

Research papers

Optimization of an improved calcium-looping process for thermochemical energy storage in concentrating solar power plants

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ABSTRACT

The calcium-looping (CaL) process comprises an endothermic calcination reaction, where CaO and CO₂ are generated from CaCO₃, and its reverse exothermic carbonation reaction. CaL is promising for thermochemical energy storage (TCES) in concentrating solar power plants. The CaL-TCES process includes a calciner where solar energy is transformed into thermochemical energy; a carbonator where the stored energy is released; turbines for electrical power generation; and tanks where the reaction products are stored. In this work, the CaL-TCES process is simulated and optimized using gProms Process. The innovation lies in identifying process improvements: make-up and purge streams to reduce CaO deactivation after cycling; a water separation process at the calciner outlet to allow calcination with water vapor as fluidizing gas; and the use of several degrees of freedom for process optimization. The goal is to maximize the thermal-to-electrical efficiency. By optimizing the carbonator and main turbine outlet pressures, the efficiency is improved from 38.1 % in the literature to 39.2 %. When make-up and purge streams are considered, the savings in power supply owing to the purged CaO allow improving the efficiency to 43.0 %. The water separation process reduces the thermal-to-electrical efficiency to 34.7 %, but allows a higher solar-to-thermal efficiency or a smaller calcination reactor.

1. Introduction

The variability of some types of renewable energy is considered one of the main obstacles to their widespread adoption. Energy storage is essential to deal with this issue. Concentrating solar power (CSP) systems rely on the concentration of solar energy in a receiver, allowing high-temperature thermal energy storage (TES) and power dispatchability. The most common solution for TES relies on nitrate-based molten salts as heat transfer and storage medium, the operational limitations of which do not allow high efficiencies since they need to be kept between 220 °C and 560 °C. An alternative method for TES in CSP systems is thermochemical energy storage (TCES), which is based on reversible reactions. For example, a promising option is the calcium-looping

(CaL) process for TCES, which relies on a cycle that comprises (i) an endothermic calcination reaction, with a standard enthalpy of reaction of $178.4 \times 10^3 \text{ J mol}^{-1}$, in which CaO and CO₂ are generated from CaCO₃ in a solar reactor, and (ii) an exothermic carbonation reaction, in which CaCO₃ is formed from CaO and CO₂. The reaction products are stored in tanks until the reverse reaction is carried out. This process is advantageous with respect to the use of molten salts since CaO precursors such as limestone are cheap, abundant, and harmless, the energy density is large ($> 3 \text{ GJ m}^{-3}$), and carbonation can occur at high temperatures, which improves the efficiency in CSP plants [1]. A main disadvantage is CaO deactivation after several cycles, which decreases

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Optimization of an improved calcium-looping process for thermochemical energy storage in concentrating solar power plants

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Group - 5



Content

A decorative graphic spanning the width of the slide. It features a blue line graph with several data points, some of which are highlighted with larger circles. The graph is set against a background of green and yellow areas that resemble a stylized landscape or data distribution. The entire graphic is positioned above the table of contents.

1. Introduction.
2. Process of modelling and optimisation.
3. Results and Discussion.
4. Conclusions



Introduction

1

Introduction: Background



- The research aims to optimize the Calcium-Looping (CaL) process for thermochemical energy storage in concentrating solar power plants.
- The CaL-TCES process proposed by Ortiz is used as a benchmark and starting point for the simulation and optimization study.
- The research introduces three innovative aspects: optimization of key variables, consideration of make-up and purge streams, and a proposed water separation process.



Introduction: Literature Comparisons



Literature Comparison	Literature Gaps
Optimization of carbonator and main turbine outlet pressures without purge or water separation process	Failed to consider the inclusion of make-up and purge streams for improved efficiency gains
Consideration of calcination under water vapor with optimal solids purge split fraction.	Failed to consider the detailed heat integration analysis and the tradeoff between thermal-to-electrical efficiency and solar-to-thermal efficiency.
Proposal of a water separation process for the use of water vapor in the solar calciner	Failed to consider the increase in residual conversion of CaCO_3/CaO mixture and its effect on the overall efficiency

Goals and Objectives



- Optimization of the carbonator and main turbine outlet pressures to improve thermal-to-electrical efficiency.
- Study the effect of varying solids purge split fraction on the CaL-TCES process and its impact on efficiency.
- Analyze the tradeoff between maximizing thermal-to-electrical efficiency and solar-to-thermal efficiency in the CaL-TCES process.

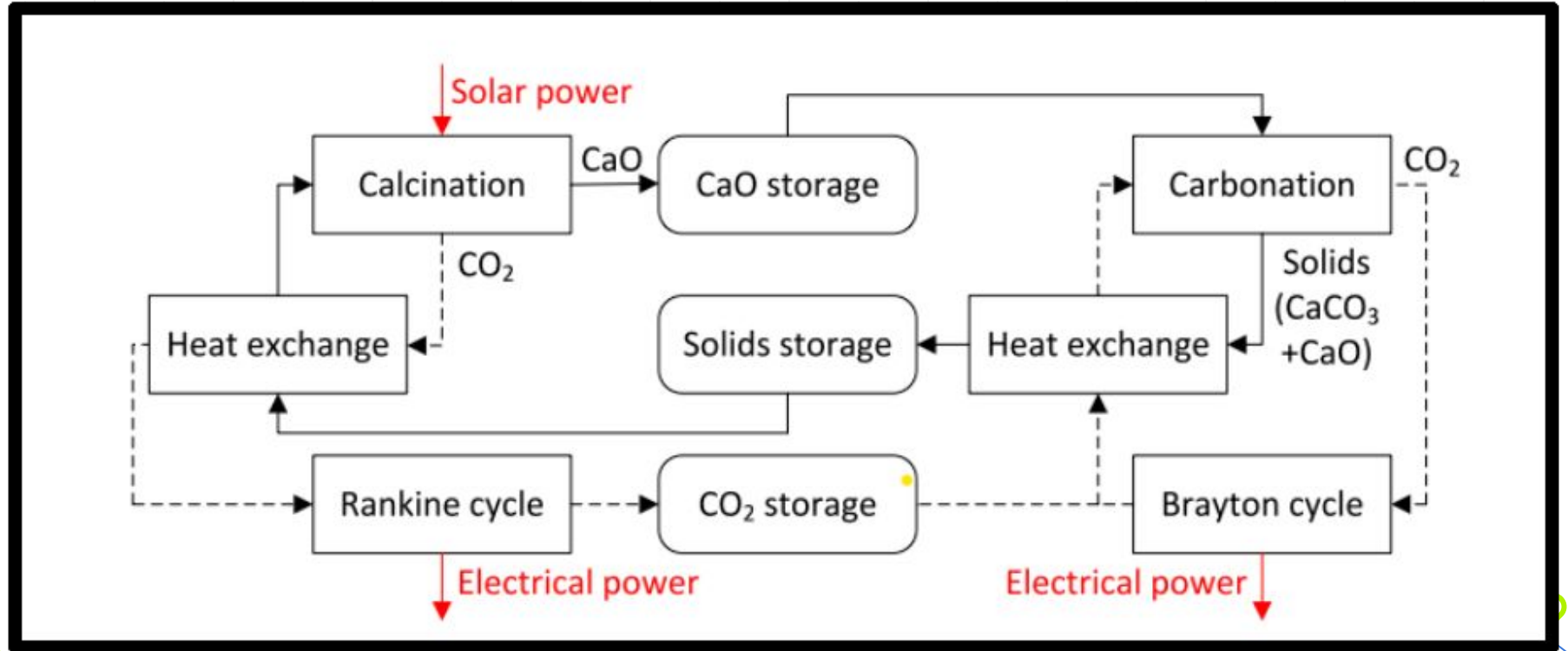




Process of modelling and optimisation

2

Schematic Diagram of the Process



CaL-TCES process



- The CaL-TCES process involves a solar calciner (CALC) and a carbonator (CARB) that convert CaCO_3 to CaO and CO_2 , and vice versa, respectively.
- Turbines are used for electrical power generation, and tanks are used to store the reaction products.
- Heat exchangers are employed to enable heat integration within the reactors.
- When solar radiation is available, calcination occurs in the solar calciner, and CO_2 is used to heat up solids and generate steam for power generation.
- The carbonator side of the process operates continuously, while the calciner side operates only when solar radiation is available.



Description of the water separation process



- The process aims to separate the gas outlet stream of the solar calcination reactor into two streams: one with a high fraction of water to be recycled and another with a high fraction of CO₂.
- The separation process should ensure that both outlet streams reach the same temperature and pressure as the gas outlet stream of the calcination reactor.
- The proposed process includes multiple stages of unit operations, initial cooling, and final separation and heating steps.
- Heat integration is utilized between condensation/cooling and evaporation/heating in each separation stage and between the initial cooling and final heating steps.
- Compressors are used to increase the pressure of the vapor streams, and the pressure ratios in the compressors are the only available degrees of freedom in the separation process.

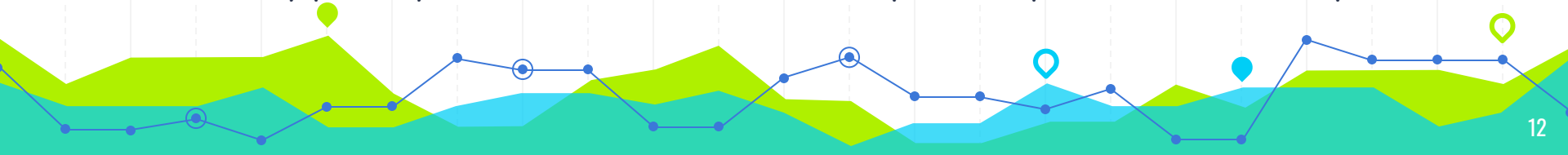
Optimization procedure

- The goal of the study is to maximize the thermal-to-electrical efficiency of the CaL-TCES process while considering various constraints.
- A nonlinear program (NLP) is used to optimize the process and achieve improved efficiency.
- The study focuses on modifying the main turbine outlet pressure, carbonator outlet pressure, and conversion in the carbonator to maximize efficiency.
- The inclusion of make-up and purge streams allows for energy savings and consideration of CaO leaving the process.
- A process for water separation from the gas outlet stream of the calcination reactor is proposed to reduce calcination temperature and residence time, and the pressure ratios in the compressors are optimized to minimize power consumption.

Process configurations



- Optimization of carbonator and main turbine outlet pressures without purge or water separation process, assuming 15% residual conversion in the carbonator and CO₂ as the fluidizing gas in the calciner.
- Introduction of a varying solids purge split fraction (fp) between 0 and 1, considering optimal carbonator and main turbine outlet pressures, CO₂ in the calciner, and the purge split fraction.
- Calcination under water vapor considered for the optimal value of fp in case (2), assuming equal mass flow rates of water vapor and solids at the calciner inlet. Efficiency penalty associated with the water separation process is also computed.





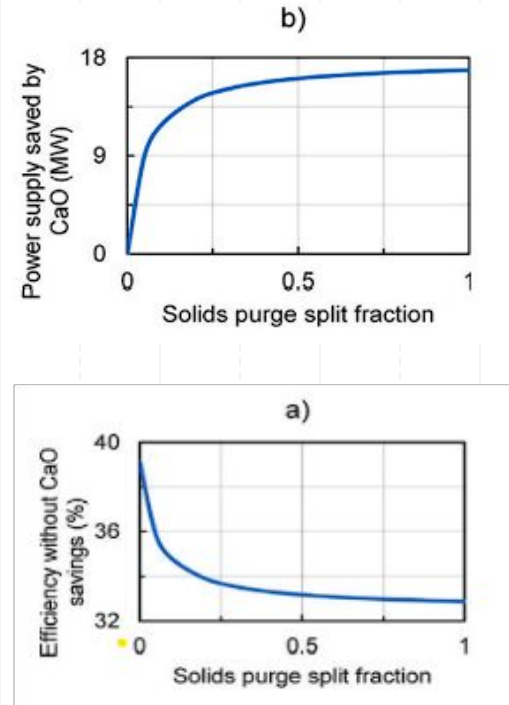
Results and discussion

3

Optimization of the carbonator and main turbine outlet pressures



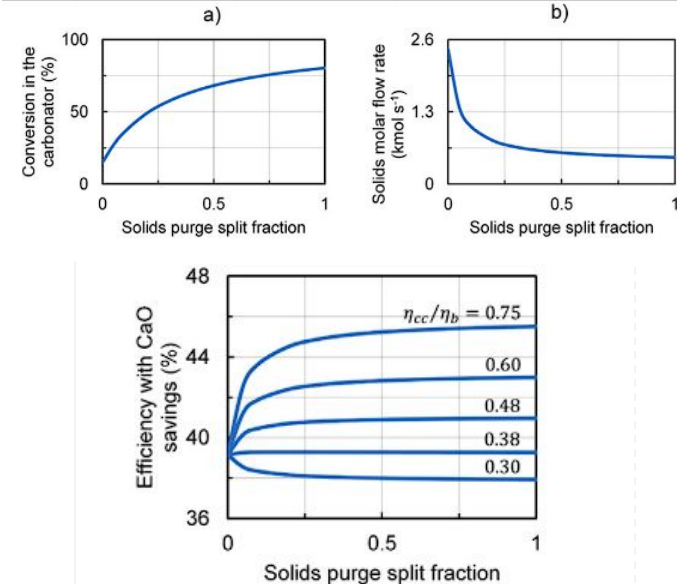
By changing the carbonator and main turbine outlet pressures from 3 bar and 1 bar to 1.485 bar and 0.293 bar respectively, the efficiency can be improved from 38.1% to 39.2%. This highlights the importance of optimizing these decision variables to enhance efficiency.



Effect of the solids purge split fraction



- Raising the solids purge rate (f_p) in the CaL-TCES process leads to a decrease in efficiency while resulting in power savings. The optimal f_p value is contingent upon the efficiency ratio, with a maximum attainable efficiency of 43% under ideal conditions. As f_p increases, the carbonator conversion rate rises, but the flow of solids decreases due to a higher proportion of CaCO_3 being transformed into CaO



Effect of the water separation process



- Increasing the solids purge split fraction (f_p) from 0 to 1 can improve the efficiency (η_2) of the process.
- The exact improvement in efficiency depends on the efficiency ratio (η_{cc}/η_b) considered.
- Without considering the savings from the CaO leaving the process in the solids purge (η_1), the efficiency decreases from 39.2% to 32.9% as f_p increases from 0 to 1.
- However, the savings owing to the CaO leaving the process (Q_p) increase from 0% to 16.9% of the solar input as f_p increases from 0 to 1.
- The best strategy is to set f_p equal to 1 (without a recycle stream) if and only if the efficiency ratio (η_{cc}/η_b) is larger than 0.38. For $\eta_{cc}/\eta_b = 0.60$, the efficiency increases from 39.2% to 43.0%.





Conclusion 4

Conclusion



- Water vapor as a fluidizing gas: The use of water vapor in the calcination process affects the residual conversion of the CaCO_3/CaO mixture, which in turn impacts the conversion in the carbonator and the overall efficiency.
- Efficiency improvement: The incorporation of water vapor leads to a significant increase in solar-to-thermal efficiency, resulting in a more efficient utilization of solar energy.
- Smaller calcination reactor: By utilizing water vapor, it becomes possible to design a smaller calcination reactor. This not only saves space but also reduces costs associated with construction and materials.



Conclusion



- Tradeoff between objectives: There is a tradeoff between maximizing thermal-to-electrical efficiency and maximizing solar-to-thermal efficiency. The use of water vapor for calcination optimizes the former objective while considering the latter.
- Temperature considerations: The study also explores the effect of the water separation process at a lower calcination temperature of 800°C. It is found that the benefits of using water vapor, such as increased efficiency and savings, remain consistent even at this lower temperature.

