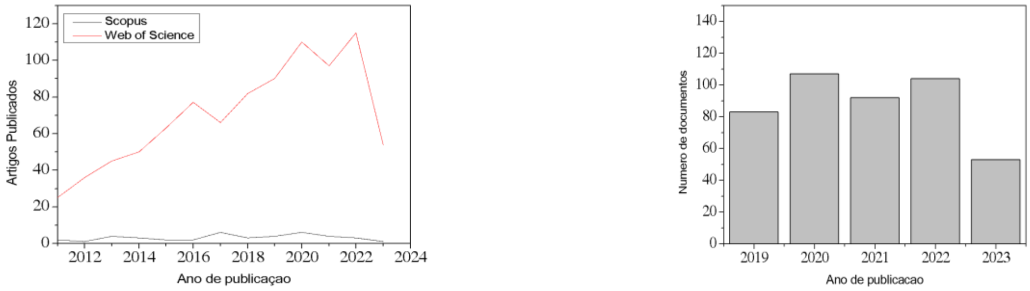
For this study, we employed two primary databases, Scopus and Web of Science, to ensure a comprehensive coverage of articles published in this field. Keywords were selected and used as presented in Table 1, separated by "AND" or "OR" where appropriate, especially when similar words conveyed the same concept.

3. RESULTS AND DISCUSSION

Table 1. Choice of keywords inserted in the bibliometric study in the databases.

Importance Level	Keywords	Scopus Results	Web of Science Results
1	Calcium Looping OR Ca Looping	1862	1064
2	Fluidized Bed	418	1019
4	Reactor design	41	985
5	Limited to 5 years	20	444

For instance, when we aggregate the literary production over these 13 years, we can calculate the average number of publications on the subject of research. The resulting average publications per year are 3 ± 0.15 for Scopus and 65 ± 3.00 for Web of Science. Notably, there has been a consistent upward trend in recent years, reaching its peak in 2020. It's worth mentioning that the Web of Science exceeded 100 articles per year during this period. One contributing factor to the increase in publications from 2020 could be the outbreak of the coronavirus pandemic in March of that year.



(a) (b)

Figure 1. Trend of publications on Calcium Looping. a) last 13 years and b) last 5 years.

3.1. Assessment of the Relevance of the Subject

To better assess this aspect, the articles from both databases were merged to create a unified database. This process involved the removal or inclusion of Scopus articles in the Web of Science database. Consequently, a consolidated database spanning the last 5 years was generated, as presented in Figure 1b. This figure represents the total number of publications in the last 5 years for the processed database. Notably, there is an annual fluctuation in the number of publications, but the overall trend remains promising with sustained growth in this research area. While there were fewer publications in 2019 and 2021, both years were followed by a surge in publications in subsequent years. Following this pattern, it is reasonable to anticipate that 2023 will exhibit a similar trend.

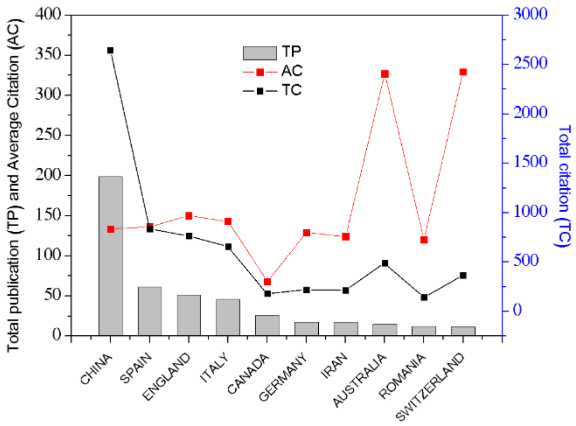
The articles were categorized and organized by countries, authors, and journals, and the results are presented along with Figures 2a, 2b, and 2c and its tables. However, analyzing only the total number of publications (TP) and total citations (TC) can sometimes lead to confusion in bibliometric analysis, as it may include less relevant publications. To gauge relevance, the average number of citations is calculated (AC), which involves dividing the total number of citations by the total number of publications. This metric was applied to evaluate the ten most productive countries, authors, and journals. The outcomes are presented in Figure 2.

In Figure 2a, we can observe the ten most productive countries in the field of Calcium Looping. The countries with the highest number of publications were China, Spain, England, Italy, and Canada, and they also had significant citation counts, with the exception of Canada, which was surpassed by Australia in terms of citations. However, when we evaluate the relevance of these countries, we notice that despite China having the highest number of publications and citations, it wasn't the most relevant. In terms of relevance, Sweden and Australia, both with fewer publications, outshone China, followed by England, Italy, and Spain. Surprisingly, Switzerland, with just 11 publications in the field, had the highest notoriety ranking with an ACx10 = 329 citations, surpassing countries with a higher volume of documents produced. Australia (ACx10 = 327) was the second country with highly relevant publications, boasting an average citation count similar to Switzerland (ACx10 = 329). England and Italy secured the third and fourth positions in terms of relevance.

Another relevant aspect in bibliometric analysis is the classification of the most cited authors in the field. As shown in Figure 2b, the authors with the highest publication counts in the last 5 years were Li, Valverde, Wang, and Zhao. However, it's noteworthy that publications by authors like Ortiz and Chacartegui and even Valverde, demonstrated higher relevance, as indicated by their average citation counts. Despite having a smaller number of publications, these authors received a greater number of citations. For instance, Ortiz, with 14 published articles, accumulated 353 citations, achieving the highest average citation count of 25. In contrast, Li, who led in terms of the volume of published articles, maintained an average citation count of 14.

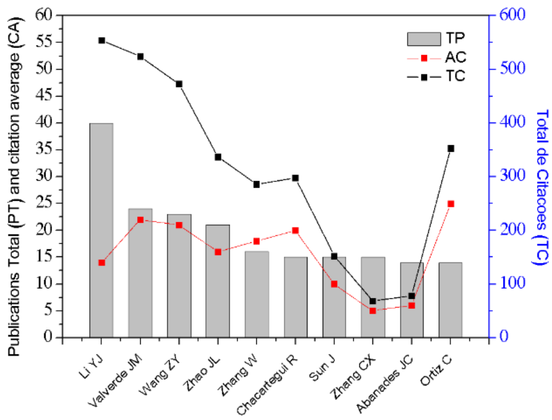
When assessing international journals and the relevance of articles published on the subject of Calcium Looping (CaL), we note that the journal with the highest publication count, as indicated in Figure 2c, was "Chemical Engineering Journal," with 50 publications, followed by "Energy Conversion and Management," which had 30 publications in the last 5 years. However, the scientific journal "Energies," with just 18 publications on the subject, managed to accumulate 399 citations, matching the average of the journal with the highest publication count. This indicates a higher level of relevance in the articles published. It's important to note that "Energies" is an Open Access journal, which may have influenced the higher citation count.

(a)



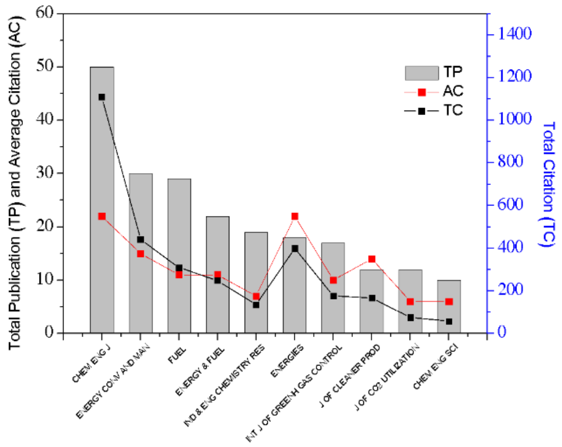
Country	TP	TC	ACx10*
China	199	2643	133
Spain	61	832	136
England	51	763	149
Italy	46	657	143
Canada	26	178	68
Germany	17	219	129
Iran	17	211	124
Australia	15	490	327
Romania	12	144	120
Switzerland	11	362	329

(b)



Authors	TP	TC	AC
Li Y. J.	40	554	14
Valverde J. M.	24	524	22
Wang Z. Y.	23	473	21
Zhao J. L.	21	337	16
Zhang W.	16	286	18
Chacartegui R.	15	298	20
Sun J.	15	152	10
Zhang C. X.	15	68	5
Abanades J. C.	14	78	6
Ortiz C.	14	353	25

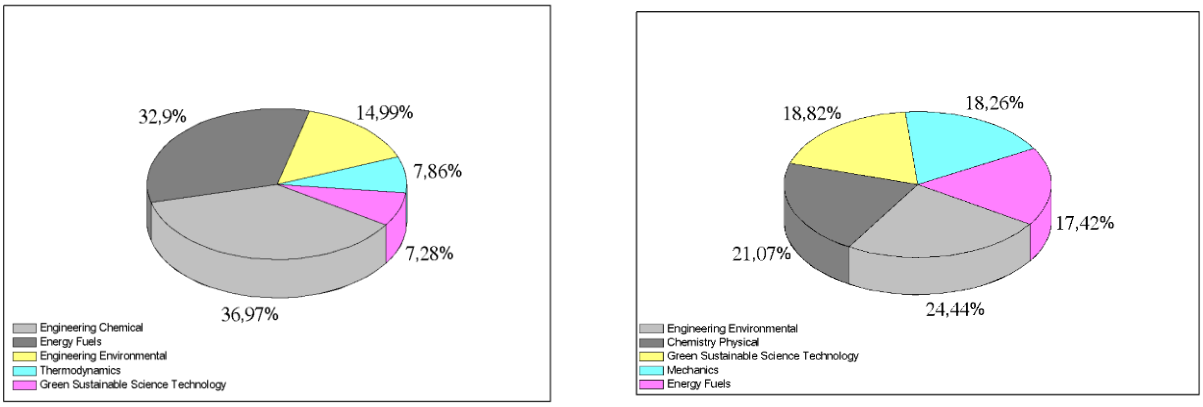
(c)



Journals	TP	TC	AC
Chem. Eng. J.	50	1109	22
Energy Conv. And Man	30	440	15
Fuel	29	308	11
Energy & Fuel	22	248	11
Ind. & Eng. Chemistry Res.	19	134	7
Energies	18	399	22
Int. J. of Greenh. Gas Control	17	177	10
J. of Cleaner Prod.	12	166	14
J. of CO2 Utilization	12	75	6
Chem. Eng. Sci	10	57	6

Figure 2. Total number of publications and their relevance in the area of Calcium Looping. a) ten most productive countries b) ten most productive authors and c) ten most productive journals. *ACx10 is average citation multiplicated for 10.

Among the evaluated authors, we can further narrow our bibliometric review by considering research areas. Figure 3 illustrates the top 5 areas with the most published articles, revealing that Chemical Engineering, Energy and Fuels, and Environmental Engineering are the leading areas, representing 39.97%, 32.9%, and 14.99% of the publications, respectively.However, when we evaluate the ranking by relevance (as shown in Figure 3b and Table 3.2), Environmental Engineering, Chemistry, and Sustainable Sciences emerge as the areas with the most relevant publications.



(a) (b)

Figure 3. Areas where most issues about Calcium Looping are published.

An interesting observation in our research is the absence of Brazil in the research ranking, despite the country's vast potential for renewable energy production and its role as a limestone ($CaCO_3$) producer.

3.1.1 Most cited articles in calcium looping research

From Figure 2b, we have identified the most cited articles from the most relevant authors, as presented in Table 2. In our search for the most relevant author, Ortiz C, we noted that he shares the most cited article with other highly relevant authors, including Chacartegui and Valverde. This suggests they are part of the same research group. The article was published in 2019 in the "Renewable and Sustainable Energy Reviews," and it has accumulated 179 citations to date.

Table 2. Most cited articles by the most relevant authors in calcium looping research.

Authors	Article Name	Journal	Year	Citations
Ortiz, C; Valverde, JM; Chacartegui, R; Perez-Maqueda, LA; Gimenez, P	The Calcium-Looping (CaCO3/CaO) process for thermochemical energy storage in **Concentrating Solar Power plants**	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	2019	179
Ma, XT; Li, YJ; Yan, XY; Zhang, W; Zhao, JL; Wang, ZY	Preparation of a morph-genetic **CaO-based sorbent** using paper fibre as a biotemplate for enhanced CO2 capture	CHEMICAL ENGINEERING JOURNAL	2019	175
Martinez, I; Fernandez, JR; Martini, M; Gallucci, F; Annaland, MV; Romano, MC; Abanades, JC	Recent progress of the Ca-Cu technology **for decarbonisation of power plants** and carbon intensive industries	INTERNATIONAL JOURNAL OF GREENHOUSE GAS CONTROL	2019	81

Ortiz et al. (2019), discusses the Calcium Looping (CaL) process as a promising technology to be applied in Solar Energy Thermochemical Concentrators (TCES). In the CaL process, concentrated solar energy is used to facilitate the endothermic calcination reaction, resulting in the release of CO_2 and CaO as separate products for storage. CaL offers several advantages: 1) including a higher energy storage density and the potential to operate at significantly higher power cycle temperatures; 2) Another advantage highlighted is the use of natural CaO precursors like limestone or dolomite, which are cost-effective, readily available, and environmentally friendly. These factors make CaL a suitable candidate for large-scale TCES energy storage systems. Ortiz et al. also notes that the utility of the CaL process for energy storage has historically been underestimated, primarily due to the multi-cyclic deactivation of CaO observed in laboratory-scale tests. However, it's pointed out that the CaL process for CO_2 capture has already reached a large pilot-scale demonstration stage (TRL7), indicating its readiness for further development and deployment. Overall, Ortiz et al. underscores the potential of the CaL process for concentrated solar power systems and the need for continued research and development to harness its full benefits. The text further suggests that by implementing CaL conditions that involve carbonation under pure CO_2 at high temperatures and using fine particles (with a particle size of approximately 45 μm) to prevent pore clogging, it is possible to achieve a high residual multi-cycle conversion of CaO derived from limestone, up to X = 0.5. Additionally, it notes the cost-effectiveness of using natural CaO precursors, such as limestone or dolomite, which are readily available and inexpensive. These qualities allow for the periodic replacement of solids with fresh materials and contribute to the favorable results achieved when using natural dolomite as a CaO precursor, given its abundance and affordability. Furthermore, the authors explains that the presence of inert MgO in CaO grains helps to mitigate sintering and aggregation of the CaO grains, as well as pore clogging. This results in increased effective conversion of CaO. The use of dolomite as a CaO precursor is expected to enhance carbonation efficiency, leading to the release of thermal energy. Residual values of effective multi-cycle CaO conversion can be as high as X = 0.7–0.8 when using calcium magnesium acetate or steel slag as CaO precursors. The potential use of these precursors should be evaluated further. In addition, the text mentions that in scaling up the CaL process, the choice of reaction conditions and the type of CaO precursor should consider not only material performance but also the integration of the process and various technological and economic aspects. Ortiz et al. (2019) reported global plant efficiencies have exceeded 45%, but this does not consider the solar receiver efficiency when serving as a calciner, a critical component of the technology that still requires development. Achieving an optimized solar receiver/calciner design is crucial for the overall performance of the plant and poses a significant technical challenge. Various specific designs have been proposed and tested, but they have not fully met some of the key requirements, including scalability, high thermal efficiency, and the need for a particle residence time that is long enough to ensure complete calcination. The text concludes by emphasizing that further advances are needed in defining the solar receiver and addressing economic viability, as these tasks are essential for a comprehensive evaluation of the potential of the Calcium Looping (CaL) process for energy storage in Concentrating Solar Power (CSP) plants.

The second article, authored by Ma and Coauthored by Wang, who is the fourth most relevant author. The article was published in 2019 and has accumulated 178 citations. Notably, Wang shares the same highly cited article with Zhang, Zhao, Zhan, and Li, indicating that they are part of the same research group or collaboration. According Ma et al. (2019), a morpho-genetic sorbent primarily composed of CaO and $Ca_{12}Al_{14}O_{33}$ exhibits a formation of a hollow tubular structure. This sorbent, denoted as BT 7.5, demonstrates the highest CO_2 capture capacity of 0.42 g/g when calcined in an atmosphere with a high concentration of CO_2. This capture capacity is 2.02 times greater than that of carbide slag. The improved CO_2 capture performance of the morphogenetic sorbent is attributed to its hollow tube-like structure, which increases the contact surface area for CO_2 capture and provides support from $Ca_{12}Al_{14}O_{33}$. The authors provides insight into the research on morpho-genetic sorbents and their enhanced CO_2 capture capabilities due to their unique structural characteristics.

The third article, which is the most cited work by the fifth most relevant author, Abanades. This review article was published in the International Journal of Greenhouse Gas Control in 2019 and has currently garnered 81 citations. According to Martinez et al. (2019), highly efficient pre-combustion systems offer sustainable alternatives for hydrogen production with a reduced carbon footprint. The Ca-Cu looping process is introduced as a new CO_2 capture method that combines Sorption Enhanced Reforming (SER) to produce nearly pure H_2 with a redox Cu/CuO cycle for regenerating the CO_2 sorbent. Importantly, this regeneration process incurs a low energy penalty and has the potential to reduce capture costs.The Ca-Cu looping process is recognized as a promising pre-combustion CO_2 capture technology, allowing for energy-intensive sorbent regeneration with a modest energy penalty. While this technology can be implemented in various reactor configurations, experimental demonstrations of the viability of each reaction step have so far reached only TRL 4-5 in packed-bed reactors. Additionally, there have been notable advancements in modeling and simulating processes, with a focus on energy generation and integration into industrial applications, such as hydrogen production, ammonia production, and steel manufacturing. However, more research is needed to facilitate the development of the Ca-Cu process on a large scale. Regarding functional materials, significant advances have been made so far, but future investigations need to focus on improving their long-term mechanical stability under changes in temperature, pressure and redox atmospheres, as a necessary step towards scaling up the technology. Furthermore, the chemical performance of materials over an extensive number of cycles (ie thousands of cycles) and under industrial conditions (pressure, temperature and gas composition) must also be studied. Martinez et al (2019) indicate that the design of reactors for this type of processes is not yet well cemented, for Ca-Cu packed bed systems, reducing the volume of the reactors to the maximum allows reducing the pressure drops in the reactors and the amount of functional material, thus reducing operating and capital costs. However, reducing the volume of reactors can be limited by fluid dynamics and manufacturing constraints and the resulting short cycles can cause excessive stress to the valves, increasing the importance of auxiliary purge, rinsing, pressurization and depressurization steps, often neglected in the analysis. of processes reported by other authors. In addition, the technical feasibility of using alternative fuels (other than natural gas) as reducing agents in the calcination/reduction operation (e.g. coal or biomass) can be assessed to reduce operating cost, energy penalty and/or emissions. of CO_2. Finally, economic analyzes are needed to confirm the recently published results in power and hydrogen plants and to provide the first evaluation of the economic indicators for the integrated Ca-Cu process in ammonia and steel plants.

This section identified three primary areas in which calcium looping (CaL) has been extensively researched. These areas are:

1. Energy storage for solar thermal power stations (CSP)
2. Development of stable sorbents at high temperatures
3. Application of CaL in the production of hydrogen (H_2)

3.1.2 Recent Development of the Calcium Looping Process

To delve into these areas, the analysis considers the ten most cited articles published in the last five years, and these articles are presented in Table 3. This analysis aims to provide a comprehensive overview of the key research and developments in each of these areas.

Table 3. The 5 most cited articles in the period 2019 – 2023.

Authors	Article name	Journal	Article type	Citations
Ortiz, C; Valverde, JM; Chacartegui, R; Perez-Maqueda, LA; Gimenez, P	The Calcium-Looping (CaCO3/CaO) process for thermochemical energy storage in Concentrating Solar Power plants	RENEWABLE & SUSTAINABLE ENERGY REVIEWS	Review	179
Chen, J; Duan, LB; Sun, ZK	Review on the Development of Sorbents for Calcium Looping	ENERGY & FUELS	Review	267
Sun, HM; Wang, JQ; Zhao, JH; Shen, BX; Shi, J; Huang, J; Wu, CF	Dual functional catalytic materials of Ni over Ce-modified CaO sorbents for integrated CO2 capture and conversion	APPLIED CATALYSIS B-ENVIRONMENTAL	Article	74
Jimenez, PES; Perejon, A; Guerrero, MB; Valverde, JM; Ortiz, C; Perez-Maqueda, LA	High-performance and low-cost macroporous calcium oxide based materials for thermochemical energy storage in concentrated solar power plants	APPLIED ENERGY	Article	62
Voldsund, M; Gardarsdottir, SO; De Lena, E; Perez-Calvo, JF; Jamali, A; Berstad, D; Fu, C; Romano, M; Roussanaly, S; Anantharaman, R; Hoppe, H; Sutter, D; Mazzotti, M; Gazzani, M; Cinti, G; Jordal, K	Comparison of Technologies for CO2 Capture from Cement ProductionPart 1: Technical Evaluation	ENERGIES	Article	58

The article by Chen et al. (2019) provides an overview of the recent developments in the Calcium Looping (CaL) process worldwide, with a particular focus on its progress in China. The primary emphasis is on the advancement of the design and enhancement of CaO-based sorbents for CO_2 capture. The article discusses various activation strategies that have been developed to improve the cyclic performance of CaO-based sorbents. These strategies include doping, chemical pre-treatment, the incorporation of supports with high Tammann temperatures, and structural modification. These approaches have shown promise in extending the sorbents' lifecycles. However, there are still challenges in the development of CaO-based sorbents, such as addressing the cost of the synthesis route, scaling up production, evaluating cyclic performance under mild conditions, and considering mechanical strength and resistance to weathering and friction. As a result, the article suggests that life cycle assessment and techno-economic analysis are crucial when synthesizing CaO-based sorbents. The article also stresses the need for more research conducted under industrially relevant conditions, particularly in fluidized bed reactors and pilot-scale reactors. These conditions are closer to real industrial situations and would provide valuable insights for the further development of the CaL process. Among the various activation strategies discussed, doping and the incorporation of high-temperature supports are considered the most promising, with the potential to accelerate the industrial application of the CaL process. In contrast, chemical pretreatment and the development of unsupported materials with high surface areas may not be as favorable due to potential cost issues and short-term enhancement effects.

According to Sun et al. (2019), they propose a CO_2 capture and conversion process that integrates the Reverse Water-gas shift (RWGS) process directly. This process utilizes Dual-Function Materials (DFMs), which are synthesized via the one-pot method and contain a sorbent coupled with a catalyst component. In this integrated process, the sorbent's regeneration and CO_2 conversion are performed simultaneously within a single reactor, eliminating the need for additional heat input. As a result, synthetic natural gas can be recycled to an industrial facility, leading to fuel savings and a reduction in CO_2 emissions. The Ce-doped DFMs are highlighted for their excellent stability, even after 20 cycles of integrated CO_2 capture and conversion. This stability is attributed to the well-dispersed CeO_2 component, which serves as a physical barrier, effectively preventing the growth and agglomeration of CaO crystallites and NiO species. This innovation demonstrates promising results in the area of CO_2 capture and conversion, with potential applications in reducing greenhouse gas emissions and improving fuel efficiency in industrial processes.

Jimenez et al. (2019) emphasize the critical characteristics that thermochemical energy storage systems must possess for viable integration into concentrating solar power plants (CSP). These characteristics include high energy density, cyclic stability, low cost, and scalability. The article notes that while no single system has yet fully satisfied all these requirements, the reversible CaO/$CaCO_3$ reaction in the calcination/carbonation (CaL) process is among the most promising options. The natural precursors of CaO are widely accessible and abundant on Earth. However, one of the challenges with the CaL process is that CaO particles become progressively deactivated due to morphological changes caused by sintering during repeated cycles of carbonation and calcination. In response to this challenge, the authors developed sorbents based on calcium acetate and calcium and magnesium acetate. These sorbents crystallized as elongated fibers and produced plaque-like structures composed of CaO nanoparticles after calcination. The inclusion of MgO nanoparticles was found to stabilize the highly porous structure of the sorbents against sintering. Remarkably, the effective conversion value achieved with these materials was around 0.7, and this high level of conversion was maintained even after 30 calcination/carbonation cycles. This is in contrast to a residual conversion of only 0.15 for natural limestone. Importantly, the precipitation method used for synthesizing these materials does not require complex equipment, expensive reagents, or environmentally harmful solvents, making them cost-effective and suitable for real applications. Additionally, the relatively large particle size of these materials is advantageous for large-scale use in fluidized bed reactors. Using calcium and magnesium acetate as a CaO precursor instead of limestone is projected to increase the overall process efficiency by approximately 3% over conventional limestone. This development shows great potential for enhancing the performance and economic feasibility of the CaL process in thermochemical energy storage systems.

The study by Voldsund et al. (2020) provides valuable insights into the comparison of different carbon capture technologies in the cement industry. Here are some key findings from their research: 1) CO_2 Equivalent Avoided: The Calcium Looping (CaL) process shows significant promise, with CO_2 equivalent emissions avoidance ranging from 73% to 90%. In contrast, the MEA (Monoethanolamine) process achieves 64% CO_2 equivalent emissions reduction. 2) Primary Energy Consumption: The CaL process is more energy-efficient, with specific primary energy consumption for avoided CO_2 ranging from 1.63 to 4.07 MJ/kg CO_2. In comparison, the MEA process has a higher energy consumption of 7.08 MJ/kg CO_2; 3) Emission Reduction Potential: Among the evaluated technologies, CaL demonstrates the greatest potential for reducing emissions, while the oxyfuel process stands out for its energy performance; 4) Cost-Effectiveness: Post-combustion technologies are more cost-effective compared to oxy-fuel processes and integrated calcium looping technologies. The cost of CO_2 avoidance varies between €42/t CO_2 for oxy-fuel capture and €84/t CO_2 for membrane-based assisted liquefaction capture, while MEA-based capture technology has a cost of €80/t CO_2; 5) Local Factors: The choice of the most suitable technology for a specific cement plant should take into account local factors such as the source of steam, electricity mix, electricity prices, fuel prices, and specific plant characteristics. 6) Clinker Cost: The cost of clinker production increases significantly, ranging from 49% to 92%, when implementing CO_2 capture technologies, compared to the cost of clinker production without capture. This research underscores the importance of considering a portfolio of technologies for CO_2 capture in the cement industry, rather than a one-size-fits-all approach. The choice of technology should be tailored to the specific circumstances and constraints of each plant, taking into account local energy sources, emissions reduction potential, and cost-effectiveness.

3.2 Overview of Calcium-looping in Brazil

It's interesting to note that there has been some research on Calcium Looping (CaL) in Brazil over the last five years, but the international reach and impact of these articles have been relatively limited, with fewer than 20 citations. The focus of these articles seems to be primarily on techno-economic evaluations of the CaL process in sugarcane thermoelectric plants and its potential integration into the Brazilian energy matrix. This research may have particular relevance to the Brazilian context, where sugarcane-based bioenergy plays a significant role (Neto et al., 2021; Moore et al 2022 and Moore and Kulay 2019). One of the articles you mentioned (Pinto et al., 2019) discusses the production of new sorbents, which is an essential aspect of CaL technology, as the development of effective and durable sorbents is a critical factor in the success of the process. A review article (Toledo et al., 2023) can also be valuable for summarizing the current state of CaL research in Brazil and providing an overview of the progress and challenges in this area.

While the articles might not have received a high number of citations, they contribute to the growing body of research on CaL and its potential applications in Brazil's energy sector. Local research can provide valuable insights and solutions that are specific to the country's unique energy landscape and challenges. However, for broader international recognition, it may be important for Brazilian researchers to collaborate with international counterparts, publish in well-recognized international journals, and present their work at relevant international conferences to increase the visibility and impact of their research.

4. CONCLUSION

The conclusion drawn from your analysis highlights the versatility and ongoing research efforts in the field of Calcium Looping (CaL). CaL is applied in various areas, including hydrogen production and heat storage for solar thermal power plants. While CaL for post-combustion CO_2 capture has been studied extensively in previous years, it's clear that research in this field continues, driven by the need to find sustainable solutions for reducing carbon emissions.

The challenges you've identified are indeed crucial for the continued development and deployment of CaL technology:

1. Sorbent Development: Creating more stable sorbents with increased capture capacity remains a central challenge. This is essential for improving the efficiency and longevity of CaL processes.

2. Reactor Design: The design of reactors for applications in zero-carbon power plants and hydrogen production is another significant challenge. These reactors must be optimized for their specific functions, ensuring that CaL processes operate efficiently and effectively.

3. Overall, CaL holds promise as a key technology in the effort to reduce carbon emissions and combat climate change. To overcome these challenges, interdisciplinary research efforts involving chemistry, materials science, engineering, and energy systems are crucial. Collaborations between researchers, institutions, and industry stakeholders can help drive advancements in CaL technology and its application in various sectors.

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